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 \(S_{\text{tot}} = 1, 2, 3\).

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 polarized 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.


**Keywords:** spin, density, neutron

**MS.66.5**


**Interplay between structure and functional properties in spin crossover frameworks**

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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 be realised when chronic, 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, [Fe(dpX)Ag(CN)]\(_2\)(ClO\(_4\))\(_2\)\(_{\text{guest}}\) (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 helicities 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 [Fe(dpX)M(CN)]\(_2\)(ClO\(_4\))\(_2\)\(_{\text{guest}}\) (where X = S or Se, and M\(^{2+}\) = Ag\(^+\) or Au\(^+\)) unexpectedly display identical magnetic properties despite elemental substitutions at the chalcogen and/or M\(^{2+}\) 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.


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

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

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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 (RO)\(_2\)Si–R–Si(OR')\(_2\) (R = alkyl, aromatic or alkyl-aromatic moiety; R' = 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

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