Single crystal x-ray diffraction study of a bismuth metal-organic framework showing adaptive behaviour during the interaction of framework atoms with guest-molecules.

F. Esteban, P. Pena-Sánchez, E. Gutiérrez-Puebla, M. A. Monge, F. Gándara

Materials Science Institute of Madrid, Spanish National Research Council (ICMM-CSIC), Sor Juana Inés de la Cruz 3, Madrid, 28049, Spain

gandara@icmm.csic.es

Keywords: Bismuth, metal-organic frameworks, single-crystal to single-crystal transformation

The use of bismuth as metal center for the preparation of metal-organic frameworks, MOFs, is scarce despite the low toxicity and high abundance of this element. Recently, we have reported a new MOF synthesized with the use of bismuth and the organic linker 4,4',4'',4'''-methanetetrayltetrazenoic acid [1]. This microporous material, denoted BiPF-7, is highly robust and chemically stable, and it shows remarkable activity as heterogeneous Lewis acid catalyst for the Strecker reaction of ketones. Interestingly, this material exhibits an adaptive behavior to presence of different adsorbed molecules. Thus, with the use of single-crystal X-ray diffraction, we found that while the crystals are immersed in different catalytic substrates, the guest molecules interact with accessible bismuth sites, triggering a change in the coordination environment of metal atoms located in different parts of the framework. Currently, we are investigating the reversible nature of this structural change, as well as the different response of the material when in presence of various types of guest molecules. The single crystal x-ray diffraction study is showing that molecules with different size and polarity interact at similar position with the metal sites that are exposed in the pores, and that this interaction is responsible for an increase in the lattice cell volume, resulting from an enlargement in the distance between bismuth atoms, and the rearrangement of coordinated and hydrogen-bonded water molecules.

Figure 1. On the left, a view of the three-dimensional structure of BiPF-7 is shown. In the right, a representation of the interaction between guest molecules and bismuth atoms, with the associated changes in coordination environment of different metal sites. Bismuth atoms are drawn in polyhedral representation.