

# Ionothermal synthesis of a metal-organic framework constructed by magnesium(II) and 4,4'-oxybis(benzoic acid) ligand

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## ABSTRACT

By using the ionic liquid 1-butyl-2,3-dimethylimidazolium bromide ([Bmmim]Br) as solvent and reactant, a magnesium(II) metal complex, namely, [Bmmim][Mg<sub>3</sub>(oba)<sub>3</sub>(obaH)] (**1**) (obaH<sub>2</sub> = 4,4'-oxybis(benzoic acid)) has been synthesized ionothermally, which represents the first Mg(II)-oba metal-organic framework. Single-crystal X-ray analysis indicated that the structure of **1** featured a three-dimensionally anionic framework of [Mg<sub>3</sub>(oba)<sub>3</sub>(obaH)]<sub>n</sub><sup>n-</sup>. Photoluminescence measurements revealed that **1** exhibited strong emission at 387 nm ascribed to ligand-to-metal charge transfer.

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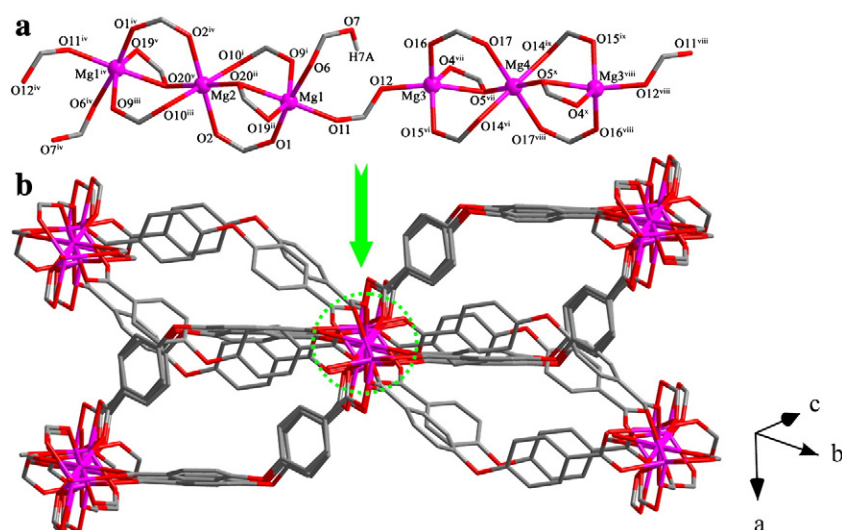
Metal-organic frameworks (MOFs) are of current interest in the fields of crystal engineering and material chemistry owing to their intriguing architectures as well as potential applications in gas storage [1], separation [2], drug delivery [3] and catalysis [4]. Recently, the light-weight metal MOFs have caused the climax of research, which may mainly be attributed to the enhancement of gravimetric gas storage capacity of materials due to the introduction of lighter metal ions such as Li<sup>+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup> [5–8]. Although many achievements have been made in this research field, thus far only a few examples of magnesium based MOFs have been reported, most of which were synthesized by the traditional hydro(solvo)thermal methods [9–11]. Moreover, the previous studies have focused on the assembly of Mg-MOFs by the combination of the Mg(II) with the rigid ligands such as terephthalic acid [12], pyromellitic acid [13], naphthalene-2,6-dicarboxylic acid (NDCH<sub>2</sub>), and pyrene-2,7-dicarboxylic acid [14]. To our knowledge, the Mg-MOFs based on flexible ligands have not been obtained. It has been demonstrated that 4,4'-oxybis(benzoic acid) (obaH<sub>2</sub>) was a good flexible ligand for constructing flexible MOF and chiral structure [15–17].

Ionic liquids (ILs) have been applied in many processes of material science. Using ILs as reaction media, template, and/or charge-compensating agent in elevated temperature, ionothermal synthesis turns out to be a highly promising synthetic method for MOFs over recent years [18,19]. In case of the preparation of Mg-MOFs in ILs, only recently we reported on the first ionothermal synthesis of Mg-MOF, in which the rigid 1,4-naphthalenedicarboxylic acid was used as organic linker [20]. Herein we report on the ionothermal synthesis, structure and characterization of [Bmmim][Mg<sub>3</sub>(oba)<sub>3</sub>(obaH)] (**1**).

Significantly, compound **1** represents the first Mg(II)-MOF built from the flexible oba ligand.

Colorless prismatic crystals of **1** were obtained through an ionothermal reaction of a mixture of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, obaH<sub>2</sub>, and [Bmmim]Br at 160 °C for 6 days [21]. The crystal structure of **1** was characterized by single-crystal X-ray diffraction analysis [22]. Compound **1** belongs to the space group *P*-1. Its structure features a three-dimensionally (3D) anionic framework with two types of trinuclear magnesium clusters as secondary building units (SBUs). The crystallographically asymmetric unit of **1** is composed of two Mg(II) ions (Mg(1)<sup>2+</sup> and Mg(3)<sup>2+</sup>) in general positions, two half a Mg(II) ions (Mg(2)<sup>2+</sup> and Mg(4)<sup>2+</sup>) ions in inversion centers, three double-deprotonated oba ligands, one mono-deprotonated obaH, and one disordered [Bmmim]<sup>+</sup> cation (Fig. S1). As shown in Fig. 1, the Mg(1)<sup>2+</sup> ion is coordinated with six carboxylate oxygen atoms, four of which are from three oba ligands and a obaH ligand in monodentate mode, and two of which are from a oba ligand in chelating fashion. Whereas the Mg(3)<sup>2+</sup> ion is rarely penta-coordinated by five carboxylate oxygen atoms from three oba ligands in monodentate mode and one oba ligand in chelating fashion, respectively. Both the Mg(2) and Mg(4) ions are six-coordinated by carboxylate oxygen atoms from six different oba ligands in monodentate mode. The Mg–O lengths fall in the range of 1.9655(12) and 2.2081(13) Å, which are comparable with those of the reported [9–14]. As illustrated in Fig. 2, the three independent deprotonated oba ligands (L1, L3, L4) and one mono-protonated obaH ligand (L2) adopt distinct coordination modes with the Mg(II) ions. Two centrosymmetric linear trinuclear units are evident as the SBUs of the structure. One is [Mg<sub>3</sub>(oba)<sub>10</sub>] containing one Mg(2) in the center and two Mg(1) in both ends, in which the Mg(1) and Mg(2) ions are inter-connected by three bridging carboxylate groups of L1, L2 and L4 ligands (Fig. 1a). The other is [Mg<sub>3</sub>(oba)<sub>8</sub>] including one Mg(4) in

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**Fig. 1.** (a) Alternating arrangements of the two distinct SBUs result in an infinite one-dimensional chain extended along the  $[1 - 1 1]$  direction, symmetry transformations used to generate equivalent atoms: i  $-x+1, -y, -z$ ; ii  $-x+2, -y, -z$ ; iii  $x, y+1, z$ ; iv  $-x+1, -y+1, -z$ ; v  $x-1, y+1, z$ ; vi  $-x+2, -y+1, -z+1$ ; vii  $-x+1, -y+1, -z+1$ ; viii  $-x+2, -y, -z+1$ ; ix  $x, y-1, z$ ; x  $x+1, y-1, z$ . (b) The linking mode of the 1D chains.

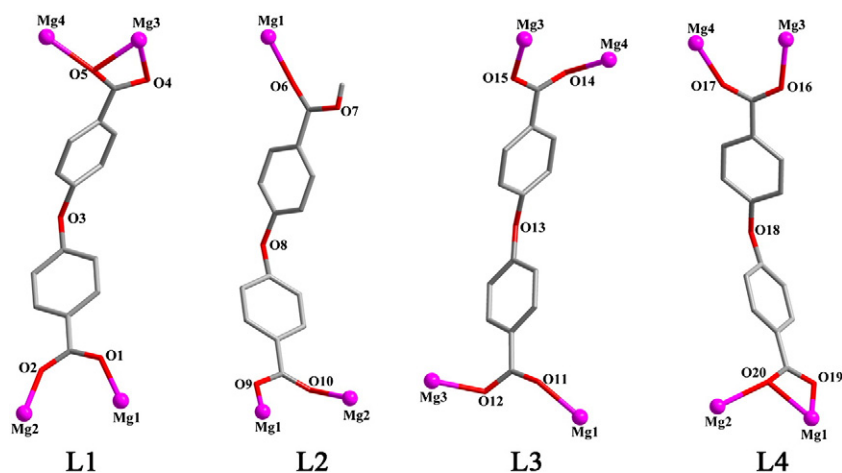
the centric and two Mg(3) in both ends, in which the Mg(3) and Mg(4) ions are also inter-connected by three bridging carboxylate groups of L1, L3 and L4 ligands. Within the trinuclear units the distances between the Mg(1)<sup>2+</sup> and Mg(2)<sup>2+</sup>, Mg(3)<sup>2+</sup> and Mg(4)<sup>2+</sup> are 3.5369(5) and 3.3930(5) Å, respectively. The two distinct SBUs are bridged by one COO<sup>-</sup> group of L3 ligand and the distances of Mg(1)<sup>2+</sup> and Mg(3)<sup>2+</sup> between two adjacent SBUs are 5.6093(7) Å. Alternating arrangements of the two distinct SBUs result in an infinite one-dimensional (1D) chain extended along the  $[1 - 1 1]$  direction. Then each 1D chain is further linked to two adjacent chains by the L1 and L4 oba ligands along the  $[-1 1 1]$  direction and linked to another two adjacent chains by the L2 and L3 oba ligands along the  $[1 1 1]$  direction (Fig. 1b). Thus a 3D anionic framework of  $[\text{Mg}_3(\text{oba})_3(\text{obaH})]_n^-$  with caves is formed (Fig. 3a). The cave can be viewed as a cage formed by eight oba ligands as the linkers bridging four Mg3 linear trinuclear units (two Mg(1)–Mg(2)–Mg(1) and two Mg(3)–Mg(4)–Mg(3)) as corners, in which there exist double oba ligand bridges between each two Mg3 units. The  $[\text{Bmmim}]^+$  cations are located in the caves acting as charge balance agents (Fig. 3a). From the topological point of view, the 3D network of **1** possesses a  $(4.5^2)_2(4^2.5^{10}.6.7^2)(5^8.6^4.8^3)$  topology (Fig. 3b), regarding the Mg(1)–Mg(2)–Mg(1) and Mg(3)–Mg(4)–Mg(3) units as 6-connected nodes, and the ligand L3 as 3-connected node, respectively.

Although a few Mg-MOFs based on the rigid organic ligands have been reported, hitherto the flexible ligands such as 4,4'-oxybis(benzoic

acid) haven't been used to construct the Mg-MOFs. Undoubtedly the current compound is the first Mg-MOFs built from the obaH<sub>2</sub> ligand. The linear trinuclear magnesium clusters in **1** are similar with those in  $\text{Mg}_3(\text{O}_2\text{C-C}_{10}\text{H}_6\text{-CO}_2)_3$  [9],  $\text{Mg}_3(\text{bdc})_3(\text{DMA})_4$ ,  $\text{Mg}_3(\text{bdc})_3(\text{EtOH})_2$  ( $\text{H}_2\text{bdc} = 1,4\text{-benzenedicarboxylic acid}$ ;  $\text{DMA} = \text{dimethylacetamide}$ ) and  $\text{Mg}_3(\text{bpd})_3(\text{DMA})_4$  ( $\text{H}_2\text{bpd} = 4,4'\text{-biphenyldicarboxylic acid}$ ) [12], and  $[\text{Mg}_3(\text{DMF})_4(\mu\text{-NDC})_3]$  [14]. It is different that the Mg(3)<sup>2+</sup> ion in **1** is rarely penta-coordinated, whereas the Mg<sup>2+</sup> ions in the other reported linear trinuclear magnesium clusters are commonly six-coordinated [23, 24]. In addition, it is found that the oba ligand only forms mononuclear or dinuclear paddle-wheel SBUs with the transition metals in MOFs, such as  $[\{\text{Mn}(\text{OH})_2(\text{oba})_2\}]$  [16] and  $[\text{Zn}_2(\text{oba})_2(\text{DMF})_2] \cdot 2\text{DMF}$  [17]. By contrary, the Mg(II) ions form trinuclear units with the oba/obaH ligands in the title compound.

**1** was examined by elemental analysis, and the purity of the bulk product was confirmed by comparing the experimental and simulated X-ray powder diffraction patterns (Fig. S2). Thermogravimetric analyses (TGA) were carried out on the pure powder samples from room temperature to 850 °C at a heating rate of 5 °C/min under a nitrogen atmosphere. The TG curve of **1** is shown in Fig. S3. The 12.3% weight loss between 100 °C and 388 °C could be attributed to the loss of the  $[\text{Bmmim}]^+$  (calcd.: 12.2%).

Photoluminescence analysis was measured on powder samples using a Cary Eclipse fluorescence spectrophotometer at room temperature. As



**Fig. 2.** The four different coordination modes of the oba (or obaH) ligands (L1, L2, L3 and L4).

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