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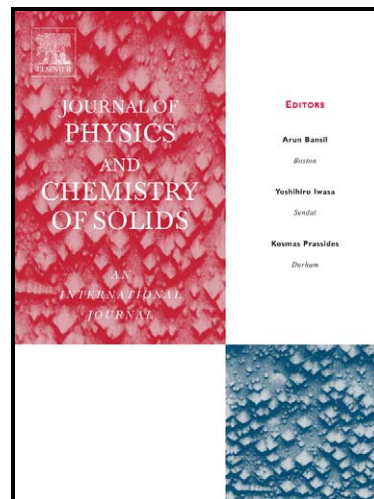
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## Two-gap magnetic structure of the two-stack anion-radical salt (N-Me-3,5-Di-Me-Py)(TCNQ)<sub>2</sub> (Py is pyridine)

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### Abstract

We performed the synthesis of a (N-Me-3,5-di-Me-Py)(TCNQ)<sub>2</sub> single crystal and we resolved the crystallic and molecular structure of this salt. Magnetic susceptibility measurements were performed in the temperature range from 2 K to 300 K. The results are studied with respect to two energy gaps in the magnetic excitations spectra which could signify that the Peierls dielectric phase forms in two grades.

Keywords: A. organic compounds; B. chemical synthesis; C. X-ray diffraction; D. magnetic properties;

### 1. Introduction

Organic materials based on TCNQ are considered as a proper systems for the study of low-dimensional magnetic models due to their significant property - small modification of their crystal structure has a substantial impact on their physical properties. Recently we have studied magnetic and thermodynamic properties of samples (N-Me-2,5-di-Me-Pz)(TCNQ)<sub>2</sub> [1] described with a dimerized Heisenberg spin 1/2 chain model and (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub> [2] described with a spin-ladder model. These compounds have very similar composition, in which only the position of the methyl group on the cation core is varying, but they differ significantly in the crystal structure, due to small changes in cation molecules.

It was theoretically predicted in the past that the low-dimensional systems may exhibit the spin-Peierls transition [3-5]. This transition was experimentally observed for the first time in charge-transfer complexes (TTF)[M{S<sub>2</sub>C<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>}] (TTF = tetrathiafulvalene) (*M* = Cu, Au) [6, 7] and MEM-(TCNQ)<sub>2</sub> (MEM = methyl-ethyl-morpholinium) [8]. Decades later, the spin-Peierls transition was observed also in inorganic compounds, firstly in CuGeO<sub>3</sub> [9], which is a main representant of spin-Peierls inorganic systems, and later also in (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> [10], which is a model system of interacting chains. Moreover, in the latter compound two energy gaps were observed [11].

Two-gap systems are insufficiently described in the literature. The so-called double gap model was introduced for the first time in 1999 [10], for (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. The authors introduced two kinds of coexisting magnetic chains in this model, behaving as alternating spin chains with two independent energy gaps. It was the first experimental evidence of the coexistence of two different ground states in a quite near distance and

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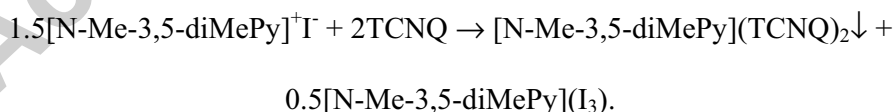
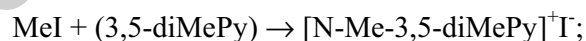
in quite similar spin chains and the  $(VO)_2P_2O_7$  can be considered as a typical gauge of unusual low-dimensional compounds.

In the crystal structure of the studied compound  $(N\text{-Me-3,5-di-Me-Py})(TCNQ)_2$  two types of columns appear. This has led us to describe the magnetic properties with a model of dimerized chains with two gaps.

In this paper we present the synthesis and the crystal and molecular structure investigations of a  $(N\text{-Me-3,5-di-Me-Py})(TCNQ)_2$  single crystal. X-ray diffraction experiments were performed. Magnetic susceptibility was measured in the temperature range from 2 K to 300 K. Analysis of the low-temperature susceptibility revealed that two energy gaps occur in the magnetic excitations spectra and that the spin-Peierls transition could proceed in a rather unusual way.

## 2. Experimental

TCNQ was purified by the recrystallization from acetone and after that the gradient sublimation in argon atmosphere was used. Anion-radical salt (ARS) was gained by a standard method using reaction of TCNQ reduction by N-Me-3,5-di-Me-pyridine iodide, which we get from the reaction of methyl iodide with 3,5-diMe-pyridine:



One and half residue of iodide is necessary for binding of the forming iodide. Precipitate of the salt was filtered and washed with diethyl ether and acetone mixture. In order to grow single crystals the recrystallization from acetonitrile/acetone mixture was performed. Black-violet needle crystals with length up to 2 mm were obtained.

The X-ray study of the crystal structure of the ARS was performed at room temperature using an Enraf-Nonius CAD-4 ( $\omega/2\theta$ -scanning, Mo-K $\alpha$  radiation, graphite monochromator) device. The crystal structure was solved by direct methods and subsequent Fourier synthesis using the SHELXS-97 software [12]. Structure was refined by full-matrix least squares procedures using an anisotropic approximation for all non-hydrogen atoms within the SHELXL-97 [13] software. Hydrogen atoms coordinates were calculated from the geometric condition. Nitrogen atom in each independent cation can be localized in one of three positions to which three methyl groups are bound. From these three possible positions we have calculated the one with maximal occupation. Main crystallographic data and some experimental characteristics are listed in table 1. Bond lengths and valence angles are given in table 2. CCDC 746389 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

The magnetization measurements and magnetic susceptibility measurements of polycrystalline sample (80.6 mg) were performed in a *Quantum Design* MPMS device. The temperature dependence of susceptibility was investigated in the temperature range from 2 K to 300 K in applied magnetic field 100 mT. Diamagnetic contribution to the susceptibility was estimated using Pascal's constants [14, 15] and then subtracted from the total susceptibility.

### 3. Results and Discussion

Crystal structure of the salt is formed by four TCNQ anion-radicals A, B, C and D (Fig. 1a) and two crystallographically independent 3,5-dimethyl-N-methyl-pyridine cations E and F, situated in general positions (Fig. 1b).

Performed study showed that this salt has a layered structure (Fig. 2) in which layers formed by cations  $[3,5\text{-di-Me-N-Me}]^+$  alternate along the  $a$  axis with layers consisting of TCNQ anion radicals. Anion layers separated by cation layers are inhomogeneous and consist, in turn, of the type A or B anion radicals (Fig. 3a), or the type C or D anion radicals (Fig. 3b).

Anions form layers along the  $c$  axis and irregular columns along the  $b$  axis (Fig. 3). The layers are formed by anions of only one type. In columns the anions alternate in sequences (AB)(BA) or (CD)(DC) and structural dimers formed by anions of diverse types ((AB) and (CD)) can be distinguished, differing from each other only by the deviation angle. The dihedral angles, formed by planes of anions A-A, B-B, C-C and D-D, are  $161.5^\circ$ ,  $162.2^\circ$ ,  $168.7^\circ$  and  $168.1^\circ$ , respectively. Anions in dimers are practically parallel (dihedral angle between planes laid through all carbon atoms in TCNQ anion is equal to  $0.4^\circ$ ). The distance between planes in (AB) dimers is  $3.19 \text{ \AA}$  and in (CD) dimers is  $3.28 \text{ \AA}$ .

Anion-radicals TCNQ are characterized by considerable deviations of nitrogen atoms from the carbon plane, with values  $0.07 \text{ \AA}$ ,  $0.10 \text{ \AA}$ ,  $0.16 \text{ \AA}$  and  $0.15 \text{ \AA}$  for atoms N(1A), N(4B), N(4C) and N(4D), respectively. Cations are practically planar, with maximal deviation being only  $0.01 \text{ \AA}$  and  $0.02 \text{ \AA}$  (atoms N(1E) and C(7F), respectively).

Cation layers separated by anion layers are homogeneous and formed by cations of E or F type. Inside the layer the cations differ from each other in their orientation.

Interplanar angles between planes laid through the carbon atoms of cations are  $66.7^\circ$  and  $68.7^\circ$  for the E and F type of cation, respectively.

In ARS with composition  $\text{Ct}^+(\text{TCNQ})_2^-$  (where  $\text{Ct}^+$  is cation) tetramers usually form in the TCNQ columns due to the metal-insulator transition because when the conductivity band is filled up to  $1/4$  the period must, in conformity with Peierls theorem, increase fourfold [16]. However, in our compound two types of structural dimers form – (AB) and (CD). For the interpretation of the physical properties of this ARS it is necessary to know the charge distribution on TCNQ molecules. This distribution was calculated by the method presented in [17]. From the data in Table 2a and 2b we calculated HOSE (Harmonic Oscillator Stabilization Energy) energies for quinoid and Kekule's TCNQ structures for A, B, C and D particles and their charges. The partial charges are  $-0.10 e$  (A),  $-1.09 e$  (B),  $-0.52 e$  (C) and  $-0.89 e$  (D) (Table 2c).

With regard to the accuracy of this interpretation we suppose that structural dimers (AB) and (CD) carry the charge about -1 and consequently the spin  $1/2$  and therefore with decreasing temperature further ordering should occur in the (N-Me-3,5-Di-Me-Py)(TCNQ)<sub>2</sub> crystal, caused by the spin-Peierls transition, due to which spinless structure tetramers with the charge -2 form.

The temperature dependence of magnetic susceptibility of this ARS confirms stated presumption. The magnetic susceptibility  $\chi$  of the sample shows a broad maximum at  $T_{max} = 26.5 \text{ K} \pm 1 \text{ K}$  (Fig. 4). After subtracting the diamagnetic contribution, approximated by Pascal's constants and found to be  $-13.587 \cdot 10^{-5} \text{ emu} \cdot \text{mol}^{-1}$ , the susceptibility data were fitted by the Currie-Weiss law in the temperature region from 130 K to 300 K. We determined the value of the Curie constant  $C$  to be  $0.299 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$  and that of Weiss constant  $\theta$  to be  $-48.7 \pm 2 \text{ K}$ , confirming the

presence of antiferromagnetic interactions. As can be seen in Fig. 4, this dependence is typical for quasi-one-dimensional systems with antiferromagnetic interaction.

The temperature dependence of the effective magnetic moment was fitted with formula (Fig. 5):

$$\mu_{eff} = \frac{P_1 \cdot T}{P_2 + T}, \quad (1)$$

which yields the values  $P_1 = 1.6 \mu_B/K$  and  $P_2 = 28.3 \text{ K}$ . The value of the effective moment  $1.6 \mu_B$  corresponds to 0.89 unpaired electrons.

Considering two types of structure dimers in the structure of ARS we can expect the appearance of two gaps in the magnetic excitations spectra. Therefore the temperature dependence of magnetic susceptibility was described with the formula:

$$\chi = \frac{C^*}{T} + \frac{A_1}{T} \exp\left(-\frac{\Delta_1}{T}\right) + \frac{A_2}{T} \exp\left(-\frac{\Delta_2}{T}\right), \quad (2)$$

where the first term describes the contribution from paramagnetic impurities (free fragments of magnetic structure) and the second and third terms describe the contributions from (AB) and (CD) type of dimers. This formula fits with parameters  $C^* = 0.0186 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ ,  $A_1 = 0.167 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ ,  $A_2 = 0.127 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ ,  $\Delta_1 = 74.1 \text{ K}$  and  $\Delta_2 = 26.6 \text{ K}$  (Fig. 4) satisfactorily the temperature dependence of magnetic susceptibility. The amount of paramagnetic impurities was estimated from the value of the Curie constant and is equal to 0.9 %.

As we know, the value of the exchange integral decreases exponentially with the increase of the interplanar distance. Therefore such considerable difference between the gap widths for (AB) and (CD) type of dimers can be explained by different interplanar distances in dimers (3.19 Å in A-B dimers and 3.28 Å in C-D dimers).

#### 4. Conclusion

This study shows that in the presented ARS (N-Me-3,5-Di-Me-Py)(TCNQ)<sub>2</sub> an unusual dielectric state is observed in which Peierls dielectric phase forms in two grades. At room temperature two types of structure dimers exist and doubling of the period is observed. At temperatures below 50 K further ordering occurs, with dimers coupling to tetramers. Two gaps in the magnetic excitations spectra correspond to two types of structure dimers. Nevertheless, to confirm our presumptions resulting from the crystal structure and magnetic susceptibility analyses, the measurements of magnetisation in high magnetic fields and EPR measurements should be performed.

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## Figure Captions

Fig. 1. ORTEP view and atom labeling of (N-Me-3,5-Di-Me-Py)(TCNQ)<sub>2</sub> – in anion (a) and cation (b).

Fig. 2. The crystal structure of (N-Me-3,5-Di-Me-Py)(TCNQ)<sub>2</sub>.

Fig. 3. Two types of anion-radical layers, formed by anions of different types – a) shows the layer formed by A and B type of anions, b) shows the layer formed by C and D type of anions.

Fig. 4. Temperature dependence of magnetic susceptibility (open circles) fitted with formula (2) (black solid line). Separate terms of the formula represent the contributions from paramagnetic impurities (pink dashed line), from AB structure dimers (blue dotted line) and from CD structure dimers (green dash-and-dot line).

Fig. 5. Temperature dependence of effective magnetic moment (open circles) of ARS (N-Me-3,5-Di-Me-Py)(TCNQ)<sub>2</sub> fitted with formula (1) (solid line); inset shows linear fit (solid line) of inverse susceptibility (open circles) in the temperature region from 130 K to 300 K.

Table 1. Basic crystallographic data

Compound	(N-Me-3,5-di-Me-Py)(TCNQ) <sub>2</sub>
Chemical formula	C <sub>32</sub> H <sub>20</sub> N <sub>9</sub>
Molecular mass	530.57
Crystal system	Monoclinic
Space group	<i>Pc</i>
<i>a</i> /Å	27.578(4)
<i>b</i> /Å	12.977(2)
<i>c</i> /Å	7.796(1)
$\alpha$ /°	90
$\beta$ /°	93.36(2)
$\gamma$ /°	90
<i>U</i> /Å <sup>3</sup>	2785.2(7)
<i>Z</i>	4
$\lambda$ /Å	0.7107
<i>D</i> <sub>calc</sub> , /g·cm <sup>-3</sup>	1.26
$\mu$ /mm <sup>-1</sup>	0.080
Number of measured reflections	5204
Number of independent reflections	5204
Number of observed reflections [ <i>F</i> 0 > 4 $\sigma$ ( <i>F</i> 0)]	2959
Parameters refined	740
(2 $\theta$ ) <sub>max</sub> , °	50.00
Interval for <i>h</i>	-32 ≤ <i>h</i> ≤ 32

Interval for k	$0 \leq k \leq 15$
Interval for l	$0 \leq l \leq 9$
R – factor ( $F_0 > 4\sigma(F_0)$ )	0.043

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Table 2a. Bond distances in cations

	A	B	C	D
N(1)-C(1)	1.134(6)	1.139(6)	1.151(7)	1.132(7)
N(2)-C(2)	1.145(6)	1.140(6)	1.152(6)	1.136(6)
N(3)-C(11)	1.137(6)	1.140(6)	1.155(7)	1.138(7)
N(4)-C(12)	1.140(6)	1.141(6)	1.153(6)	1.128(7)
C(1)-C(3))	1.439(6)	1.421(6)	1.411(7)	1.431(7)
C(2)-C(3)	1.432(7)	1.414(6)	1.409(6)	1.429(7)
C(3)-C(4)	1.377(8)	1.423(8)	1.400(8)	1.406(8)
C(4)-C(9)	1.446(6)	1.409(6)	1.431(6)	1.419(6)
C(4)-C(5)	1.448(6)	1.415(6)	1.435(6)	1.416(6)
C(5)-C(6)	1.334(8)	1.381(8)	1.351(8)	1.370(8)
C(6)-C(7)	1.449(6)	1.405(6)	1.437(6)	1.426(6)
C(7)-C(10)	1.367(8)	1.420(8)	1.388(8)	1.392(8)
C(7)-C(8)	1.445(6)	1.408(6)	1.425(6)	1.412(7)
C(8)-C(9)	1.336(8)	1.365(8)	1.342(8)	1.366(8)
C(10)-C(11)	1.436(6)	1.415(6)	1.405(7)	1.425(7)
C(10)-C(12)	1.439(6)	1.416(6)	1.410(6)	1.432(7)

	A	B	C	D
N(1)-C(1)-C(3)	177.6(8)	177.4(8)	177.8(9)	171.5(9)
N(2)-C(2)-C(3)	176.4(8)	176.7(8)	178.8(8)	178.1(8)
C(4)-C(3)-C(2)	122.1(5)	120.8(5)	119.8(5)	121.5(5)
C(4)-C(3)-C(1)	121.5(5)	121.1(5)	121.7(6)	121.5(6)
C(2)-C(3)-C(1)	116.3(6)	118.0(6)	118.4(6)	117.0(6)
C(3)-C(4)-C(9)	121.9(5)	122.0(5)	123.1(5)	121.1(5)
C(3)-C(4)-C(5)	122.1(5)	120.4(5)	119.7(5)	122.0(5)
C(9)-C(4)-C(5)	116.0(5)	117.6(5)	117.2(6)	116.9(6)
C(6)-C(5)-C(4)	121.2(5)	122.0(6)	120.7(6)	122.9(6)
C(5)-C(6)-C(7)	121.9(5)	118.9(6)	121.3(6)	119.2(6)

C(10)-C(7)-C(8)	121.2(4)	120.3(5)	122.3(5)	121.2(5)
C(10)-C(7)-C(6)	121.2(5)	120.0(5)	119.9(5)	120.2(5)
C(8)-C(7)-C(6)	117.6(5)	119.6(6)	117.7(6)	118.6(6)
C(9)-C(8)-C(7)	119.5(5)	120.8(6)	120.6(6)	121.3(6)
C(8)-C(9)-C(4)	123.7(5)	121.0(5)	122.2(5)	121.2(6)
C(7)-C(10)-C(11)	123.8(5)	121.7(5)	121.7(5)	124.5(5)
C(7)-C(10)-C(12)	122.9(5)	123.0(5)	124.5(5)	119.9(6)
C(11)-C(10)-C(12)	113.3(6)	115.1(6)	113.6(6)	115.6(6)
N(3)-C(11)-C(10)	179.4(9)	176.9(8)	177.5(8)	177.3(9)
N(4)-C(12)-C(10)	177.7(8)	179.3(9)	178.1(8)	179.4(9)

Table 2b. Bond distances in anions

	E	F
N(1)-C(1)	1.29(1)	1.33(1)
N(2)-C(2)	1.37(1)	1.40(1)
N(1)-C(6)	1.48(1)	1.49(1)
C(1)-C(2)	1.35(1)	1.36(1)
C(2)-C(3)	1.37(1)	1.35(1)
C(2)-C(7)	1.45(1)	1.52(1)
C(3)-C(4)	1.32(1)	1.41(1)
C(4)-C(5)	1.35(1)	1.37(1)
C(4)-C(8)	1.52(1)	1.47(1)

	E	F
C(5)-N(1)-C(1)	118.2(6)	122.1(6)
C(5)-N(1)-C(6)	120.1(7)	118.4(7)
C(1)-N(1)-C(6)	121.7(7)	119.4(7)
C(2)-C(1)-N(1)	123.0(7)	119.3(7)
C(1)-C(2)-C(3)	115.1(7)	120.5(7)
C(1)-C(2)-C(7)	121.9(8)	118.5(7)
C(3)-C(2)-C(7)	123.0(8)	121.0(7)
C(4)-C(3)-C(2)	122.7(7)	
C(3)-C(4)-C(5)	119.1(7)	
C(3)-C(4)-C(8)	120.1(7)	
C(5)-C(4)-C(8)	120.8(7)	
N(1)-C(5)-C(4)	121.9(6)	

Table 2c. Partial charges on four types of anions.

	A	B	C	D
Partial charge [ $e$ ]	-0.10	-1.09	-0.52	-0.89

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