Antiferromagnetic spin chains formed in novel TCNQ-based organic magnets

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The work devoted to the study of two novel genuine organic anion-radical salts (ARS) [N-Me-Dipy](TCNQ)$_2$CH$_3$CN (**1**) and [N-Xy-iQn](TCNQ)$_2$ (**2**), where TCNQ = 7,7,8,8- tetracyanoquinodimethane, N-Me-Dipy = N-methyl-2,2'-bipyridine, and N-Xy-iQn = N-(p-xylene)-isoquinoline, is presented.

In the past few decades molecular low-dimensional conducting materials have attracted much interest, in particular, electrical (conducting or semiconducting properties), magnetic and spectral. The uniqueness of ARS TCNQ is in a combination of electroconductivity and the ability to form magnetically ordered structures. Such structures are interesting primarily because, even though they do not have metal ions, and still exhibit magnetic properties in the role of the acceptor molecule.

The crystallographic data indicate the formation of $(TCNQ)_2^{\bullet -}$ anion-radical π-dimers in the synthesized ARS carrying spin S = 1/2. The analysis of the TCNQ bond distances allowed the estimation of the charge distribution that suggests the formation of magnetic stacks along the crystallographic a-axis. Magnetic measurements of prepared ARS were performed in a temperature range from 1.8 to 350 K in magnetic fields up to 7 T using a SQUID magnetometer. Both studied ARS display an antiferromagnetic (AFM) behavior.A broad maximum in the temperature dependence of the susceptibility was observed at ∼280 K for ARS **1** and described by a model of uniform spin chain with exchange interaction J/k_B = - 440 K, which agrees with a uniform spacing of TCNQ π-dimers in the stacks. On the other hand, an exponential-like decrease of susceptibility with decreasing temperature for ARS **2** suggests strong spin chain dimerization due to the complicated stacking of TCNQ π-dimers along the a-axis. A model of AFM alternating bond (or dimerized chain) spin chain with S =1/2 was used for the analysis. The energy gap in the excitation spectrum of the spin chain induced by dimerization was estimated from the analysis of susceptibility as $\Delta/k_B = 1322$ K with exchange interaction alternation parameter α=0.195. In both systems, low-temperature behavior is affected by a very small fraction (less than 2%) of uncoupled or end-chain spins displaying simple paramagnetism.

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