## Microsymposia

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 bahavior 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 crtystal) was suppressed at around 3 kbar but no indication of superconducting transition was observed at least down to 4.2 K. We are now examinintg 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 transtion metal complexes with extended-TTF ligands [5]. To our best knowledge, [Au(tmdt)<sub>2</sub>] is the first molecular metals 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.

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Keywords: magnetic molecular conductor, single-component molecular metal, dilectric property

#### MS.66.3

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

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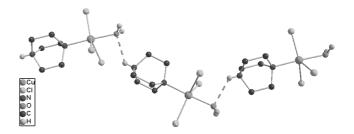
A Jahn-Teller-distorted version of the ABO<sub>3</sub>-type structures like A = organic cation, B =  $Cu^{2+}$ ,  $Ni^{2+}$  and  $Mn^{2+}$ , and O = halogen has been widely investigated due in part this effect resulting in the formation of structural phase transition. Most of cases exhibiting ABO<sub>3</sub>-type structures with phase transition are octahedron situation. For example, in the copper(I1) salts, the octahedra assumes a tetragonally elongated [4 + 2] coordination geometry such that each  $Cu^{2+}$  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.

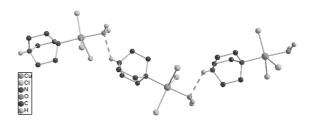
After the temperature decreases down to 80 °C, the crystal structure determination of 1 still belongs to an orthorhombic crystal system but with a noncentrosymmetric space group of  $Pna2_1$  ( $C_{2v}$ ) which belongs to a ferroelectric phase. In the solid state structure of 1 below Tc the distorted [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,  $3C_2$ ,i,  $3\sigma$ ) at the paraelectric phase (above 236 K) are halved into four (e,  $C_2$ ,  $2\sigma$ ) owing to the loss of the symmetric elements  $2C_2$ , i and  $\sigma$ , 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 *Tc* (Figure) and a good dielectric hysteresis loop just below *Tc* 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

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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  $[Cr_8Cd]$  of nanometric size provides a model of a finite antiferromagnetic chain of spins 3/2 carried by the eight  $Cr^{3+}$  ions in