



Fig. 1: The Zn(II) MOF with channels viewed along [0 0 1]

[1] S. Horike, S. Shimomura, S. Kitagawa, *Nature Chemistry* **2009**, *1*, 695-704.

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### Uncovering the action behind negative thermal expansion in MOF-5

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Materials with properties with zero or low temperature dependence find widespread applications ranging from electronic devices to dental fillings. Negative thermal expansion (NTE) materials are compounds which contract with increasing temperature. This is in contrast to most materials, which exhibit positive thermal expansion (PTE). Composites of PTE and NTE materials can be engineered to possess specific expansion properties. Understanding the mechanism behind thermal expansion on an atomic level is crucial for tailoring properties.

PTE is caused by the anharmonicity of the chemical bond potential. In NTE materials, a physical mechanism - often of vibrational character - overrules the PTE. Vibrational NTE is typically observed in flexible and porous covalent structures, which can partly absorb thermal energy as vibrational motion perpendicular to the bond direction *i.e.* as transverse motion. Such motions are known to cause NTE in some oxides and cyanides. In these compounds oxygen atoms or cyanide groups link together the metal atoms. NTE was recently discovered in some metal-organic frameworks (MOF) including the archetype coordination polymer MOF-5 ( $Zn_4O(1,4\text{-benzenedicarboxylate})_3$ ) [1] and  $Cu_3(1,3,5\text{-benzenetricarboxylate})_2$  [2,3].

Our initial studies of MOF-5 used single-crystal and powder X-ray diffraction [1]. These results have been backed up by powder and single-crystal neutron diffraction data covering the temperature range 4-400 K to obtain a more detailed picture of the NTE mechanism especially with respect to the thermal motion of the hydrogen atoms. Additionally, the metal center motion was selectively probed using X-ray absorption spectroscopy (XAS) to contrast time- and position-averaged diffraction data. The complementary findings from diffraction and XAS are shown in this presentation. Powder diffraction data reveal near-linear NTE over the temperature range 20-500 K. The vibrational motions in MOF-5 were obtained from multi-temperature single-crystal neutron Laue diffraction data (4-300 K) through extraction of positional and vibrational parameters. The exact same crystal was used in a complementary single-crystal X-ray diffraction experiment covering the temperature range 100-300 K. The crystal was a solvent-free single crystal packed in a sealed glass capillary under vacuum.

There is good overall agreement between the studies showing that NTE in MOF-5 is due to (1) concerted transverse motion of the benzenedicarboxylate linkers and (2) local motion of the metal centers. Analysis of the temperature dependent atomic displacement parameters indicates that a lattice contracting transverse motion of the aromatic ring perpendicular to the unit cell axis is significantly populated below 20 K, whereas local NTE motions of the carboxylate group become populated at slightly higher temperatures.

[1] N. Lock, Y. Wu, M. Christensen, L. J. Cameron, V. K. Peterson, A. J. Bridgeman, C. J. Kepert, B. B. Iversen, *J. Phys. Chem. C* **2010**, *114*, 16181-16186. [2] Y. Wu, A. Kobayashi, G. J. Halder, V. K. Peterson, K. W. Chapman, N. Lock, P. D. Southon, C. J. Kepert, *Angew. Chem. Int. Ed.* **2008**, *47*, 8929-8932. [3] V. K. Peterson, G. J. Kearley, Y. Wu, A. J. Ramirez-Cuesta, E. Kemner, C. J. Kepert, *Angew. Chem. Int. Ed.* **2010**, *49*, 585-588.

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### Structural analysis of metal organic frameworks with perovskite-like structure

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Hybrid materials that combine inorganic and organic components and that contain cavities and channels –the so-called metal organic frameworks (MOFs)– have been extensively studied in the last decade in view of their interesting potential applications, for example, in catalysis and gas storage [1]. In addition to nanoporous MOFs, dense hybrid framework structures have also been discovered and are receiving increasing attention as they can display a wide range of interesting functional properties [2].

A most interesting example is the recently discovered family of MOFs that crystallize in the perovskite architecture, and that display weak ferromagnetism [3], dielectric properties [4] and even multiferroic behavior [5].

As it is well-known, the “conventional” perovskite structure, of general formula  $ABX_3$  (A= lanthanide, alkaline-earth cations, etc.; B= transition metal cations; X=  $O^{2-}$ ,  $S^{2-}$ , halide ions, etc.) consists of a three-dimensional array of corner sharing  $[BX_6]$  octahedra with the larger A cation occupying the 12-coordinated cubooctahedral cavities of the 3D network. Such structure is the basis of many transition metal mixed oxides with very outstanding properties (high  $T_c$  superconductivity, colossal magnetoresistance, ferroelectricity, charge ordering, non-linear optical behaviour, catalytic properties, etc.) and extensive work has allowed to establish important structure-properties relationships.

As for the much less explored MOF compounds with perovskite architecture, up to now, all of them contain the formate ion  $HCOO^-$  in the X site, an amine cation in the A site, while different divalent cations, as  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$  and  $Mg^{2+}$  can occupy the B site [6].

In this work, and by analogy with the “conventional” perovskite, we try to find and establish systematic trends in the structural characteristics and distortions displayed by these perovskite MOFs and that can be useful to understand and even predict the properties of these compounds.

For this purpose we present a thoroughly structural analysis that we have made on two series of compounds, namely:  $M(HCOO)_3[(CH_3)_2NH_2]$  ( $M^{2+}$ :  $Mn^{2+}$  to  $Zn^{2+}$ ) and  $Mn(HCOO)_3[RH^+]$  (where R is an amine), and that allow us to rationalize the different parameters that control the resulting structure.