



A trinuclear magnesium based metal-organic framework with self-penetrated rob topology



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ABSTRACT

A new magnesium based metal-organic framework (MOF) $[\text{Mg}_3(\text{obb})_3(\text{H}_2\text{O})_2(\text{DMA})_2]\cdot 2\text{DMA}$ (**1**; $\text{H}_2\text{-obb}$ = 4,4'-oxybisbenzoic acid; DMA = N,N'-dimethyl acetamide) with $\text{Mg}_3(\text{H}_2\text{O})_2(\text{DMA})_2(\text{COO}^-)_6$ secondary building units (SBUs) has been solvothermally synthesized and structurally characterized by single crystal X-ray diffraction, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) and Elemental analysis (EA). A prominent feature of **1** is the unprecedented pillar-layered framework in which the obb ligand acts as both the linker and pillar simultaneously. In another way, The trinuclear $\text{Mg}_3(\text{H}_2\text{O})_2(\text{DMA})_2(\text{COO}^-)_6$ subunit (SBU) can be simplified as 6-connected node and the flexible obb ligand acts as the linker. Correspondingly, the compound **1** exhibits 6-connected self-penetrated **rob** topology.

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1. Introduction

Recently, the construction of metal-organic frameworks (MOFs) has been attracted much attention not only for their potential applications but also for their intriguing topologies [1,2]. Among the new numerous networks topologies, self-penetrated nets, wherein the shortest circuits within the network are penetrated by rods of the same network, are one of the most intriguing ones. For example, several 6-connected self-penetrating nets, such as **rob** ($4^8.6^6.8$) [3–10], **mab** ($4^4.6^{10}.8$) [3,11,12], **roa** ($4^4.6^{10}.8$) [3,13], ($4^4.6^{11}$) [14], and ($4^8.6^7$) [15] have been reported so far¹. A common strategy in the design of such self-penetrated networks in MOFs adopts flexible ligands, as these can promote helical or looped structural motifs through which other organic linkers can penetrate. As a typical flexible V-shaped dicarboxylate ligand, 4,4'-oxybis(benzoic acid) (H_2obb) has been widely used to promote the formation of interpenetrating and self-catenated frameworks with auxiliary organic linkers [3,4]. Although the coordination chemistry of the obb ligand has been widely explored, most of them are focused on Indium, transition-metal and lanthanide-metal based subunits (SBUs) [16–25]. The Mg-obb frameworks have never been reported to date. The main reason is that the coordination chemistry of magnesium is less flexible than that of zinc, and in most cases, the octahedral

complexes are observed [26–36]. Additionally, because of the high affinity of Mg^{2+} for oxygen donor atoms of polar solvents, the competitive coordination by water or other solvent ligands may result in low-dimensional network topologies or isolated complexes. So for the magnesium carboxylates system, it's difficult to form coordination polymers and extended three-dimensional structures. Considering that divalent magnesium has a number of similarities to the transition metal ions Zn^{2+} and Cu^{2+} , such as the octahedral coordination, the comparable ionic radius and similar hydration energy, the formation of polynuclear Mg based SBUs like the transition-metal analogues, may be the useful method to construct high-dimensional MOFs [36]. Herein, we firstly report a neutral three dimensional (3D) framework $[\text{Mg}_3(\text{obb})_3(\text{H}_2\text{O})_2(\text{DMA})_2]\cdot 2\text{DMA}$ (**1**) with the $\text{Mg}_3(\text{H}_2\text{O})_2(\text{DMA})_2(\text{COO}^-)_6$ SBUs under solvothermal conditions. A prominent feature of **1** is the unprecedented pillar-layered framework in which the obb ligand acts as both the linker and pillar simultaneously. The ligand (obb) flexibility in the structure of **1** results in the self-penetrated **rob** topology even without auxiliary ligand.

2. Experimental

2.1. Materials and methods

All reagents and solvents for the syntheses were purchased from commercial sources and used as received. The IR spectra (KBr pellets) were recorded on a Magna 750 FT-IR spectrophotometer. Powder X-ray diffraction data were recorded on a Rigaku MultiFlex diffractometer with a scan speed of 10°min^{-1} . Thermal

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¹ For definitions of three-letter abbreviations, see Reticular Chemistry Structure Resource (<http://rcsr.anu.edu.au/>).

stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer under N₂ (30–800 °C range) at a heating rate of 10 °C min^{−1}.

2.2. Synthesis of [Mg₃(obb)₃(H₂O)₂(DMA)₂]₂·2DMA (**1**)

A mixture Mg(NO₃)₂·6H₂O (0.1848 g, 0.5 mmol), H₂obb (0.1893 g, 0.5 mmol), NaOH (0.0412 g, 1 mmol) was dissolved in 5 mL of DMA or DMA/H₂O(4:1) in a 20 mL vial. The reaction vial was capped tightly and heated at 120 °C for 48 h. Cool down to room temperature and washed by ethanol, colorless block crystals were obtained (63% yield). Elemental analysis (EA) for **1**, C₅₈H₆₀N₄O₂₁Mg₃ (1222.03): Calc. C, 57.01; H, 4.95; N, 4.58. Found: C, 57.34; H, 4.53; N, 4.51%.

2.3. Crystal structure determination

X-ray diffraction data were collected on Rigaku Mercury70 CCD X-ray diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by direct method of SHELXS-97 and refined by full-matrix least-square techniques using the SHELXL-97 program [37]. The details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

3. Results and discussion

3.1. Description of crystal structure

The asymmetric unit of **1** contains one crystallographically Mg²⁺ ion (Mg1) lying on an inversion centre, half obb (denoted L1, its center oxygen atom places in binary axis including O6, O7), one crystallographically Mg²⁺ ion (Mg2), another one obb (denoted L2), one coordinated water and DMA molecules, one guest DMA (Fig. 1a). The Mg1 ion is octahedrally coordinated by six O atoms from six different carboxyl groups of obb ligands. The Mg2 is also octahedrally coordinated by six O atoms, in which O1 and O4 atoms are from two different carboxyl groups of one obb ligand (L2) in monodentate mode, O6 and O7 atoms are from one carboxyl group of the obb ligand (L1) in chelating mode, another two O atoms (O1w and O10) are from coordinated solvent molecules (Fig. 1a).

Table 1
The crystal data of compound **1**.

Compound reference	a
Chemical formula	C ₅₈ H ₆₀ N ₄ Mg ₃ O ₂₁ ·2(C ₄ H ₉ NO)
Formula mass	1222.03
Crystal system	orthorhombic
a (Å)	23.7111(13)
b (Å)	11.3748(4)
c (Å)	22.0842(10)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Unit cell volume (Å ³)	5956.3(5)
Temperature (K)	293(2)
Space group	Pccn
No. of formula units per unit cell, Z	4
No. of reflections measured	12958
No. of independent reflections	5229
R _{int}	0.0463
Final R _i values (I > 2σ(I)) ^a	0.0733
Final wR(F ²) values (I > 2σ(I)) ^b	0.1929
Final R _i values (all data)	0.1271
Final wR(F ²) values (all data)	0.2225
Goodness of fit (GOF) on F ²	1.234

^a R_i = (|F_o| − |F_c|)/|F_o|.

^b wR₂ = [w(F_o² − F_c²)/w(F_o²)]^{1/2}.

Table 2
Selected bond lengths and angles for **1**.

Mg(1)–O(2) ^{#1}	2.051(3)	Mg(2)–O(10)	1.979(4)
Mg(1)–O(2)	2.051(3)	Mg(2)–O(4) ^{#2}	2.011(3)
Mg(1)–O(3) ^{#2}	2.052(3)	Mg(2)–O(1)	2.038(3)
Mg(1)–O(3) ^{#3}	2.052(3)	Mg(2)–O(1W)	2.096(4)
Mg(1)–O(6) ^{#1}	2.173(3)	Mg(2)–O(7)	2.141(3)
Mg(1)–O(6)	2.173(3)	Mg(2)–O(6)	2.197(3)
O(2) ^{#1} –Mg(1)–O(2)	180.00(16)	O(10)–Mg(2)–O(4) ^{#2}	106.68(17)
O(2) ^{#1} –Mg(1)–O(3) ^{#2}	88.55(12)	O(10)–Mg(2)–O(1)	87.07(16)
O(2)–Mg(1)–O(3) ^{#2}	91.45(12)	O(4) ^{#2} –Mg(2)–O(1)	91.91(15)
O(2) ^{#1} –Mg(1)–O(3) ^{#3}	91.45(12)	O(10)–Mg(2)–O(1W)	86.35(17)
O(2)–Mg(1)–O(3) ^{#3}	88.55(12)	O(4) ^{#2} –Mg(2)–O(1W)	87.89(15)
O(3) ^{#2} –Mg(1)–O(3) ^{#3}	180.00(16)	O(1)–Mg(2)–O(1W)	173.06(15)
O(2) ^{#1} –Mg(1)–O(6) ^{#1}	91.62(11)	O(10)–Mg(2)–O(7)	90.54(16)
O(2)–Mg(1)–O(6) ^{#1}	88.38(11)	O(4) ^{#2} –Mg(2)–O(7)	161.21(14)
O(3) ^{#3} –Mg(1)–O(6) ^{#1}	91.19(11)	O(1)–Mg(2)–O(7)	96.54(14)
O(3) ^{#3} –Mg(1)–O(6) ^{#1}	88.81(11)	O(1W)–Mg(2)–O(7)	85.70(14)
O(2) ^{#1} –Mg(1)–O(6)	88.38(11)	O(10)–Mg(2)–O(6)	150.81(17)
O(2)–Mg(1)–O(6)	91.62(11)	O(4) ^{#2} –Mg(2)–O(6)	102.49(13)
O(3) ^{#2} –Mg(1)–O(6)	88.81(11)	O(1)–Mg(2)–O(6)	93.07(13)
O(3) ^{#3} –Mg(1)–O(6)	91.19(11)	O(1W)–Mg(2)–O(6)	93.74(14)
O(6) ^{#1} –Mg(1)–O(6)	180.0	O(7)–Mg(2)–O(6)	60.42(11)

Symmetry transformations used to generate equivalent atoms: ^{#1} −x + 1, −y + 1, −z; ^{#2} −x + 1/2, y, z − 1/2; ^{#3} x + 1/2, −y + 1, −z + 1/2.

The primary feature of **1** is the observation of the unprecedented pillar-layered framework based on the Mg₃(CO₂)₆(H₂O)₂(DMA)₂ SBUs (Fig. 1b), which consists of one central Mg1 ion and two outer Mg2 ions. According to coordination mode, the obb ligands were classified into two kinds: the obb (L1) acts as the μ₄-bridge to link two Mg1 by the carboxyl group (O6, O7) in chelating mode, linking two Mg2 by the O6 atoms in μ₂-bridge mode; the obb (L2) also acts as the μ₄-bridge, two carboxyl groups of which link two Mg1 and two Mg2 atoms by their four atoms (O1–O4) as μ₂-bridge. This slight difference of their coordination mode results in the different roles they played. The L2 ligand acts as μ₂-bridge to link aforementioned Mg3 SBUs to form 2D (4, 4) layer parallel to the ac plane (Fig. 1c). In comparison, the L1 ligand links aforementioned Mg3 SBUs to form 1D zigzag chain also as μ₂-bridge (Fig. 1d). Interestingly, for the whole framework of **1**, the obb (L1) also acts as the pillar to link adjacent (4, 4) layer above to generate a novel 3D open framework giving 1D channels along the b axis (Fig. 2a), occupied by the structural ordered DMA molecules.

From the topological view, another prominent structural feature is the presence of the **rob** topology in **1**. As analyzed above, the whole framework can be treated as the Mg3 SBUs linked by six obb ligands, all the obb ligands act as the linker and the Mg3 SBU as the six-connected node. In this way, the framework of **1** can be simplified as a uniform 6-connected **rob** network [38–40] with the point symbol of (4⁸.6⁶.8) (Fig. 2b). As mentioned before, this network is a self-penetrated one, in which the six-membered shortest circuits are penetrated by rods of the same net (highlighted in Fig. 2b). It should be noted that though the Mg₃ SBU of **1** is very similar to the one reported by Long [13], the frameworks and topology of them are much different. Compared to the rigid linear ndc ligand (H₂ndc = 2,6-naphthalic acid), the obb ligand is flexible and bent, and the length of obb is longer than that of ndc, which results in that the compound **1** adopts self-penetrated **rob** topology instead of the common 4¹²6³ primitive cubic (**pcu**, a-Po) 6-connected topology.

3.2. Powder-XRD patterns (PXRD) and thermogravimetric analysis (TGA)

The as-synthesized samples of **1** have been characterized by powder X-ray diffraction (PXRD) (Fig. 3). The experimental PXRD patterns correspond well with the results simulated from the

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