



Contribution ID: 11

Type: **Short oral presentation**

Halogen sensitive spin crossover in Mn (III) cation complex with electroactive TCNQ anion

We present the synthesis, crystal structure, electric and magnetic properties of the spin-crossover salt $[\text{Mn}(5\text{-Cl-sal-N-1,5,8,12})\text{TCNQ}1.5(2\text{CH}_3\text{CN})]$, (I), containing distinct conductive and magnetic blocks along with the solvent acetonitrile molecules. As a magnetic unit it employs the Mn (III) ion with Schiff base ligands $[\text{Mn}(5\text{-Cl-sal-N-1,5,8,12})\text{ClO}_4]$ while the conducting unit is the π -electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ). The title compound (I) exhibits the semiconducting behavior with room temperature conductivity $RT = 2 \cdot 10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$ and activation gap $E_a = 0.21 \text{ eV}$. In the range 73 - 123 K, it experiences hysteretic phase transition accompanied by a crossover between low spin $S = 1$ and high spin $S = 2$ states of Mn (III) ions and sharp changes in bond lengths within MnN_4O_2 octahedra. The pronounced shrinkage of basal Mn - N bonds at the spin crossover in (I) suggests that the $d_{x^2-y^2}$ orbital is occupied/deoccupied at this transition. Interestingly, the Br isostructural counterpart $[\text{Mn}(5\text{-Br-sal-N-1,5,8,12})\text{TCNQ}1.5(2\text{CH}_3\text{CN})]$, (II), of the title compound evidences no spin-crossover phenomena, cf. Fig. 1 and Fig. 2. The comparison of Cl and Br compounds allows distinguishing the thermal and spin-crossover contributions to the overall bond lengths variation. The difference in behavior of these salts is ascribed to enhanced anharmonicity of the stretching Mn - N vibrations due to the mixing with bending N - C - Cl vibrations in (I) as compared to the mixing with N - C - Br vibrations in (II). The only difference between (I) and (II) compounds concerns the mass of the halogen ions. The spin-crossover in (I) must be assigned to a mode which has mixed character due to the overlap of stretching Mn - N vibrations and bending N - C - Cl vibrations.

Primary author: Dr MAXIMOVA, Olga (National University of Science and Technology "MISIS", Lomonosov Moscow State University)

Co-authors: Dr KAZAKOVA, Anna (Institute of Problems of Chemical Physics); Prof. YAGUBSKII, Eduard (Institute of Problems of Chemical Physics); Dr KORCHAGIN, Denis (Institute of Problems of Chemical Physics); Prof. ZVEREV, Vladimir (Institute of Solid State Physics)

Presenter: Dr MAXIMOVA, Olga (National University of Science and Technology "MISIS", Lomonosov Moscow State University)