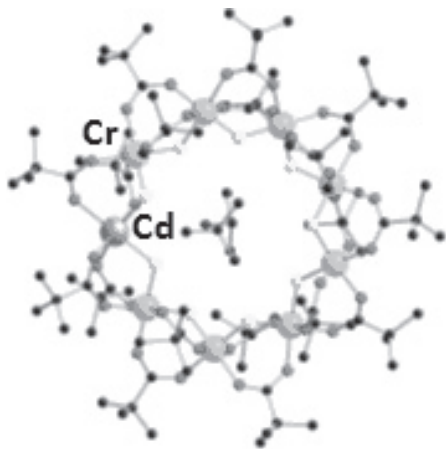


the ring which is interrupted by a diamagnetic Cd^{2+} ion [1] (see figure below).



Antiferromagnetic coupling between first nearest neighbors Cr^{3+} ions, via the bridging organic ligands, leads to a singlet spin ground state $S_{\text{tot}} = 0$ and to excited states with integer spin values $S_{\text{tot}} = 1, \dots$. Application of a high magnetic field at low temperature induces a lifting of degeneracy of the excited states and the existence of $S_{\text{tot}} \neq 0$ spin states with lower energy than the $S_{\text{tot}} = 0$ zero-field ground state.

The experimental induced spin density in two different states ($S_{\text{tot}} = 1$) and ($S_{\text{tot}} = 2$), reached by applying a field of 4.6 and 9 Tesla respectively, was determined from polarised neutron diffraction measurements on a single crystal at 2K (D3, ILL and 5C1, LLB). A non-uniform distribution of the induced magnetic moments on the Cr^{3+} finite chain is observed, with accumulation of positive spin density at the extremities of the chain.

[1] Y. Furukawa, K. Kiuchi, K. Kumagai, Y. Ajiro, Y. Narumi, M. Iwaki, K. Kindo, A. Bianchi, S. Carretta, G.A. Timco, R.E.P. Winpenny, *Phys. Rev. B* **2008**, 78, 092402.

Keywords: spin, density, neutron

MS.66.5

Acta Cryst. (2011) **A67**, C151

Interplay between structure and functional properties in spin crossover frameworks

Natasha F. Sciortino,^a Gregory J. Halder,^{a,b} Boujemaa Moubaraki,^c Keith S. Murray,^c Jean-François Létard,^d Cameron J. Kepert,^a ^a*School of Chemistry, University of Sydney, Sydney, (Australia)*. ^b*Materials Science Division, Argonne National Lab, Illinois, (USA)*. ^c*School of Chemistry, Monash University, Melbourne, (Australia)*. ^d*Laboratoire des Sciences Moléculaires CMCB, CNRS, Université Bordeaux, Bordeaux, (France)*. E-mail: sciort_n@chem.usyd.edu.au

The recent integration of spin-crossover capabilities (electronic spin-state switching) into nanoporous metal-organic framework materials (MOFs) gives rise to a unique molecular scenario where factors that govern the switching responses to external perturbations (e.g. magnetic field, temperature, pressure, light, and guest/chemical environment) are newly intertwined with factors governing structure-function relationships and host-host/host-guest chemistry [1]. Consequently, these nanoporous spin-crossover MOFs display rare and unprecedented synergistic structure-function properties that offer a new opportunity to develop advanced 'smart' materials capable of a dynamic response to their environment. For example, molecular sensing capabilities become realised when chromic, electronic and magnetic switching properties characteristic of spin-crossover materials can be

reversibly and selectively controlled on the molecular level by specific host-guest interactions.

Here we present a porous bimetallic spin-crossover framework material with an unprecedented 3D Kagome-type topology, $[\text{Fe}(\text{dps})\text{Ag}(\text{CN})_2](\text{ClO}_4)\text{-guest}$ (where dps = 4,4'-dipyridylsulfide) which exhibits a unique structural response to spin-crossover in addition to spin-crossover behaviour that is responsive to guest- and light-induced perturbations. The framework lattice, comprising hexagonal and triangular helices with the Fe(II) centres at the vertices, contains a network where no simple alternating arrangement of high-spin (HS) and low-spin (LS) Fe(II) sites can occur, creating a molecular scenario loosely analogous to magnetically frustrated materials. Consequently, an interplay between electronic spin-state switching with both internal host-guest pressure and geometric frustration effects manifests as a volume-quadrupling structural modulation. Furthermore, the extended family of isostructural analogues $[\text{Fe}(\text{dpX})\text{M}'(\text{CN})_2](\text{ClO}_4)\text{-guest}$ (where X = S or Se, and $\text{M}' = \text{Ag}^+$ or Au^+) unexpectedly display identical magnetic properties despite elemental substitutions at the chalcogen and/or M' positions. This unorthodox behaviour can be interpreted as another facet of the structure function-relationship.

To the best of our knowledge, the physical realization of a true 3D Kagome-type topology, the structure-function relationship of a modulation arising from a complex 3D ordering of HS-LS Fe(II) sites and the apparent insensitivity of the spin-crossover behavior of a material to elemental substitutions have not been reported to date. Thermo-chromic, optical and photomagnetic phenomena as well as the large porous architecture with host-guest specific properties also add to the multifunctionality displayed by this series of framework materials.

[1] P.D. Southon, L. Liu, E.A. Fellows, D.J. Price, G.J. Halder, K.W. Chapman, B. Moubaraki, K.S. Murray, J.-F. Létard, C.J. Kepert, *Journal of the American Chemical Society* **2009**, 131, 10998-11009.

Keywords: spin-crossover, metal-organic framework, modulation

MS.67.1

Acta Cryst. (2011) **A67**, C151-C152

News from the world of eni carbon silicate (ECS) materials

Roberto Millini, *eni s.p.a. – refining & marketing division, San Donato Milanese Research Center, Via F. Maritano 26, I-20097 San Donato Milanese (Italy)*. E-mail: roberto.millini@eni.com

ECS (Eni Carbon Silicate) materials form a new class of crystalline organic-inorganic hybrid aluminosilicates recently discovered in eni's laboratories [1]. Synthesis of ECSs resembles that of zeolites, involving the hydrothermal treatment at 100°C of a reaction mixture being composed by NaAlO_2 as source of alumina, NaOH and/or KOH, demineralized water and a bis-trialkoxysilylated organic precursors of general formula $(\text{R}'\text{O})_2\text{Si}-\text{R}-\text{Si}(\text{OR}')_2$ (R = alkyl, aromatic or alkyl-aromatic moiety; $\text{R}' = \text{Me}$ or Et) as source of silica.

A set of ECS materials has been synthesized so far, by appropriately varying the nature of the bis-silylated precursor and the synthesis conditions. The extensive physico-chemical characterization of these materials demonstrated that most part of the silica precursors do not undergo Si-C hydrolysis and are kept unchanged in the crystalline phase. Only trace amounts of conventional, low-silica zeolite phases (e.g. Sodalite, Na-P1) were occasionally found as by-products.

The determination of the crystal structure of some ECS materials was fundamental for clarifying their properties. The structural characterization of these materials proved to be a challenging problem because of the complexity of the X-ray powder diffraction patterns and even for the impossibility to grow samples suitable for single crystal data collection. In spite of that, for some ECS phases the structure