

superconducting ground state,  $\lambda'$ -BETS<sub>2</sub>GaBr<sub>4</sub> exhibited an insulating transition at about 50 K below which the susceptibility decreased with lowering temperature (after the subtraction of the contribution from Curie impurities), indicating the non-magnetic insulating ground state. The low-temperature resistivity behavior exhibited a fairly large sample-dependence probably due to the relatively low stability of  $\lambda'$ -BETS<sub>2</sub>MBr<sub>4</sub> (M=Ga, Fe). Recently it was confirmed that the MI transition (of good quality crystal) was suppressed at around 3 kbar but no indication of superconducting transition was observed at least down to 4.2 K. We are now examining analogous system  $\lambda'$ -BETS<sub>2</sub>FeBr<sub>4</sub>, which exhibited an electrical behavior quite similar to that of  $\lambda'$ -BETS<sub>2</sub>GaBr<sub>4</sub>.

For the last decade, we have developed various single-component molecular metals based on the transition metal complexes with extended-TTF ligands [5]. To our best knowledge, [Au(tmdt)<sub>2</sub>] is the first molecular metal where magnetic order and metallic electrons coexists above 100 K. We are now trying to develop single-component molecular conductors with diluted paramagnetic molecules (Cu(tmdt)<sub>2</sub>), [Ni<sub>1-x</sub>Cu<sub>x</sub>(tmdt)<sub>2</sub>] (molecular Kondo alloy).

Besides the magnetic molecular conductors, we are examining the dielectric properties of molecular crystals such as coordination polymer complexes and classical charge transfer complexes, which will be also briefly mentioned.

[1] A. Kobayashi, T. Udagawa, H. Tomita, T. Naito, H. Kobayashi, *Chem. Lett.* **1993**, 2179-2182. [2] H. Kobayashi, H. Cui, A. Kobayashi, *Chem. Rev.* **2004** *104*, 5265-5288. [3] H. Akiba, S. Nakano, Y. Nishio, K. Kajita, B. Zhou, A. Kobayashi, H. Kobayashi, *J. Phys. Soc. Jpn.* **2009**, *78*, 033601. [4] H. Tanaka, A. Kobayashi, H. Kobayashi, *Chem. Lett.* **1999**, 133-134. [5] A. Kobayashi, E. Fujiwara, H. Kobayashi, *Chem. Rev.* **2004**, *104*, 5243-5264.

**Keywords:** magnetic molecular conductor, single-component molecular metal, dielectric property

## MS.66.3

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### Jahn-teller effect and ferroelectric phase transition in a metal-organic complex

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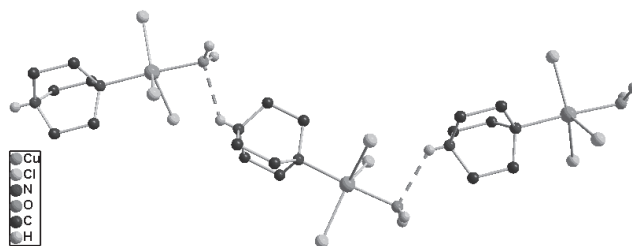
A Jahn-Teller-distorted version of the ABO<sub>3</sub>-type structures like A = organic cation, B = Cu<sup>2+</sup>, Ni<sup>2+</sup> and Mn<sup>2+</sup>, and O = halogen has been widely investigated due in part this effect resulting in the formation of structural phase transition. Most of cases exhibiting ABO<sub>3</sub>-type structures with phase transition are octahedron situation. For example, in the copper(II) salts, the octahedra assumes a tetragonally elongated [4 + 2] coordination geometry such that each Cu<sup>2+</sup> ion has four short (~2.3Å) and two long (2.8–3.2Å) Cu–Cl bonds.

In our case [(Hdbco)CuCl<sub>3</sub>(H<sub>2</sub>O)] (**1**, dbco = 1,4-diazabicyclo[2.2.2]octane), the coordination geometry of the Cu(II) is a distorted trigonal bipyramidal with one oxygen atom and N atom of monoprotonated Hdbco occupying the axial positions while three Cl anion is composed of a equatorial plane. Interestingly, strong H-bonds through a proton H<sup>+</sup> on N of dbco can be formed between H<sup>+</sup> and one of coordinated H<sub>2</sub>O to result in the formation of 1D zigzag chain (Figure). The crystal structure of **1** at room temperature belongs to a centrosymmetric space group *Pnma* (D<sub>2h</sub>) and a distorted Hdbco is found in this situation.

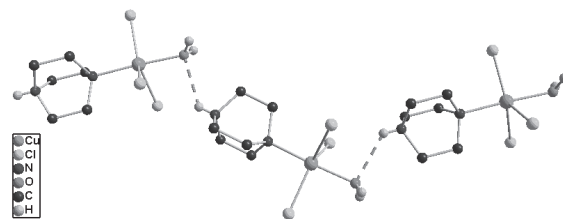
After the temperature decreases down to 80 °C, the crystal structure determination of **1** still belongs to an orthorhombic crystal system but with a noncentrosymmetric space group of *Pna2<sub>1</sub>* (C<sub>2v</sub>) which belongs to a ferroelectric phase. In the solid state structure of **1** below *T<sub>c</sub>* the distorted [Hdbco] cation clearly becomes more regular while the

central Cu atom in **1** becomes a relatively-regular trigonal bipyramidal coordinated environment. Typical bond length changes of Cu–Cl both in paraelectric and ferroelectric phases suggest that a similar Jahn-Teller effect-like distortion may exist in the case of **1**.

Thus, in the cooling process symmetry breaking takes place with an Aizu notation of *mmmFmm2*, that is, the eight symmetric elements (e, 3C<sub>2</sub>, i, 3σ) at the paraelectric phase (above 236 K) are halved into four (e, C<sub>2</sub>, 2σ) owing to the loss of the symmetric elements 2C<sub>2</sub>, i and σ, which is attributed to a typical second-order feature according to Landau phase transition theory.<sup>[1-7]</sup>



A round-like peak in specific heat curve appears at ca. 231 K, manifesting the presence of a typical second-order phase transition like that of triglycine sulfate. The large value of dielectric constant around *T<sub>c</sub>* (Figure) and a good dielectric hysteresis loop just below *T<sub>c</sub>* all suggest that the phase transition should be a ferroelectric one.



[1] R.-G. Xiong, et al, *J. Am. Chem. Soc.* **2009**, *131*, 12544. [2] R.-G. Xiong, et al, *J. Am. Chem. Soc.* **2010**, *132*, 7300. [3] R.-G. Xiong, et al, *Chem. Soc. Rev.* **2011**, DOI: 10.1039/c0cs00226g. [4] Z.-M. Wang, S. Gao, et al, *J. Am. Chem. Soc.* **2010**, *132*, 9588. [5] R.-G. Xiong, et al, *Inorg. Chem. Commun.* **2010**, *13*, 1590. [6] R.-G. Xiong, et al, *Coord. Chem. Rev.* **2009**, *253*, 2980. [7] W. Zhang, R.-G. Xiong, et al, *Angew. Chem. Int. Ed.* **2010**, *49*, 6608.

**Keywords:** copper, Jahn-Teller, ferroelectric

## MS.66.4

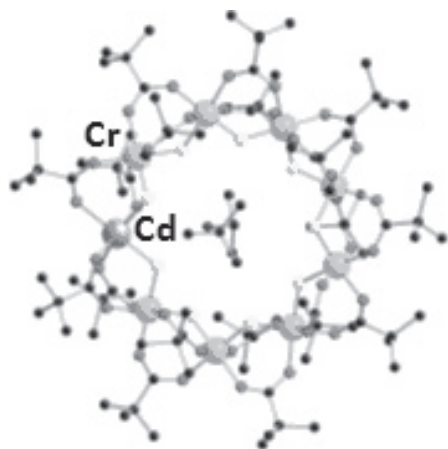
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### Finite size effects in a quantum chain of antiferromagnetically coupled spins 3/2

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Molecular nanomagnets are isolated magnetic systems formed by a finite number of magnetic atoms which present therefore quantum effects in contrast to classical systems with infinite size. The molecular wheel [Cr<sub>8</sub>Cd] of nanometric size provides a model of a finite antiferromagnetic chain of spins 3/2 carried by the eight Cr<sup>3+</sup> ions in

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



Antiferromagnetic coupling between first nearest neighbors  $\text{Cr}^{3+}$  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  $\text{Cr}^{3+}$  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.

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## MS.66.5

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### 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 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  $\text{Au}^+$ ) unexpectedly display identical magnetic properties despite elemental substitutions at the chalcogen and/or  $\text{M}'$  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.

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

## MS.67.1

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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  $\text{NaAlO}_2$  as source of alumina, NaOH and/or KOH, demineralized water and a bis-trialkoxysilylated organic precursors of general formula  $(\text{R}'\text{O})_3\text{Si-R-Si}(\text{OR}')_3$  (R = alkyl, aromatic or alkyl-aromatic moiety;  $\text{R}' = \text{Me}$  or  $\text{Et}$ ) 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