

The experiments we have carried out with these compounds in gel media demonstrate the formation of different and new structures, even in the same U-tube (see Figure). This kind of experiment shows the possibility to tune the conditions to prepare new phases of these coordination polymers.

[1] L. Carlucci, G. Ciani, J.M. García-Ruiz, M. Moret, D.M. Proserpio, S. Rizzato, *Crystal Growth & Design* **2009**, *9* (12), 5024–5034. [2] C. Daiguebonne, A. Deluzet, M. Camara, K. Boubekeur, N. Audebrand, Y. Gérault, C. Baux, O. Guillou, *Crystal Growth & Design* **2003**, *3* (6), 1015–1020. [3] L.-P. Hsu, J.-Y. Wu, K.-L. Lu, *J.Inorg.Organomet.Polym.Mater.* **2007**, *17* (1), 259-265. [4] F. A. Almeida Paz, Y.Z. Khimyak, J. Klinowski, *Acta Cryst.* **2003**, *E59*, m8-m10.

Keywords: gel media, crystal growth, coordination polymers.

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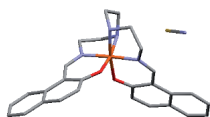
New iron (III) two-step spin crossover compounds

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In recent years researcher's developed an effort to obtain molecular-based functional materials exhibiting properties of technological interest. Spin Crossover (SCO) emerges as a very powerful tool to be employed in such research.

In octahedral ligand fields, transition metal ions with d4-d7 configuration can assume a high-spin (HS) or a low-spin (LS) electronic arrangement, depending if the crystal field energy is lower or higher than the main spin pairing energy. In some of these cases bistability can take place, i.e. LS-HS transitions occur at different temperatures, they can be gradual or occur abruptly, eventually with an hysteresis loop. These materials possess increased interest in view of their possible application as display, memory and switching devices [1,2].

The two-step spin crossover of a new iron(III) compound [Fe^{III}(Nst)]SCN is studied by magnetic and crystallographic methods revealing two spin transitions with an ordered intermediate phase built by the repetition of the [HS-LS] motif. Crystallographic data were collected on a single crystal temperatures between ; 50 and 294K. The structures collected at 50, 150 and 294 K are reported here.



[1] P. Gütllich, A. Hauser, H.C. Spiering, *Angew. Chem. Int. Ed.* **1994**, *33*, 2024. [2] J.A. Real, A.B. Gaspar, M.C. Munoz, *J Chem. Soc. Dalton Trans.* **2005**, 2062 .

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Solid-state synthesis and structure solution of chiral co-crystals and salts

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Co-crystallization provides a new strategy for altering the chemical and physical properties of molecular solid forms. The possibility of co-crystallization has to take into account the competition with kinetic factors associated with the nucleation stage of the crystallization processes. A way to overcome the thermodynamic-kinetic dualism is the "solvent-free" condition. It has also been shown that, in some systems, chiral recognition can affect solid state reactions just as it does in solution chemistry, and that products of grinding and solution experiments can be different [1],[2].

In the present work we make use of solution experiments and mechano-chemical techniques to obtain co-crystals or salts of chiral compounds [3]. For this purpose, serine(-), serine(+), serine-/+ and dicarboxylic acids were chosen as starting materials. Salts and co-crystals obtained were studied by single-crystal and powder X-ray diffraction methods, showing the formation of different polymorphs depending on the synthetic method (crystallization from solution, grinding or kneading). The new salts were also studied by thermal analysis (DSC, TG) and variable-temperature X-ray powder diffraction to check their thermal stability.

[1] R. Kuroda, Y. Imai and T. Sato, *Chirality* **2001**, *13*, 588; [2] S. Chen, H. Xi, R. F. Henry, I. Marsden and G. G. Z. Zhang, *CrystEngComm* **2009**, *11*,427; [3] D. Braga, F. Grepioni and G. I. Lampronti, *CrystEngComm* **2011**, Advance Article DOI: 10.1039/C0CE00576B

Keywords: polymorphism, X-ray, amino acids

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Single-crystal to single-crystal transformations of a flexible porous Zn(II) framework

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Host-guest complexation by metal-organic frameworks (MOF's) is a highly topical area of research owing to applications in storage, separation and delivery of guest molecules. In particular, dynamic frameworks with guest responsive properties are essential for improved selectivity and controlled uptake and storage purposes [1]. Guest removal and exchange processes often result in collapse of a host framework and/or loss of the single-crystal quality of the material. In exceptional cases, these processes occur as single-crystal to single-crystal transformations that can be studied directly using single crystal X-ray diffraction.

Our investigation centers on the permanent porosity and exchange of guest molecules, by a three-dimensional Zn(II) MOF ([Zn(L)₂(H₂O)₂]CH₃OH, see Fig. 1) that has well-defined one-dimensional, square-shaped channels. Significant structural changes occur when the host framework accommodates different guest molecules whilst retaining its single crystal-nature.

The MOF consists of two-dimensional layers or nets stacked on top of one another and interconnected by polymeric metal-water-metal coordination. The as-synthesized framework includes methanol molecules hydrogen bonded to the framework. The crystals are remarkably robust and remain transparent following removal of the methanol molecules at 150°C under reduced pressure. A series of exchange experiments were carried out, all of which occurred *via* a single-crystal to single-crystal process.

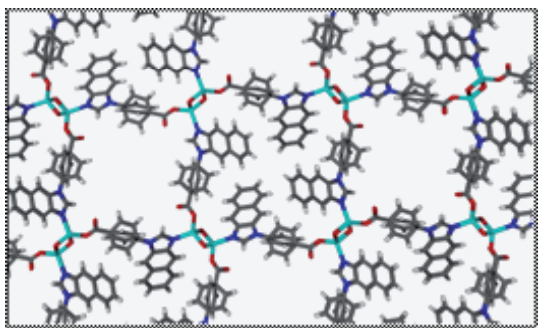


Fig. 1: The Zn(II) MOF with channels viewed along [0 0 1]

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

Keywords: host-guest, metal-organic framework, porosity

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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.

Keywords: metal-organic frameworks, negative thermal expansion, neutron diffraction

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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.