

Single-crystal-to-single-crystal phenomena in novel Lutetium(III) metal-organic framework

M. Almáši¹, V. Zelenák¹

¹Department of Inorganic Chemistry, Faculty of Natural Science, P.J.Šafárik University, Moyzesova 11, 040 01 Košice, Slovak Republic

Porous metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) are constructed by three-dimensional porous polymeric frameworks, which consist of the inorganic building units (connectors), bridged by organic ligands (linkers). High porosity and high specific surface area of MOFs can lead to many potential applications in gas storage and separation processes, ion exchange, enantioselective separation and catalysis, sensor technology, drug delivery and fabrication of metal nanoparticles¹.

The history of porous MOFs started at the end of the last century with the discovery of important compound HKUST-1 [20], which is the polymorph of copper trimesate with composition $\{[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]\}_n$. In the present work we have focused on preparation of novel MOF using the same connector, but Lu(III) cation as metal center. Here we report selected physicochemical properties of complex with formula $\{[\text{Lu}(\text{BTC})(\text{H}_2\text{O})\cdot\text{DMF}]\}_n$ (**1**) (DMF = N,N'-dimethylformamide), which is isostructural with MOF-76. The compound was characterized by elemental analysis, IR spectroscopy, TGA, single crystal X-ray diffraction and high energy X-ray diffraction (HEXRD). HEXRD measurements were carried out at wiggler beamline BW5 of Doris positron storage ring in DESY (Hamburg, Germany) with energy 100 keV corresponding to a wavelength of 0.123984 Å.

The compound **1** exhibits single-crystal-to-single-crystal (SCSC) phenomenon. The first SCSC phenomenon was reported by Kepert in 2000. They prepared compound $\{[\text{Ni}_2(4,4'\text{-bipyridine})_3](\text{NO}_3)_4\cdot 6\text{EtOH}\}_n$, which has $6 \times 3 \text{ \AA}^2$ channels, which can reversibly uptake H_2O and other guest molecules at room temperature. The desolvation process at 100°C caused just a 2.4% decrease in cell volume and the mosaicity of the crystal remained intact. The SCSC phenomenon in compound **1** can be seen from Fig. 1. Figure 1a shows comparison of experimental HEXRD pattern of **1** and the pattern calculated from single crystal X-ray data. As it can be seen from Fig. 1a, very good agreement between the measured and the calculated data was observed, indicating pure phase of **1**. HEXRD patterns of **1** measured during *in-situ* heating (Fig. 1b) showed that **1** undergoes structural changes upon removal of the DMF and water molecules, from tetragonal phase to monoclinic and then back to tetragonal. Measured patterns demonstrate, that structure of **1** started to change from first to second phase after heating to 130°C (red lines). Subsequent heating to 220°C resulted only in minor shifts of the peak positions. At 230°C compound **1** transformed to a third phase (green lines in XRD). A fourth phase (black lines) started to form above 390°C and this phase was stable up to the collapse of the framework above 600°C (see Fig. 1c). Similar SCSC transformation was observed in Nd(III) analogue published by Zou in 2010.²

Thermogravimetric analysis of complex **1** is shown in Fig. 1c. In the first step of thermal decomposition, in the temperature range 80-380°C, stepwise elimination of water and DMF molecules was observed. Activated framework is then stable to 630°C. Further heating led to collapse of the framework.

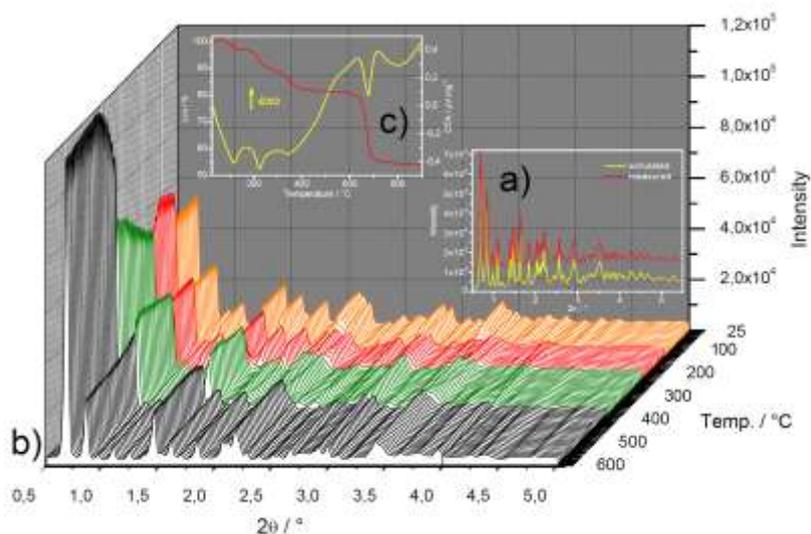


Fig. 1a) Comparison HEXRD patterns of as synthesized sample **1** (red line) and calculated pattern from single X-ray diffraction data (yellow line); b) HEXRD experiments during *in-situ* heating; c) TG/DTA curves of thermal decomposition of **1**.

The N₂ sorption isotherm of complex **1** is shown in Fig. 2. Obtained N₂ adsorption-desorption isotherms can be classified as type *I* according to IUPAC classification of physisorption isotherms, which is typical for microporous materials. Applying BET model the determined surface area of the compound was 655 m²·g⁻¹. Pore size distribution analysis calculated by DFT method showed size of the pores about 16.3 Å and pore volume 0.28 cm³·g⁻¹.

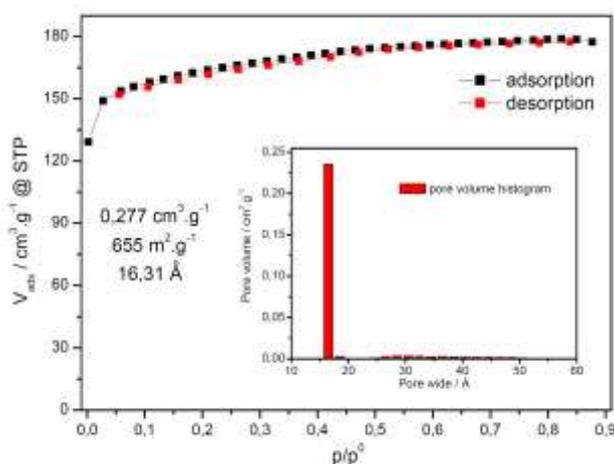


Fig. 2 N₂ adsorption isotherm and pore volume histogram of complex $\{[\text{Lu}(\text{BTC})(\text{H}_2\text{O})\cdot\text{DMF}]\}_n$.

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