

## THE EFFECT OF THE SOLVENT ON THE DIMENSIONALITY OF THE Mg-MOF FRAMEWORK

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### ABSTRACT

MOF materials have been growing increasingly popular because of their vast potential in applications. In an attempt to synthesise new structures, the emphasis was also put on the variation of the solvents. Previous study of the influence of solvent on the structure and dimensionality has shown that the solvent can play an important role in the structure formation.

We used <sup>1</sup>H, <sup>13</sup>C and <sup>25</sup>Mg liquid and solid-state NMR spectroscopy to observe the framework formation of four new magnesium tricarboxylates. The solvent plays an important role in the dimensionality of the system and different H<sub>2</sub>O:EtOH ratios result in 0D, 1D, 2D or 3D phases. By NMR we were able to observe the assembly of individual building blocks into coordination polymers during the synthesis procedure. We determined that the crucial difference in the framework formation takes place already in the initial mixture of the reagents. 1,3,5-benzenetricarboxylic acid reacts with Mg ions and forms an unordered structure that closely resembles the final crystalline product. By <sup>25</sup>Mg NMR spectroscopy we determined that interaction of magnesium ions with the solvent is very important in determining the dimensionality because the same magnesium complexes that are present in the final compounds are already formed in the solution.

Keywords: NMR, MOF, magnesium.

### INTRODUCTION

Hybrid inorganic-organic coordination polymers or metal-organic framework (MOF) materials represent an extensive group of materials where inorganic building units are interconnected through rigid organic molecules (typically polycarboxylates) forming crystalline structure [1,2]. In the last decade, interest on MOFs research is increasing rapidly due to their vast potential in a variety of applications [3] such as heterogeneous catalysis, ion exchange, gas separation and storage, heat storage and drug delivery. In an attempt to design new structure, the emphasis was also put on the effect of the solvent. The important role of the solvent in the structure formation and its dimensionalities was studied previously [4]. In this work we discuss the role of the solvent on the structure and formation of some new magnesium tricarboxylate phases.

### EXPERIMENTAL

The synthesis of all compounds was carried out with constant magnesium acetate tetrahydrate (Mg(ac)<sub>2</sub>·4H<sub>2</sub>O, 99%, Fluka) and 1,3,5-benzenetricarboxylic acid (BTC, 95%, Aldrich) molar ratio of 1, while the molar ratios of ethanol (EtOH, 99%, Aldrich) and deionised water varied between 0 and 1. The components were mixed and then solvothermally treated at 423 K for 24 h. Depending on the H<sub>2</sub>O:EtOH ratio we obtained mononuclear complex (0D) [Mg(H<sub>2</sub>O)<sub>4</sub>(BTC-H<sub>2</sub>)<sub>2</sub>], one- (1D) [Mg<sub>3</sub>(BTC)<sub>2</sub>(H<sub>2</sub>O)<sub>12</sub>], two- (2D) [Mg<sub>2</sub>(H-BTC)(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] or three-dimensional (3D) Mg tricarboxylate structure

[Mg(H-BTC)]. The structures of all four final materials were solved from single-crystal X-ray diffraction data collected on Nonius Kappa diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Mononuclear complex was proven to be isostructural to the [Fe(H<sub>2</sub>O)<sub>4</sub>(BTC-H<sub>2</sub>)<sub>2</sub>] [5].

The framework formation was studied by <sup>1</sup>H, <sup>13</sup>C and <sup>25</sup>Mg NMR on a Varian VNMRS 600 MHz (14.1 T) spectrometer equipped with a 3.2 mm T3 MAS solids probe.

The size and morphology of the crystals in the product were studied with scanning electron microscope Zeiss Supra<sup>TM</sup> 3VP.

## RESULTS AND DISCUSSION

*Crystal structures description.* Compound **0D** consists of discrete units built of MgO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> and two trimesate ligands ( $P2_1/c$ ,  $a = 5.1286(1)$  Å,  $b = 12.9832(4)$  Å,  $c = 15.1717(4)$  Å,  $\beta = 97.172(2)^\circ$ ). Compound **1D** have chain-like structure of isolated MgO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> octahedra units linked through trimesate ligands ( $C2$ ,  $a = 17.2532(5)$  Å,  $b = 12.9657(4)$  Å,  $c = 6.6115(2)$  Å,  $\beta = 111.443(2)^\circ$ ). Compound **2D** have layered structure with unique edge- and corner-sharing Mg-centered octahedral building units ( $P\bar{1}$ ,  $a = 7.8423(5)$  Å,  $b = 8.7463(5)$  Å,  $c = 10.7163(8)$  Å,  $\alpha = 101.274(3)^\circ$ ,  $\beta = 111.443(2)^\circ$ ,  $\gamma = 96.042(3)^\circ$ ). Compound **3D** with dense, three-dimensional structure ( $P\bar{1}$ ,  $a = 7.7922(2)$  Å,  $b = 7.7932(2)$  Å,  $c = 7.7929(2)$  Å,  $\alpha = 66.135(4)^\circ$ ,  $\beta = 66.148(4)^\circ$ ,  $\gamma = 66.148(4)^\circ$ ) is built from edge-sharing Mg-centered octahedra connected through trimesate linkers. Schematic representations of all four structures are presented in Figure 1.

*Framework formation investigations.* We used <sup>1</sup>H, <sup>13</sup>C and <sup>25</sup>Mg liquid and solid-state NMR spectroscopy to observe the framework formation of Mg MOF materials. We were able to observe the assembly of individual building blocks into coordination polymers during the synthesis procedure. Four distinct magnesium-based trimesates with different dimensionalities using solvents with different H<sub>2</sub>O/EtOH ratios were studied (Figure 1).

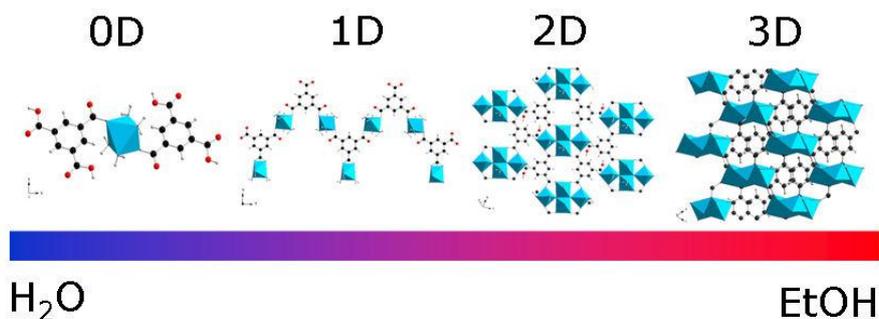


Figure 1. The dimensionality of the magnesium tricarboxylate framework depends solely on the molar ratio between water and ethanol in the solvent.

We were able to determine that the crucial difference in the framework formation takes place already in the initial mixture of the reagents, before heating (Figure 2). 1,3,5-benzenetricarboxylic acid reacts with Mg ions and forms an unordered structure that closely resembles the final crystalline product.

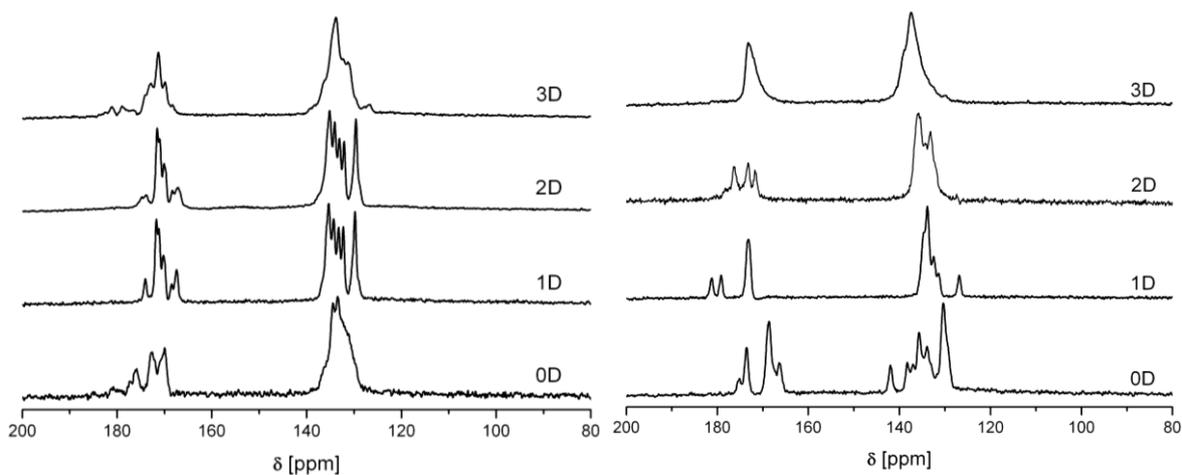


Figure 2. Figure shows  $^1\text{H}$ - $^{13}\text{C}$  CPMAS NMR spectra of the initial gels (left) and final Mg-MOF products (right hand side). We were able to determine that the crucial difference in the framework formation takes place already in the initial mixture of the reagents, before heating. 1,3,5-benzenetricarboxylic acid reacts with Mg ions and forms an unordered structure that closely resembles the final crystalline product.

$^{25}\text{Mg}$  NMR spectroscopy of Mg acetate dissolved in different  $\text{H}_2\text{O}:\text{EtOH}$  ratios showed that the crucial factor determining the dimensionality of the final crystallite is the interaction between the solvent and the magnesium ions. Magnesium acetate dissolves well in water and Mg ions in the solution are very mobile which results in narrow signals in  $^{25}\text{Mg}$  NMR spectra. Dissolution of  $\text{Mg}(\text{CH}_3\text{COO})_2$  in the solvent with higher ratios of ethanol is lower and the signals in NMR spectra are broadened. We believe that the same magnesium clusters or complexes that are present in the final compounds are formed, which broadens the  $^{25}\text{Mg}$  NMR signals.

## CONCLUSION

The solvent composition of the synthesis gel influences the dimensionality of the obtained crystalline MgMOF system. More precisely, as shown by  $^{25}\text{Mg}$  NMR spectroscopy, the dimensionality of the system is determined by the interaction of magnesium ions with the solvent. By understanding the principles behind the framework formation we can tailor the structure of MOFs.

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