

**MS37-O3** Pressure induced chemisorption in isoreticular Metal Organic FrameworksPiero Macchi<sup>1</sup>, Arianna Lanza<sup>1</sup>, Luzia German<sup>1</sup>, Martin Fisch<sup>1</sup>, Nicola Casati<sup>2</sup>1. Department of Chemistry and Biochemistry, University of Bern  
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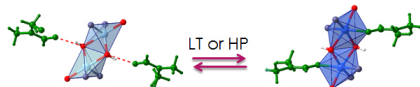
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MOFs with stereochemically accessible unsaturated metal centres may enable chemisorption of small molecules at the metal sites, to be distinguished from the classical physisorption occurring through weaker interactions between the guest and the internal active surface of the MOF.

Chemisorption and framework flexibility are desirable features for the design of promising catalysts, selective sieves or absorbents. Moreover, by varying metal centers, oxidation states, organic linkers, guest molecules, stereochemical features etc., the potential and complexity of MOFs can be tuned towards the desired properties. Efforts to rationalize the synthesis of frameworks with specific features would therefore benefit from comparative studies involving systematic variations of their structure, which can be induced by external stimuli (temperature, pressure) as well as chemical modifications.

In this work, we investigated the role of controlled structural modifications on the physico-chemical properties of a family of isostructural MOFs. We discuss here about isomeric, iso-reticular MOFs based on M<sup>II</sup> connectors (Co<sup>II</sup>, Zn<sup>II</sup> or Mn<sup>II</sup>) and benzotriazolide-5-carboxylato (btca) linkers that were found to selectively react with guest molecules (like methanol or dimethylformamide) trapped in the channels during the sample preparation or after an exchange process. A mild compression or cooling are enough to induce a reversible nucleophilic addition of the guest molecules to the metal ion. Depending on the guest or the metal, the coordination may increase stepwise up to saturation. A preliminary study on the CoII MOF was recently published.<sup>1</sup>

[1] Lanza, A.; Germann, L. S.; Fisch, M.; Casati, N.; Macchi, P. J. Am. Chem. Soc., 2015, 137, 13072–13078



**Figure 1.** Schematic representation of the ligand addition stimulated by the crystal contraction in  $[\text{Co}_3(\text{OH})_2(\text{btca})_3]$

**Keywords:** MOFs, high pressure crystallography, chemisorption

**MS37-O4** High-pressure effects in carbohydrate-based crystalsEwa Patyk<sup>1</sup>, Andrzej Katrusiak<sup>1</sup>

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Carbohydrates create one of the most important groups of organic compounds. Their diverse properties result in their wide application in various industries. Lately, a new group of metal-organic frameworks based on  $\gamma$ -cyclodextrin molecules ( $\gamma$ -CD-MOF) was introduced,<sup>1</sup> allowing new ways of implementation of carbohydrates. All sugars, regardless the size, share the same characteristic feature, *i.e.* multiple hydrogen donors and acceptors taking part in creation of extensive hydrogen-bond network. It was recently shown that even slight structural change in their unique code of hydroxyl groups can result in quite different high-pressure behavior and stability.<sup>2,3</sup> Yet, some of the observed pressure effects are consistent for all mono- and disaccharides studied till now.<sup>2-4</sup> The information gathered for simple carbohydrates can be of an importance when more complex systems build of well-known monosaccharides are investigated at high pressure. In this research a high pressure study of  $\gamma$ -CD-MOF was performed in order to determine its stability and compare its behavior with the  $\alpha$ -D-glucose.

For this study the Merrill-Bassett diamond–anvil cell<sup>5</sup> (DAC) was used. Either single crystals of the sample obtained at ambient conditions were placed in the DAC along with the cellulose fiber to fix its position, or it was recrystallized *in situ* at high pressure. In all cases a small ruby chip was placed inside the DAC to measure the pressure. All sample crystals were measured with 4-circle diffractometer and either X-ray or synchrotron radiation.

Collected data allowed to determine the pressure stability of both compounds and to investigate how extreme conditions influence their H-bonding pattern and aggregation, as well as to compare these effects in both systems.

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**Keywords:** high pressure, carbohydrates, glucose,  $\gamma$ -CD-MOF