SYNTHESIS AND STRUCTURE INVESTIGATION OF NEW POROUS METAL CARBOXYLATES FOR GAS CAPTURE AND STORAGE

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INTRODUCTION

Metal-organic framework (MOF) structures are crystalline nanoporous solids that are known for about a decade and show a great perspective in gas capture and storage [1-5]. The unprecedented surface area (up to 6000 m^2/g) that far exceeds those achieved for porous carbons and zeolites and precise chemical and structural control over their crystalline structure provide limitless potential for selective adsorption of different gasses. At the present time MOFs are the only materials that are close to having high enough capacity for adsorptive hydrogen storage (e.g. 7 wt.% being reported for MOF-177 at 77 K and 70 bar), because of their extremely low density (< 1g/cm^3) [6]. More recently, it was demonstrated that metal-organic frameworks show remarkable CO_2 adsorption capacities (e.g. MOF-177 exhibits a CO_2 capacity of 33.5 mmol/g or 147 wt.% at 298 K and 32 bar) [7] and MIL-101 40 mmol/g at 303 K and 50 bar condition [8].

Recently a number of divalent or trivalent transition metal cations were used for the formation of open MOF frameworks forming different building unit motifs with different nuclearities [1]. Our research was focused on the development of new MOF materials for gas sorption with improved/selective sorption performance for CO_2 and H_2 by using cost-effective synthesis procedures. The pore volume/surface area, specific weight, hydrophobicity/hydrophilicity, etc. were controlled with a proper choice of reactants (aromatic tri-carboxylic acids and Mg-, Zn- and Fe-salts) and optimisation of syntheses procedures. The use of lighter metals (e.g. Mg, Ca) in the materials preparation is especially beneficial for hydrogen storage. Mg- and Fe-MOFs as biocompatible crystalline solids are interesting for drug delivery applications [9]. In this contribution we report on the hydrothermal crystallisation and structural determination of new magnesium, zinc and iron 1,3,5-benzene tricarboxylates with chain-like, layered and open framework structures.

EXPERIMENTAL

The syntheses were carried out hydrothermally or solvothermally. Two Mg-trimesate compounds were synthesised from the reaction gel with molar ratios of reactants Mg(ac)$_2$.4H$_2$O : BTC (1,3,5-benzene tricarboxylic or trimesic acid) : 100 EtOH : 100 H$_2$O with pH 4, which was transferred into 45 ml Teflon- lined autoclaves. Hydrothermal treatments were performed at 432 K for 48 h (Mg-MOF-1) and 72 h (Mg-MOF-2). The third Mg-trimesate compound crystallised from the gel with the molar ratios of reactants Mg(ac)$_2$.4H$_2$O : BTC : 100 EtOH after solvothermal treatment at 463 K for 2 days (Mg-MOF-3). The Zn-trimesate was prepared in water/ethanol medium in the presence of 1,3-diaminopropane (DAP) as structure directing agent and hydrofluoric acid. The pure product crystallised from gel with molar ratios of reactants Zn(ac).2H$_2$O : 0.57 BTC : 50 H$_2$O : 5 HF : 0.4 DAP after solvothermal treatment at 463 K for 1 day (Zn-MOF-1). The Fe-trimesate compound crystallised from the gel with molar ratios of reactants FeCl$_3$·6H$_2$O : 1,5 BTC : 62 H$_2$O : 66,5 acetone after solvothermal treatment at 463 K for 7 days. The pH was adjusted to 2.5 using 10% NaOH ((Fe-MOF-1). All crystalline solids were collected by filtration, continuously rinsed with deionised water and dried at ambient conditions.

The basic characterisation methods for synthesised materials were X-ray powder diffraction (XRD), elemental analysis, scanning electron microscopy (SEM) and thermal analysis (TG/DTG/DSC). Detailed structural characterisation was performed using single-crystal X-ray diffraction. The room temperature single-crystal diffraction data of all samples were collected on a laboratory Nonius Kappa CCD diffractometer by using the MoKα radiation. All structures were solved using the SHELX program package.

RESULTS AND DISCUSSION

In all analysed Mg-trimesate phases magnesium form octahedral coordination with carboxylic oxygen atoms and water molecules. Magnesium octahedra form clusters of up to 4 corner or edge sharing MgO$_6$ polyhedra. Most of the carboxylate oxygen atoms form covalent bonds with magnesium (Figure 1). Formation of particular phase is extremely sensitive to synthesis parameters (i.e. the solvent and temperature/time of crystallisation); e.g. the increase of synthesis time and temperature led to the structural evolution from one-dimensional chain structure to two-dimensional layered structure from the same synthesis gel (Figure 1).
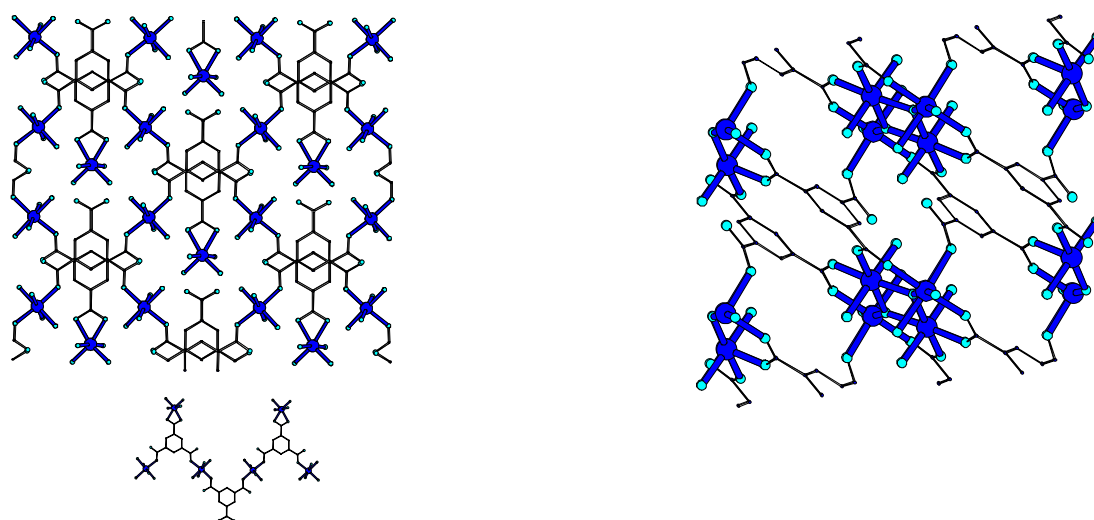

Figure 1: Chain (left) and layered (right) Mg-trimesate structures projected along [001] direction (Mg=blue, O=cyan, C=black).

Table 1: Crystal data for Mg-trimesate structures.

	Mg-MOF-1	Mg-MOF-2	Mg-MOF-3
space group	monoclinic *C2*	triclinic *P-1*	triclinic *P-1*
a (Å)	17.2532(5)	7.8423(5)	7.7922(2)
b (Å)	12.9657(4)	8.7463(5)	7.7932(2)
c (Å)	6.6115(2)	10.7163(8)	7.7929(2)
α (°)	90	101.274(3)	66.135(4)
β (°)	111.443(2)	91.868(3)	66.148(4)
γ (°)	90	96.042(3)	66.148(4)

Three-dimensional porous structure was formed only in the absence of water in the reaction gel (Figure 2). Crystal data are summarised in Table 1. The low density of the Mg-MOF-3 structure makes this material promising for H$_2$ storage.
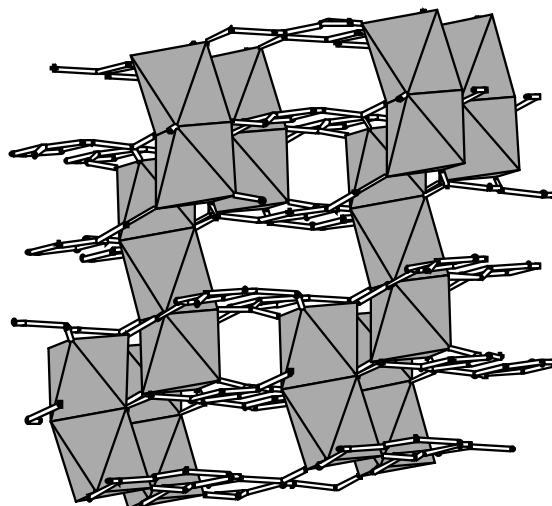
Figure 2: Framework Mg-trimesate structures along [010] direction. MgO$_6$ units are presented as grey octahedra.

The Zn-MOF-1 structure, shown on Figure 3, with monoclinic $P2_1/a$ symmetry and cell parameters $a = 7.5674(2)$ Å, $b = 18.8476(4)$ Å, $c = 9.8779(2)$ Å, $\beta = 100.668(2)$ ^{o}, $V = 1237.59(5)$ Å^3 is built up from two five-coordinated Zn(O$_4$F) units, where three oxygens belongs to carboxylate anions, one to water molecule, and one six-coordinated Zn(O$_4$F$_2$) unit forming edge-sharing trimer. Trimers are connected with trimesate anions and thus forming 3-D porous structure. 1,3-propanediammonium cations, which are located in the pores are disordered over two positions and connected with framework through hydrogen bonds. Thermal properties of the material were investigated by TG and HT-XRD. TG measurements show weight loss in four major steps. First step up to 363 K represents the loss of physisorbed water. In second and third step at 420 K and 580 K is 5.6 wt.% and 4.1 wt.% respectively, weightloss correspond to template degradation. In the first step of template removal process CH chain degradation occurs, leaving the pores opened, however amine groups still remain attached to the framework by strong hydrogen bonds. Amine groups are removed in second step of template removal at 580 K. This degradation process was also confirmed by HT-XRD. Thermodiffractometry showed that the structure is thermally stable up to 623 K. Specific two-step template degradation enables to activate and functionalize framework structure with amine groups at 473 K. This makes the material promising for CO$_2$ storage.
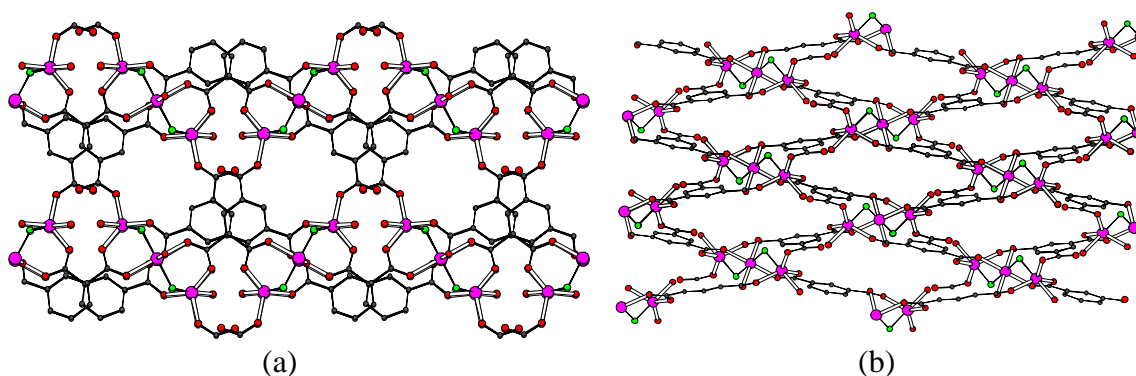

(a)   (b)

Figure 3: Zn-trimesate structure (a) along [100] and (b) along [101] directions (Zn=magenta, F=green, O=red, C=black).

Fe-trimesate (Fe-MOF-1) structure with monoclinic *P2/c* symmetry and cell parameters *a* = 9.6790(1) *Å, b* = 12.5770(1) *Å, c* = 14.081 (2) *Å, β* = 110.1370(1) ^{o}, *V* = 1609.3(3) *Å^3* is built up from chains of FeO_6 octahedra, where all oxygens belongs to carboxylate anions. Chains are connected with trimesate anions to form 3D porous framework structure (Figure 4). The material is a promising adsorbent for different gasses due to high porosity of the structure.
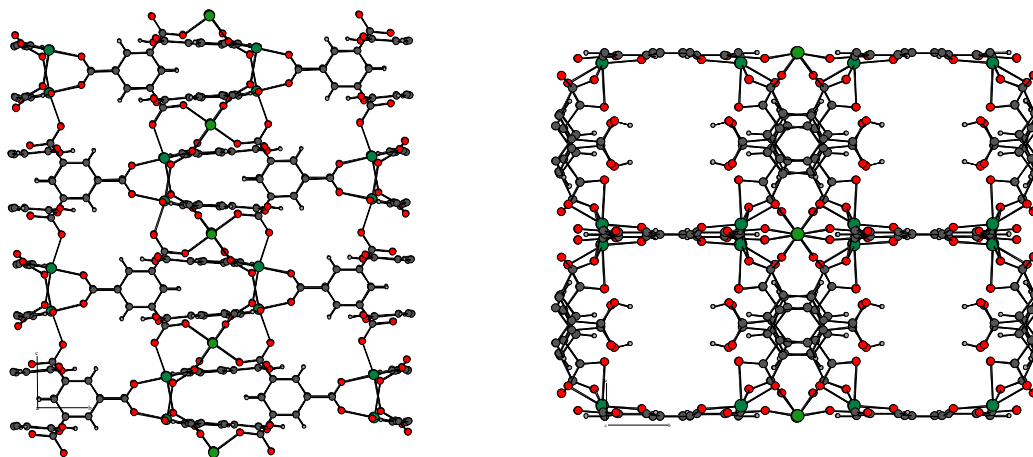

Figure 4: Fe-trimesate structure along [100] (left) and [001] (right) directions (Fe=green, O=red, C=black).

CONCLUSION

1,3,5-benzene tricarboxylic acid was successfully used in the synthesis of crystalline framework metal-organic structures with different divalent metal ions (Mg(II), Zn(II), Fe(II)) in the absence or in the presence of structure-directing agents. A precise control over synthesis parameters was concentrated on the choice of the solvent, crystallisation temperature/time and pH of the reaction gel.

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