

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 isomorphous 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 (MgIm₂), which, based on the nature of Mg²⁺ 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 MgIm₂ was found to be amorphous, annealing at relatively high temperatures yields the crystalline and porous MgIm₂.

Herein, we present our results on the synthesis, characterization and some properties of newly obtained MgIm₂.

[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.

Keywords: zeolitic imidazolate framework, magnesium imidazolate, porous structure, crystal structure, physical properties

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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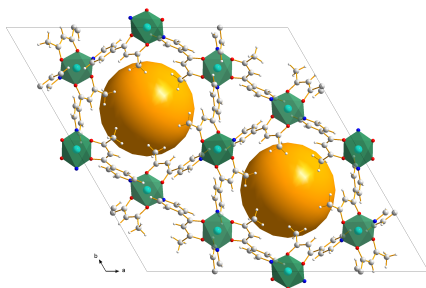


Figure 1. The ambient pressure structure of CuPyr-I viewed perpendicular to the *a*, *b* face. This is a one-dimensional porous material with large channels 9 Å in diameter at their widest point, shown in the figure by the orange spheres.

Keywords: MOF, High Pressure, Phase Transition

MS37-P10 Crystal structures of novel polydentate N,O-ligands

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Polydentate molecules are of growing interest as they are widely applied as scaffolds in the combinatorial synthesis of artificial receptors for ions with medical and environmental potential. Among the broad variety of synthetic molecules, polyazaoxa ligands have received special attention due to their outstanding coordination abilities. A particular goal involves the construction of ligands with an appropriate order and predictable arrangement of two or more molecular components with possibility to form hydrogen bonds, which play the pivotal role in molecular recognition by synthetic receptors.

Herein, we present a study on the crystal structures of a series of novel polydentate N,O-ligands possessing unsymmetrical urea fragments attached to a *p*-cresol scaffold. The compounds are obtained by a fast and simple protocol from *p*-cresol-based symmetrical bis-amine, phosgene, and primary amine. Their structures are assigned by 1D and 2D NMR spectra in solution and by single crystal XRD in solid phase. Ortep drawings of selected crystal phases are presented on Figure 1.

The ligands can be generally divided in two groups: open-chain substituted aromatics with at least one unsymmetrical urea unit (a) and fused aryloxazinones with unsymmetrical urea fragment (b). The concept is to design polydentate ligands with variable coordination abilities controlled by the difference in the molecule geometry.

The single crystal XRD analysis showed that the open-chain substituted molecules are oriented towards optimal intramolecular H-bonding of the ureas' heteroatoms, while the preferred geometry of oxazinones is driven by intermolecular bonding.

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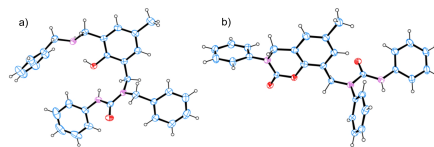


Figure 1. ORTEP drawings of selected samples

Keywords: polydentate N,O-ligands , singal crystal XRD