Spin-Peierls transition in genuine organic TCNQ salt with pyrazine-based cation (N-Me-2,5-di-Me-Pz)(TCNQ)$_2$

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Abstract. The magnetic susceptibility measurements in the temperature range from 2 K to 300 K have been performed on a novel genuine organic TCNQ salt (N-Me-2,5-di-Me-Pz)(TCNQ)$_2$. Based on previous study of similar material spin-ladder like behaviour was expected. However, obtained experimental data are analyzed in terms of the Heisenberg linear chain model. Transition with spin-Peierls features occurs due to the peculiarities of crystalline structure.

1. Introduction
Charge transfer complexes have exhibited considerable multitude of physical attributes, such as insulating, semiconducting, metallic or superconducting behavior, attended by a large variability of magnetic ordering phenomena, that makes them highly suitable for practical applications. Organic donor-acceptor radical-ion charge-transfer salts are molecular compounds in which the ionization potential of the donor molecule is relatively small and electron affinity of the acceptor molecule is relatively large. The result is a charge-transfer salt with unpaired electrons appearing on the acceptor or donor, or on both. The existence of unpaired electrons in the lowest unoccupied molecular orbitals (LUMO) allows such a system to be potentially a magnetic insulator or a metal, depending on the crystal structure, the strengths of the various interactions involved, and the temperature.

The most interesting systems studied so far have been based on the acceptor molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ) [1]. Recently, they have been in the focus of attention also because of the search for genuine organic magnetic semiconductors [2]. Although anion-radical salts (ARS) with TCNQ anions have been well known for more than 40 years, they have been designated as quasi-one-dimensional systems up until now. First quasi-two-dimensional salts with pyrazine based cation have been synthesized lately [3].

Recently, experimental study of novel ARS (N-Me-2,6-di-Me-Pz)(TCNQ)$_2$ was performed. It was presented that sample shows some features of a spin-ladder [4]. However, description of this material with spin-ladder model was not fully satisfactory. Therefore another ARS with simpler crystal structure was synthesized and studied, namely (N-Me-2,5-di-Me-Pz)(TCNQ)$_2$, which has only one type of TCNQ anions in contrast with the three anion types in the previous ARS. Our preliminary results point out that in contrast with the previous sample magnetic behaviour of novel sample can be described by the Heisenberg linear chain model and the spin-Peierls transition can occur due to the dimerization of anions followed by possible further tetramerization of anions.

2. Sample preparation and structure
The sample was prepared by electrocrystallization method and the detail crystal structure characterization, IR absorption and electric conductivity studies of presented ARS sample were reported previously [5].

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was shown that electrical conductivity of the salt develops characteristics of quasi two-dimensional behavior, and the activation energy was estimated and compared with the IR absorption spectra.

Investigated salt has layered structure where layers consisting of \([\text{N-Me-2,5-di-Me-Pz}]^+\) cation alternate along the \(c\) axis with layers consisting of TCNQ anion-radicals. The planar molecules of anions, parallel to each other, form stacks along the \(a\) axis, where they are situated in pairs shifted with respect to each other, and characterized by two overlapping manners (Fig.1). Within the pairs, molecules are eclipsed to a higher degree than between the pairs. That is why we suggest that TCNQ dimerization may appear in stacks with decreasing temperature, despite the fact that interplanar distances within and between the pairs are almost the same (3.24 Å and 3.27 Å, respectively). The TCNQ molecule was estimated to carry the charge of \(-0.44\) e and inhomogeneous charge distribution is present.

Figure 1. Fragment of crystal structure of \((\text{N-Me-2,5-di-Me-Pz})(\text{TCNQ})_2\) in two different directions: a) overlapping of molecules in TCNQ layers without cations; b) overlapping of anions and weak interactions between cations and anions illustrated by dashed lines

3. Results and discussion

Temperature dependence of susceptibility was investigated in the temperature range from 2 K to 300 K in applied magnetic fields 100 mT and 1 T, using commercial Quantum Design MPMS device. Diamagnetic contribution to the susceptibility was estimated using Pascal’s constants and subtracted from the total susceptibility.

The magnetic susceptibility \(\chi_M\) of \((\text{N-Me-2,5-di-Me-Pz})(\text{TCNQ})_2\) slowly increases with decreasing temperature and has a broad maximum at \(T_{\text{max}} = 38\) K \(\pm\) 1 K (Fig.2.). Maximum in susceptibility is typical for short range correlations of a low-dimensional \(S = 1/2\) spin system and is probably due to the dimerization of TCNQ anions. The effect is emphasized when magnetic field is applied. The \(\chi_M\) follows the Curie-Weiss law with a Curie constant of \(0.568\) K-emu·mol\(^{-1}\) and a negative Weiss constant \(\Theta = -87\) \(\pm\) 1 K in the temperature region from 70 K to 200 K (Fig.3). The value of \(\chi_M T\) at 300 K was estimated as 0.484 K-emu·mol\(^{-1}\). The value of \(\mu_{\text{eff}} = 1.98\) \(\mu_B\) is very close to that of one unpaired electron, as expected from the crystal structure.
Figure 2. Temperature dependence of magnetic susceptibility of (N-Me-2,5-di-Me-Pz)(TCNQ)$_2$ (circles), fitted to a Heisenberg linear chain model with the function (2) (solid line).

Figure 3. Temperature dependence of inverse magnetic susceptibility of (N-Me-2,5-di-Me-Pz)(TCNQ)$_2$ (circles) analysed using Curie-Weiss law, in the temperature range from 70 K to 200 K (solid line). Temperature dependence of $\chi T$ is shown in the inset.
Following the results on (N-Me-2,6-di-Me-Pz)(TCNQ)$_2$ we expected a spin-ladder like behaviour [4] also for the (N-Me-2,5-di-Me-Pz)(TCNQ)$_2$ sample. However, spin-ladder fit-to-data was not satisfactory therefore, starting with the crystal structure, we applied another model, namely Heisenberg linear chain model described by Hamiltonian [6]

\[ H = -2J \sum_{i=1}^{n} \left( \hat{S}_{2i} \hat{S}_{2i-1} + \alpha \hat{S}_{2i} \hat{S}_{2i+1} \right), \]  

where $J$ is the exchange integral between a spin and its right neighbor and $\alpha$ is the exchange integral between a spin and its left neighbor.

The experimental data were fitted with the equation, derived from [6, 7],

\[ \chi = \frac{G}{T} \cdot \frac{A + BT^{-1} + CT^{-2}}{1 + DT^{-1} + ET^{-2} + FT^{-3}}, \]

where A, B, C, D, E, F and G are function of $J$ and $\alpha$, where $\alpha$ is a parameter that takes into account the distortion in the chain and can vary from $\alpha = 0$ (corresponding to isolated TCNQ$^-$ dimmers) to $\alpha = 1$ (corresponding a uniform chain of $S = \frac{1}{2}$ spins). Experimental data fitted with equation (2) are shown in figure 2. From the crystal structure point of view it is suggested that weak structural dimerization in the stacks of anions leads to the dimerization of spins and possible further tetramerization of spins via spin-Peierls transition.

Nevertheless, we can not gain the parameters $J$ and $\alpha$ from the fit untill the g-factor is known. For exact establishing of the g-factor further analysis of the heat capacity and experimental study with EPR method is planned.

4. Conclusion
Temperature dependence of magnetic susceptibility was studied on a novel ARS based on TCNQ, namely (N-Me-2,5-di-Me-Pz)(TCNQ)$_2$. We conclude that this material shows antiferromagnetic type of interaction with unusually large absolute value of the Weiss constant. Moreover, probable weak structural dimerization leads to spin dimerization and their possible further tetramerization via spin-Peierls transition, which may be considered as interesting magnetic behaviour. To establish the values of $J$ and $\alpha$ in the Heisenberg linear chain model it is necessary to know the value of g-factor which will be derived from prepared EPR measurements.

5. Acknowledgements
This work was supported by the Slovak Research and Development Support Agency APVV LPP-0102-06 and MVTS NSF/08 project. The financial support of U.S.Steel – DZ Energetika Košice is acknowledged.

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