MS37-P8 Magnesium Imidazolate – a First Porous Zeolitic Imidazolate Framework with Alkali and Alkaline Earth Metals

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Zeolitic imidazolate frameworks (ZIFs) are an outstanding class of MOFs, constructed from tetrahedrally configured transition metal cations linked through bridging imidazolate (Im) spacers. ZIFs are structurally isiomorphic to zeolites since the metal-Im-metal angle is similar to the Si–O–Si angle (145°) in the latter compounds. This feature was exploited to produce a huge variety of porous transition metal-based ZIFs. Our initial goal was to combine Im and alkali metal borohydrides in the same structure with the formation of porous borohydride compounds, where Im serves as a structural unit of the framework, while borohydride anions provide with a functionality. However, alkali and alkaline earth metal-based imidazolates are not structurally characterized so far. Thus, the coordination chemistry of Im towards alkali and alkaline earth metal cations remains a challenge. With this in mind and inspired by the storage properties of ZIFs, we have recently turned our attention to Im-based coordination compounds with Li^+, Na^+ and K^+ [1]. Unfortunately, these imidazolates form dense and hypercoordinated structures. The coordinative demand of the metal cation increases with an increase of the ionic radii. The Li^+ cation exhibits a strong propensity to form heteroleptic structures, while the K^+ cation allows to coordinate the Im ring through the π-system.

Our next challenge was to obtain magnesium imidazolate ($MgIm_2$), which, based on the nature of Mg^{2+} as well as its coordination chemistry, was considered as a much more promising complexing agent in comparison with alkali metal cations. While, the freshly synthesized $MgIm_2$ was found to be amorphous, annealing at relatively high temperatures yields the crystalline and porous $MgIm_2$.

Herein, we present our results on the synthesis, characterization and some properties of newly obtained $MgIm_2$.

[1] D. A. Safin, K. Robeyns, N. A. Tumanov, V. Ban, Y. Filinchuk, *Dense Hypercoordinated vs. Porous ZIFs of Alkali and Alkaline Earth Metals: Single Source Precursors for Hybrid Borohydrides.* 42nd International Conference on Coordination Chemistry, July 3–8, 2016, Brest, France.

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MS37-P9 High-Pressure Guest Included Phase Transitions, Amorphisation and Negative Linear Compressibility on a Porous Copper-Based Metal Organic Framework

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Porous materials such as zeolites and porous organic polymers have long been considered good candidates for storing and separating molecules based on their size. More recently, metal organic frameworks (MOFs) have attracted further interest with many aspects of their functional and mechanical properties investigated.[1] The porous channels found in MOFs are ideal for the uptake of guests of different shapes and sizes, and with careful design they can show high selectivity for particular species from a mixture.[2] Adsorption properties of MOFs have been thoroughly studied,[3] however obtaining in depth 'structural' insight into the adsorption/desorption mechanism is not so common place.

Over the last 6 years, we have been using high-pressure crystallographic techniques to explore the uptake of guest species in the pores of MOFs. This is done by selecting a hydrostatic medium that can penetrate the pores on increasing pressure and has revealed unexpected flexibility,[4] explained unusual adsorption phenomena under milder gas pressures, and increased reactivity in MOFs.[5]

Here, we present a high-pressure and low-temperature crystallographic study on the Cu-based MOF, bis[1-(4-pyridyl)butane-1,3-dione]copper(II), (CuPyr-I) which crystallises in the rhombohedral space group *R*-3. Under ambient temperature and pressure, the structure of CuPyr-I is composed of Jahn-Teller distorted octahedral Cu-centres, which link via the dione linkers to form a one-dimensional porous framework material. On increasing pressure to 3.34 GPa using methanol as a hydrostatic medium, CuPyr-I undergoes an isosymmetric single-crystal to single-crystal phase transition which results in a doubling of the *a*- and *b*-axes, while the *c*-axis displays negative linear compressibility caused by a subtle twisting of the framework in order to accommodate the uptake of methanol into the pores. In comparison, on direct compression using a nonpenetrative hydrostatic medium (FC-70), amorphisation occurs above 1.60 GPa, with no associated phase transition.

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