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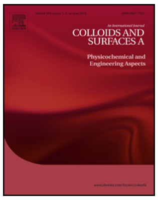

New members of MOF-76 family containing Ho(III) and Tm(III) ions: Characterization, stability and gas adsorption properties

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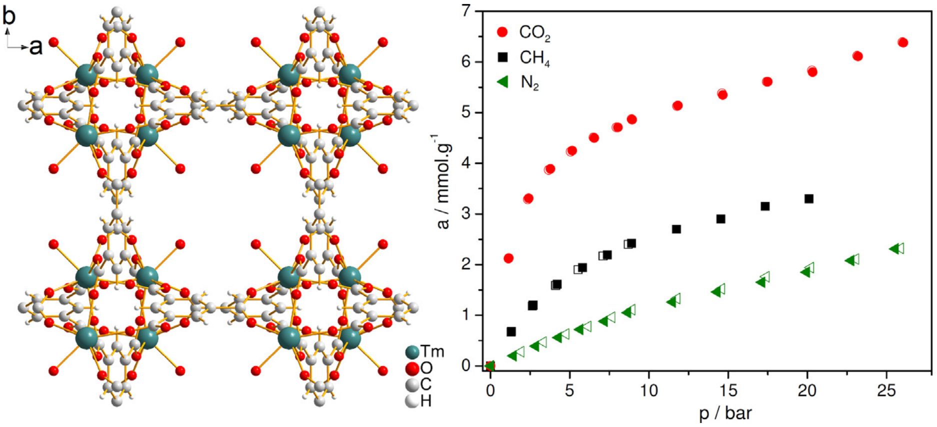
HIGHLIGHTS

- Two new metal-organic frameworks of MOF-76 family were prepared and studied.
- Both frameworks exhibit the open porosity and high thermal stability.
- Tm(III) compound shows "single-crystal-to-single-crystal transformation".
- High pressure adsorption of CO_2 is 2–3 times higher in comparison with CH_4 and N_2.

GRAPHICAL ABSTRACT



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ABSTRACT

Two novel three-dimensional microporous coordination polymers with composition $\{[Ln(\mu_6\text{-}BTC)(H_2O)]\cdot DMF\}_n$ (Ln = Ho(III) (**1**) and Tm(III) (**2**); BTC-benzene-1,3,5-tricarboxylate) have been solvothermally synthesized and their preparation conditions were optimized. Single crystal X-ray diffraction experiments showed, that both compounds display similar structures with (6, 6)-connected nets and 1D sinusoidally shaped channels with sizes about 6.7 × 6.7 Å^2. Activation process and stability of the frameworks were studied by infrared spectroscopy measured at different temperatures, thermogravimetry coupled with evolved gas analysis and by high energy powder X-ray diffraction experiments measured during *in-situ* heating. The compounds exhibited high thermal stability, up to 600 °C. Nitrogen and carbon dioxide measurements at low pressures showed BET surface area of 600 m^2 g^{-1} for the sample **1** and 590 m^2 g^{-1} for the sample **2**. The carbon dioxide uptake at 0 °C and 1 atm was ~12 wt.% for both compounds. The adsorption behaviour of **2** has been also investigated by high pressure adsorption measurements of pure methane, carbon dioxide, and nitrogen at 30 °C and pressures up to 26 bar. The measured maximal adsorption capacities were 5.03 wt.% of CH_4 at 20 bar, 6.10 wt.% of N_2 and 21.95 wt.% of CO_2 at 26 bar and 30 °C.

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1. Introduction

Building new molecular organizations with controlled structure is an important point of interest in supra-molecular chemistry, crystal engineering and materials science. The assembly of organic molecules and metal ions may yield novel types of three-dimensional networks that contain channels with various sizes and shapes and which are denoted as metal-organic frameworks (MOFs). MOFs represent an interesting and relatively new class of crystalline hybrid inorganic–organic porous materials, which have attracted a great deal of research interest due to their promising applications in the fields like gas storage and separation [1–4], heterogeneous catalysis [5–7], drug delivery [8,9], sensor technology [10,11], fabrication of nanoparticles [12,13] and others.

The MOF materials are often based on aromatic polycarboxylic acids [14–16]. One of the often used polycarboxylate linker is benzene-1,3,5-tricarboxylic acid (trimesic acid; H_3BTC), due to its rigidity and stability of the final porous framework. The dimensionality of the framework depends on several factors such as selection of the central ion, molar ratio of the reactants, solvents, reaction temperature and reaction time used in the synthesis and the strength of base employed for deprotonation of H_3BTC [17–22].

Lanthanides are sometimes regarded as unsuitable metal centres for the creation of MOFs due to their high coordination numbers and hard to control the coordination geometries. In comparison to traditional transitional metals, inner-transitional metals are unavoidable to coordinate with solvent molecules at terminal positions. However, the removal of such coordinated solvent molecules from the lanthanide ions could lead to the formation of primary adsorption sites, which are essential for catalysis and adsorption. It has been demonstrated that some MOFs with pore surfaces lined by unsaturated coordination sites possess stronger affinities for H_2, CH_4 and CO_2 [23–30].

Many metal-organic frameworks are often considered as an unstable compounds comparing to zeolites, due to weak chemical, mechanical or physical stability (mainly temperature) of their building blocks. But instability is not always a negative point of view. It was shown recently that defects in MOFs can be used for tailoring material properties, which opens up novel opportunities in gas adsorption, catalysis, band gap as well as magnetic and electrical-conductive properties [31–33].

MOF-76 represents a large family of compounds, which consists of predominantly lanthanide ions and benzene-1,3,5-tricarboxylate linker. According to our search of CCDC database, crystal structures of compounds of 10 lanthanide ions has been reported up to date, namely M(III) = Y [34], Ce [35], Nd [36,37], Eu [38,39], Gd [40], Tb [34,41,42], Dy [34,43,44], Er [34], Yb [34] and Lu [35,45]. These 3D transformable frameworks exhibit permanent porosity and extremely high thermal stability (cerium(III) analogue is an exception [35]). However, according to our best knowledge and based on the search of CCDC database, no compounds containing Ho(III) and Tm(III) ions of MOF-76 group were reported up till now.

In our previous work, we have investigated stability, gas adsorption properties and catalytic activity in Knoevenagel condensation reactions of MOF-76 (Ce) and MOF-76 (Lu) [35]. In the present work, we describe two novel members of MOF-76 family with holmium(III) and thulium(III) ions, namely $\{[Ho(\mu_6\text{-}BTC)(H_2O)]\cdot DMF\}_n$ (**1**) and $\{[Tm(\mu_6\text{-}BTC)(H_2O)]\cdot DMF\}_n$ (**2**). The conditions of activation and framework stability were investigated using different techniques (FT-IR, TG/DTG-DTA-EGA and *in-situ* HE-PXRD). After activation, complexes exhibit stable porous frameworks with large surface areas and high adsorption capacities to carbon dioxide at 0 °C and 1 atm. Moreover, adsorption measurements of nitrogen, methane and carbon dioxide over **2** were performed at 30 °C and up to 26 bar.

2. Experimental

2.1. Materials

All chemicals used in the synthesis of compounds **1** and **2** were obtained from Sigma–Aldrich company in the highest available purity and used without further purification.

2.2. Synthesis of $\{[Ho(\mu_6\text{-}BTC)(H_2O)]\cdot DMF\}_n$ and $\{[Tm(\mu_6\text{-}BTC)(H_2O)]\cdot DMF\}_n$

50 mg of $Ln(NO_3)_3\cdot 5H_2O$ (Ln(III) = Ho, Tm; 0.1134 mmol (Ho), 0.1124 mmol (Tm)) and 10 mg of H_3BTC (0.0476 mmol) were dissolved in the mixture of 3 ml DMF, 3 ml EtOH and 2.4 ml of water. The reaction mixtures were put in glass Ace® autoclaves and inserted into an oven equipped with thermoregulator. Mixtures were heated to 80 °C with heating rate 3 °C min^{-1} and kept at this temperature for 12 h. After this time the reaction mixtures were cooled to ambient temperature with cooling rate 1 °C min^{-1}. Pink (complex **1**) and colourless (complex **2**) needle-shaped crystals were filtered off and slightly washed with DMF and dried in the stream of air. Yields of **1** and **2**, were approximately ~98% for both compounds. Elemental analysis for $Ho_1C_{12}H_{12}N_1O_9$ (463.16 g mol^{-1}): Calcd. C 31.12%, H 2.61%, N 3.02%. Found. C 30.82%, H 2.39%, N 2.96%. Elemental analysis for $Tm_1C_{12}H_{12}N_1O_9$ (467.16 g mol^{-1}): Calcd. C 30.85%, H 2.59%, N 3.00%. Found. C 29.94%, H 2.45%, N 2.91%.

To optimize the synthesis conditions and yields, similar experiments with 20, 30, 40, 50, 60 mg of H_3BTC were carried out (for details see also paragraph 3.3 Rationalization of the synthesis).

2.3. Characterization

2.3.1. CHNS analyses

The elemental analysis was performed with CHNOS elemental analyzer vario MICRO from elementar analysensysteme GmbH with sample weight within 2–3 mg.

2.3.2. UV–vis spectroscopy

Solid-state UV–vis spectra of compounds **1** and **2** were recorded on a Specord 250 spectrometer developed by Analytik Jena in the wavelength region 300–900 nm. Samples for UV–vis measurements were prepared in the form of KBr pellets (see Section 2.3.3 Infrared spectroscopy below).

2.3.3. Infrared spectroscopy

The infrared spectra at room temperature and also after step-by-step heating to selected temperatures (100, 150, 200, 250, 300, 350, 400, 450, 500, 550 and 600 °C, see Section 3.2 spectral, thermal and HE-PXRD study) were recorded with FT-IR spectrometer Avatar 6700 in the range 4000–400 cm^{-1}. The samples were prepared in the form of KBr pellets with complex/KBr mass ratio 1/100. The prepared pellets were heated at selected temperatures for a half hour, subsequently cooled to room temperature in desiccator and measured. All spectra were recorded with a resolution of 4 cm^{-1} by collecting 128 scans for a single spectrum. Before IR measurements KBr was dried at 700 °C for 3 h (m.p. 734 °C) in an oven and cooled in desiccator over molecular sieves.

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