



	Experiment title: Limits of thermal stability of metal-organic framework structures	Experiment number: 01-02-1069
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Report:

Metal-organic framework (MOF) compounds are dimensionally extended structures consisting of metal or metal cluster centers that are linked by multidentate organic ligands. This interconnectivity can result in one-, two-, or three-dimensional networks.

Typically metal-organic framework synthesis is based on bridging metal ions or clusters by rigid polydentate organic linkers. Synthesis of permanently porous MOFs with flexible linkers is often a challenge because the flexibility of the linkers might lead to structural rearrangement and loss of porosity when the guest molecules are removed from the pores. We synthesized a series of MOFs based on a 4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzoic acid which contains two asymmetric carbon atoms and a large degree of conformational freedom. These new structures were labelled CPO-49-Zn and CPO-49-Mn, corresponding to the metal ion used in the synthesis and reflecting the fact that the two compounds are isostructural.

Carboxylate groups are usually coordinated to the metal in MOF structures, but in the case of CPO-49, both hydroxyl groups are coordinated to the metal ion in addition to the carboxylate ion, resulting in formation of a 3D network with 1D channels. It is important to note, that even with flexible linker employed, both Zn and Mn frameworks are permanently porous after solvent exchange and removal on activation. However, the compounds showed different behavior upon N₂ adsorption. The high stability of the framework allowed us to determine the single crystal X-ray structure of desolvated CPO-49-Mn framework, in which the loss of coordinated solvent leads to a change in coordination mode of a carboxylate group (Figure 1, left).

Knowledge of the temperature range in which a porous framework is stable and of possible phase changes occurring therein is essential for determination of the structure-property relationships of the MOF and evaluation of its usefulness in various application areas. Thermogravimetric analysis of CPO-49-Mn and Zn showed stepwise mass loss of solvent. The desolvated compound appeared to be stable up to 400-450°C. However, TGA does not provide any information on the crystallinity of the framework on heating. For this reason we performed variable temperature powder X-ray diffraction of CPO-49-Mn and Zn at the BM01A station at the SNBL@ESRF (Figure 1, right).

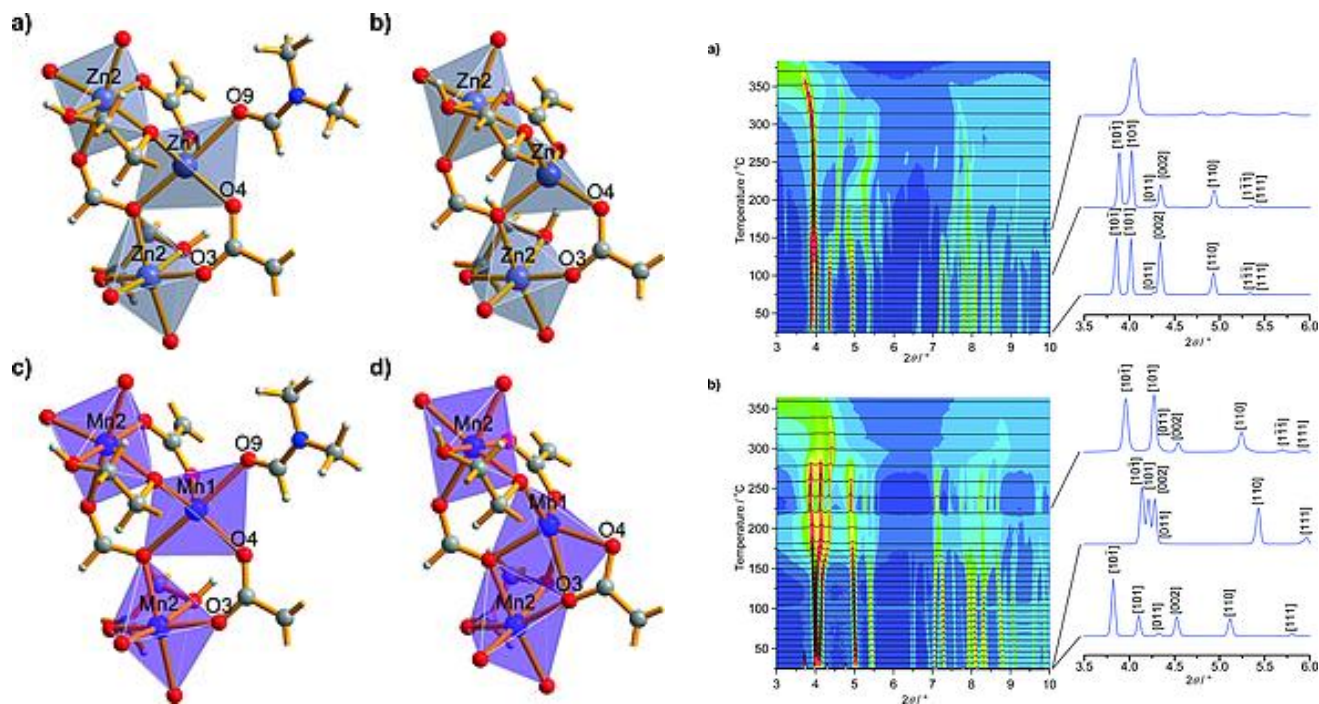


Figure 1. Left: Coordination environment of the two crystallographically unique transition metal atoms in a) as-synthesized CPO-49-Zn, b) desolvated CPO-49-Zn, c) as-synthesized CPO-49-Mn, d) desolvated CPO-49-Mn; Right: Variable temperature powder X-ray diffraction plot of a) CPO-49-Zn in Ar flow, b) CPO-49-Mn in He flow.

The results of this investigation were disseminated in

A. A. Bezrukov, K. W. Törnroos, P. D. C. Dietzel, “Variation of desolvation behaviour in two isostructural metal-organic frameworks based on a flexible, racemic bifunctional organic linker”, *Eur. J. Inorg. Chem.* **2016**, in press, doi: 10.1002/ejic.201600681.

Abstract

A racemic mixture of the chiral ligand 4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzoic acid was used to prepare two isostructural metal-organic frameworks, CPO-49-Zn and CPO-49-Mn, which contain coordinated solvent molecules at the metal site. The compounds showed different behavior upon desolvation. The dissociation of the solvent molecule from the metal site leads to a single-crystal-to-single-crystal transformation. In CPO-49-Zn, a change of coordination geometry from trigonal bipyramidal to tetrahedral occurs at the zinc atom. In CPO-49-Mn, a rearrangement of coordination mode of a carboxylate group occurs instead, leading to a 4+1 coordination of the manganese cation in the form of a capped distorted tetrahedron. N₂ gas adsorption confirms that both desolvated structures are permanently porous. The behavior of the compounds upon heating has also been studied using variable temperature powder X-ray diffraction. The presence of a coordinated solvent molecule in the as-synthesized structures indicates the possibility to access the metal cation with reactive substrates. Both materials were evaluated in the catalytic oxidation of styrene. CPO-49-Mn showed significantly higher conversion than the CPO-49-Zn material.