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# (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub>—genuine organic anion-radical salt: a spin-ladder?

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## Abstract

The room temperature Raman spectra investigations on single crystals of an anion-radical salt (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub> with a pyrazine-based cation were performed. The infrared reflection spectra of the sample were recorded in the frequency range from 400 to 7500 cm<sup>-1</sup>, at room temperature. Magnetization measurements were performed as a function of temperature in magnetic fields up to 5 T. The heat capacity and magnetic susceptibility were measured in the temperature range from 2 to 300 K. The results are studied in terms of quasi-one-dimensional magnetic theoretical models and they indicate behavior close to a spin-ladder system.

(Some figures in this article are in colour only in the electronic version)

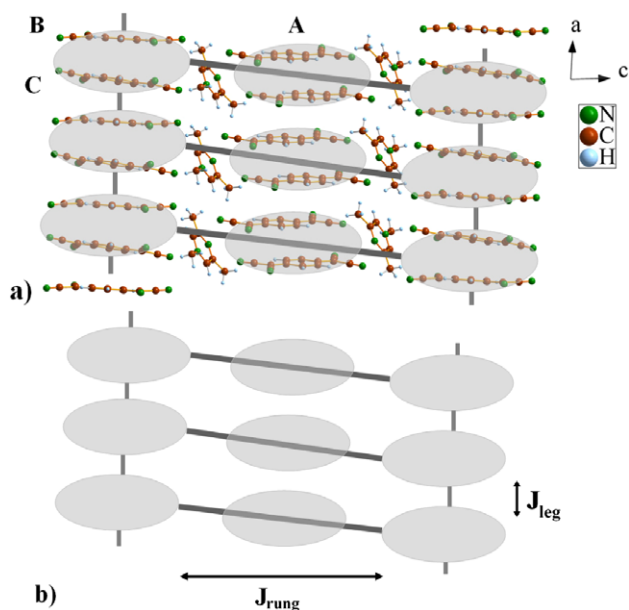
## 1. Introduction

In the past few decades, molecule-based materials have attracted much interest in relation to molecular magnetism, magnetic conductors and superconductivity. Solids made out of low molecular weight organic molecules have the tendency to self-assemble in highly ordered structures and so high-quality single crystals can be obtained. The structure–property relationship can thus be systematically explored in an ideal situation where disorder can be ignored. Over their more classical inorganic counterparts, the advantage of molecular solids is that their basic structural elements are molecules or clusters that can be designed and synthesized and subsequently they can be intentionally modified [1].

Anion-radical salts (ARS) of 7,7,8,8-tetracyanoquinodimethane (TCNQ) were the first organic objects to exhibit metallic properties [2]. They constitute a class of quasi-one-dimensional narrow-band materials. Late in the 1960s they captured attention in view of high-temperature superconductivity based on the Little model [2, 3], but the first organic superconductor was discovered only in 1980 among the cation-radical salts [4]. However, in the middle of the 1980s, conducting ARS of TCNQ were synthesized possessing

a unique ability to melt without decomposition [5–7]. This reveals the wide usage possibilities of such ARS in electronics. Such compounds might be used in the development of a new type of electrolyte capacitor that possess better operational characteristics, namely the ability for the ‘self-treatment’ of oxide layer defects [5–7].

In spite of a long history of TCNQ chemistry, no ARS with pyrazine derivatives as a cation had been known till recently [8–10]. Pyrazine is the simplest analog of phenazine, being a constituent of the first organic metal, NMP-TCNQ (NMP = *N*-methylphenazinium). TCNQ ARS with cations containing an additional donor atom (e.g. pyrazine-based cations) can be used to deposit conducting organic coatings over a metallic substrate. In these ARS, there is a possibility of additional interactions (besides the electrostatic ones) between anion-radical TCNQ stacks and cations via the non-alkylated nitrogen atom of pyrazine. This may result in structures unusual for TCNQ ARS. Using this approach the quasi-two-dimensional TCNQ ARS of (N-Et-Pz)(TCNQ)<sub>3</sub>, (N-Et-2,5-di-Me-Pz)(TCNQ)<sub>2</sub> and (N-Me-NH<sub>2</sub>-Pz)(TCNQ)<sub>2</sub> composition were synthesized for the first time [11–13]. The quasi-two-dimensional character of these ARS follows from their crystal



**Figure 1.** (a) The crystal structure of the sample (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub>—cation and anion layers alternate along the *c* axis, two different overlapping manners of TCNQ anion molecules can be seen in the *a* axis direction; (b) schematic representation of a spin-ladder, where antiferromagnetic interactions are represented by lines and circles represent effective spin 1/2 situated on a structural TCNQ dimer.

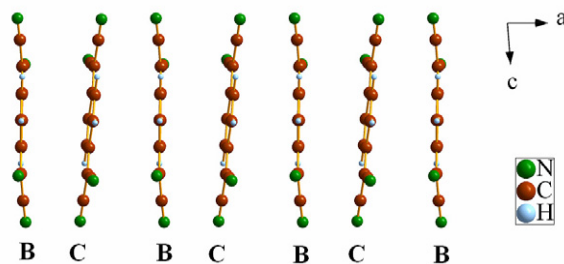
structure investigations and from the analysis of their electro-physical and optical properties.

In this paper we present results of our study of spectral data, obtained mainly by the Raman scattering method, and magnetic and thermodynamic properties of a novel (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub> salt, which we prepared in the form of single crystals. Although previous results of structural analysis and electrical conductivity measurements indicate a quasi-two-dimensional character of both the crystal and electronic structure of this salt [14], comparison of the results of low-temperature susceptibility and heat capacity investigations with the one-dimensional and two-dimensional theoretical models indicates that the magnetic system of this salt may be described by a spin-ladder model.

## 2. Experimental details

The ARS precipitate prepared by the usual method [8] was filtered, washed with ether and hexane, and dried in vacuum. In order to grow single crystals and for purification, recrystallization from acetonitrile and acetone was used. Black-violet needle crystals of up to 25 mm length have been obtained. The ARS composition was determined using spectrophotometry. The exact description of sample preparation and detailed crystallographical characterization is reviewed in a recent paper [14].

The room temperature Raman spectra of single crystals were collected with a Horiba Jobin Yvon LabRam HR800 spectrometer with a He–Ne laser excitation beam ( $\lambda_{\text{ex}} = 633 \text{ nm}$ ). The power of the beam at the sample was less than



**Figure 2.** Anions in the BC layer, where two types of TCNQ molecules alternate.

1 mW to avoid damage to the sample. The infrared reflection spectra of the samples were recorded in the frequency range from 400 to 7500  $\text{cm}^{-1}$ , at room temperature, for two polarizations of the beam: parallel and perpendicular to the longer crystal axis. These investigations were performed with an FT-IR Bruker Equinox 55 spectrometer equipped with a Hyperion 1000 microscope.

The magnetic susceptibility measurements and magnetization measurements were performed in a Quantum Design MPMS. Temperature dependence of the susceptibility of the powder sample was investigated in the temperature range from 2 to 300 K in applied magnetic fields of 100 mT and 1 T. The diamagnetic contribution of the material to the susceptibility was estimated using Pascal's constants and subtracted from the total susceptibility. Field dependence of magnetization was measured in magnetic fields from 0 to 5 T at five different temperatures. Temperature dependence of the heat capacity of the single-crystal sample was investigated in the temperature range from 2 to 300 K in zero magnetic field using a Quantum Design PPMS.

## 3. Crystal structure

The sample (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub> has a layered structure which was revealed by the x-ray structural analysis [14]. The crystal structure is formed by [N-Me-2,6-di-Me-Pz]<sup>+</sup> cations in general position and three TCNQ<sup>−</sup> anions (A, B, C), one of which (A) takes a general position and B and C anions are situated in special centrosymmetrical positions. Cation layers alternate along the *c* axis with layers consisting of TCNQ anion-radicals (figure 1). Anionic layers differ from each other by the molecular symmetry: the BC layers formed by the centro-symmetrical B and C anions alternate with the A layers, consisting of A anions without any crystallographic symmetry elements. In the A and BC layers, the anions overlap in various manners (figures 1 and 2): in A layers, neighboring anions are shifted with respect to each other along the long axis at a C=C distance, while in BC layers, anions are practically not overlapped. Molecules of cations and anions are practically planar.

## 4. Results and discussion

The experimental Raman spectrum of the investigated crystal together with the optical conductivity spectrum calculated from

**Table 1.** Selected totally symmetric modes of the neutral TCNQ molecule and corresponding bands observed in the spectra of (Me-2,6-di-Pz)(TCNQ)<sub>2</sub>. All frequencies are in cm<sup>-1</sup>. Values of electron–phonon coupling are in brackets.

Symmetry species (A <sub>g</sub> )	(Me-2,6-di-Pz)(TCNQ) <sub>2</sub>			Mode description <sup>b</sup>
	Reference [21] q = 0	Raman	IR <sup>a</sup>	
ν <sub>2</sub>	2229 (0.19) <sup>c</sup>	2210	2152	C≡N str + C–C <sup>w</sup> str
ν <sub>3</sub>	1602 (0.66) <sup>c</sup>	1590, 1602	1555	C=C <sup>R</sup> str + C–C <sup>R</sup> str + C–C–H b
ν <sub>4</sub>	1454 (0.27) <sup>c</sup>	1426, 1436	1289	C=C <sup>w</sup> str + C–C <sup>w</sup> str
ν <sub>5</sub>	1207 (0.19) <sup>c</sup>	1181	1100	C–C–H b + C–C≡N b + C=C <sup>R</sup> str
ν <sub>6</sub>	948 (0.25) <sup>c</sup>	975	951	C–C <sup>R</sup> str + C–C <sup>w</sup> str
ν <sub>7</sub>	711 (0.37) <sup>c</sup>	724	691	C–C <sup>R</sup> str + C–C <sup>w</sup> str + C–C–C <sup>R</sup> b
ν <sub>8</sub>	602 (0.03) <sup>c</sup>	611	595	C–C <sup>w</sup> str + C–C–H b + C–C–C <sup>w</sup> b

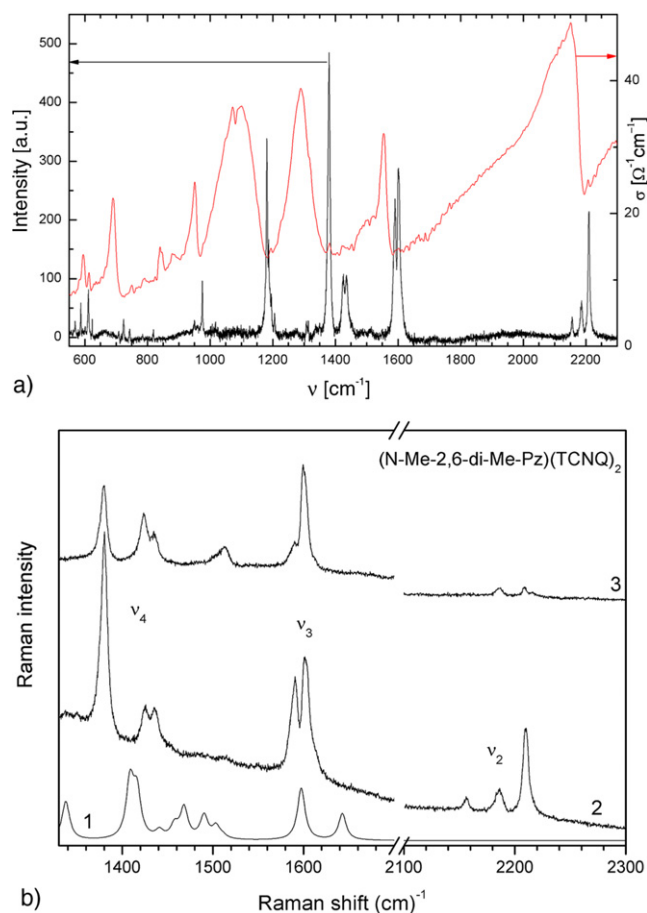
<sup>a</sup> Positions in the IR spectrum were taken from the optical conductivity spectrum.

<sup>b</sup> str = stretching, b = bending, w = wing, R = ring.

<sup>c</sup> Electron–phonon coupling constants from [22].

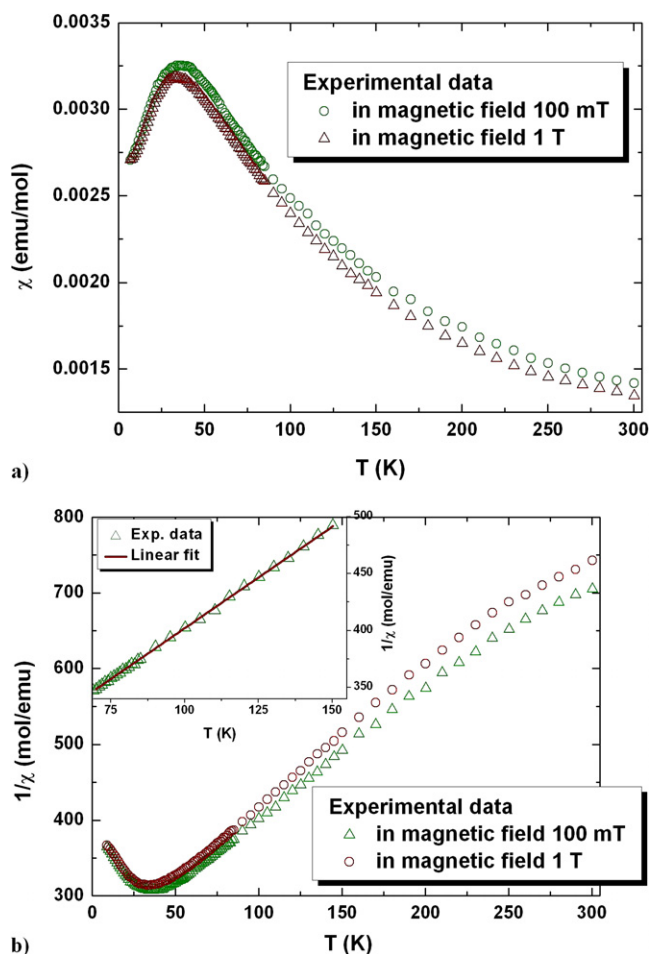
the reflectance data are presented in figure 3(a). The spectra are dominated by the intense bands related to the totally symmetric (A<sub>g</sub>) vibrations of the TCNQ anion. This is a typical situation for many TCNQ salts. The (A<sub>g</sub>) bands in the optical conductivity spectrum are activated by the electron–molecular vibration (EMV) coupling. They are usually asymmetric in shape, very intense and make the other vibrations invisible in the IR (or optical conductivity) spectrum. Our case is not an exception—we observe very intense bands related to ν<sub>2</sub>(A<sub>g</sub>), ν<sub>3</sub>(A<sub>g</sub>), ν<sub>4</sub>(A<sub>g</sub>) and ν<sub>5</sub>(A<sub>g</sub>) modes and a little less intense bands due to ν<sub>6</sub>(A<sub>g</sub>) and ν<sub>7</sub>(A<sub>g</sub>) modes (see table 1 for details of the assignment). At higher wavenumbers (above 2300 cm<sup>-1</sup>) we did not observe any distinct bands. The positions of the A<sub>g</sub> modes in the optical conductivity spectra are generally in good agreement with those obtained by Kazheva *et al* [14] (1094, 1279 and 2147 cm<sup>-1</sup>). In our case the interesting feature is an additional component of the ν<sub>5</sub>(A<sub>g</sub>) mode (at about 1100 cm<sup>-1</sup>) which was not observed by Kazheva for the sample dispersed in a KBr pellet. Usually the single-crystal spectra reveal more details than the spectra obtained by the KBr pellet technique. The above-mentioned band is most probably related to the normal mode with B<sub>3g</sub> symmetry, activated by EMV coupling. We have observed a similar feature in the (N-Me-2, 5-(Me)<sub>2</sub>-Pz)(TCNQ)<sub>2</sub> salt [15].

It is well known that the position of some A<sub>g</sub> modes in the Raman spectrum depends on the average charge on the molecule [16–18]. We can skip the analysis of the modes from ν<sub>6</sub>(A<sub>g</sub>) to ν<sub>10</sub>(A<sub>g</sub>) because of their low intensity, which makes the interpretation uncertain. The ν<sub>5</sub>(A<sub>g</sub>) and ν<sub>1</sub>(A<sub>g</sub>) modes involve mainly the C–H bonds, so they are not very sensitive to the charge on the molecule and also should not be taken into account. For that reason we will focus only on the modes from ν<sub>2</sub>(A<sub>g</sub>) to ν<sub>4</sub>(A<sub>g</sub>) (see figure 3(b)). The position of the ν<sub>3</sub>(A<sub>g</sub>) mode at 1601 cm<sup>-1</sup> is almost identical to the neutral TCNQ (1602 cm<sup>-1</sup> [16]) while the position of the ν<sub>2</sub>(A<sub>g</sub>) mode at 2209 cm<sup>-1</sup> is close to that for the TCNQ<sup>-</sup> anion (2206 cm<sup>-1</sup> [19]). However, we observe additional bands close to the ν<sub>2</sub>(A<sub>g</sub>) mode (2185 and 2156 cm<sup>-1</sup>) and close to the ν<sub>3</sub>(A<sub>g</sub>) mode (1590 cm<sup>-1</sup>). The appearance of these bands suggests that vibrating TCNQ molecules have a different crystal environment which may be caused by the presence of three different types of TCNQ molecules. The



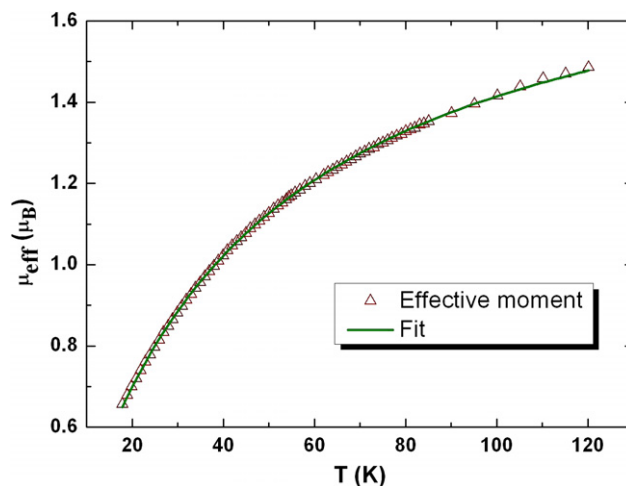
**Figure 3.** (a) Raman scattering spectrum and optical conductivity spectrum of (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub> for the direction parallel to the TCNQ stacks. (b) Theoretical Raman spectra of (N-Me-2,6-di-Me-Pz)<sup>+</sup> cation (B3LYP/6-311++ G(d, p)) (1) and experimental Raman spectra for two polarizations of the excitation beam: parallel to the TCNQ stacks (2) and perpendicular to them (3). Note that the intensities of the spectra have been changed for clarity.

ν<sub>2</sub>(A<sub>g</sub>) mode is the symmetrical stretching of C≡N bonds, so it involves external parts of the molecule and should be sensitive to the molecular environment. It explains the presence of the additional components of the ν<sub>2</sub>(A<sub>g</sub>) mode. In the case of the ν<sub>3</sub>(A<sub>g</sub>) mode, we observe only one additional band at



**Figure 4.** Magnetic susceptibility of (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub> (a) and inverse susceptibility (b). Inset of (b) shows the susceptibility data (triangles) in the temperature range from 70 to 150 K, analyzed using the Curie–Weiss law and the results are given by the solid line.

1590 cm<sup>-1</sup>, which can be caused by the same effect. The fact that we observe two bands in this region (not three like in the case of ν<sub>2</sub>(A<sub>g</sub>)) is probably connected to the nature of the ν<sub>3</sub>(A<sub>g</sub>) mode. This normal mode is mainly related to the bending of C–C–H bonds and stretching of ring C=C bonds, so it should be less sensitive to the environment than ν<sub>2</sub>(A<sub>g</sub>). On the other hand, the band at 1590 cm<sup>-1</sup> can be related to the vibrations of the cation. The position of the ν<sub>4</sub>(A<sub>g</sub>) mode is known to be a good indicator for estimation of the average charge on the TCNQ molecule. This mode is related to the stretching of wing C=C bonds and this is why its position is very sensitive to the average charge located on the molecule [20]. In our case in the appropriate spectral region we observe three bands at 1435, 1426 and 1380 cm<sup>-1</sup>. Using the linear dependence between the charge on the TCNQ anion and the wavenumber of the ν<sub>4</sub>(A<sub>g</sub>) mode [20] the average charges for these modes are -0.32e (1435 cm<sup>-1</sup>), -0.47e (1426 cm<sup>-1</sup>) and -1.25e (1380 cm<sup>-1</sup>). The first two values are in agreement with those from the structural data (0.28e and 0.6e). One can see the differences between these values but we should remember that both methods are approximate. The main issue is the band at 1380 cm<sup>-1</sup> which corresponds to the



**Figure 5.** Effective magnetic moment of (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub> fitted with formula (2).

-1.25e charge. This band is far more intense than the other bands assigned to the ν<sub>4</sub>(A<sub>g</sub>) mode and the estimated charge is different than the prediction based on the bond’s length (-0.88e). The difference in intensity can be caused by two reasons. The first one is the vibration of the cation which can take part in the creation of this band, together with the ν<sub>4</sub>(A<sub>g</sub>) mode. The second reason is the position of the molecule in the structure. There is a possibility that TCNQ molecules related to this band are in gainful position against the polarization of the excitation light while the other two types of TCNQs are not. In such a case the difference in the intensity should be smaller for different polarizations of the excitation beam (e.g. perpendicular to the previous one). Despite the fact that the Raman spectrum for this second polarization (presented in figure 3(b) and labeled as 3) is of poor quality, it is clearly visible that the mentioned difference in intensity between the 1380 cm<sup>-1</sup> band and a doublet at 1426 and 1435 cm<sup>-1</sup> is much smaller compared to the previous case.

The magnetic susceptibility χ of the sample shows a broad maximum at T<sub>max</sub> = 35 K ± 1 K, as shown in figure 4. After subtracting the diamagnetic contribution, approximated by Pascal’s constants<sup>5</sup> and found to be equal to -6.181 × 10<sup>-5</sup> emu mol<sup>-1</sup>, the susceptibility data were fitted by the Curie–Weiss law.

The χ follows the Curie–Weiss law in the temperature region from 70 to 150 K, with a Curie constant of 0.56 emu K mol<sup>-1</sup> and a negative Weiss constant Θ = -126 ± 2 K, confirming the presence of antiferromagnetic interactions.

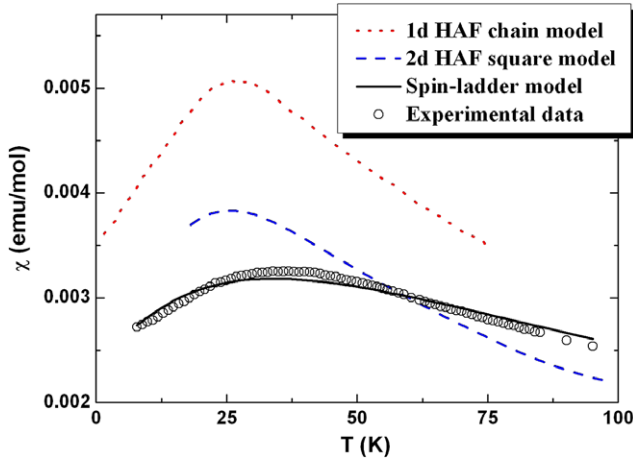
A hump in the temperature dependence of magnetic susceptibility which is typical for low-dimensional antiferromagnets is probably due to the dimerization of TCNQ anions.

The effective magnetic moment decreases monotonically with the temperature decrease (figure 5). The temperature dependence of the magnetic moment can be described by a fractional rational function:

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

<sup>5</sup> Software MaTra2.exe designed by Z Travneeek from Palacky University in Olomouc and J Marek from Masaryk University in Brno, Czech Republic.





**Figure 6.** Experimental data of magnetic susceptibility (open circles) fitted with formula (3) for spin-ladder model (solid line) proposed by Barnes and Riera [25]. Theoretical prediction of 1d Heisenberg antiferromagnetic (HAF) chain is denoted by the dashed line. The dotted line represents prediction for a spatially isotropic 2d Heisenberg antiferromagnetic square lattice.

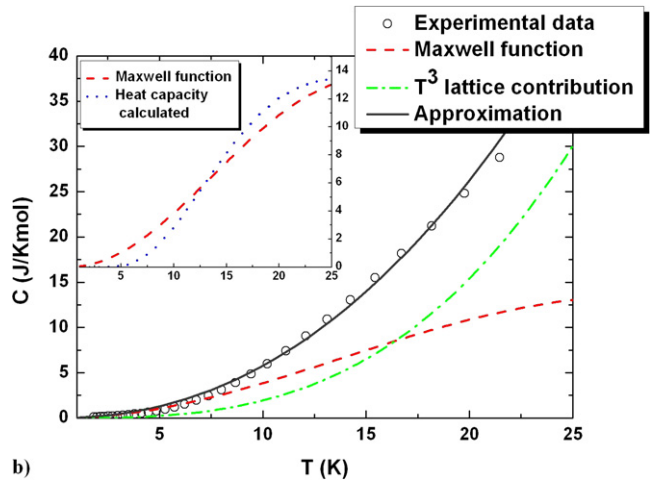
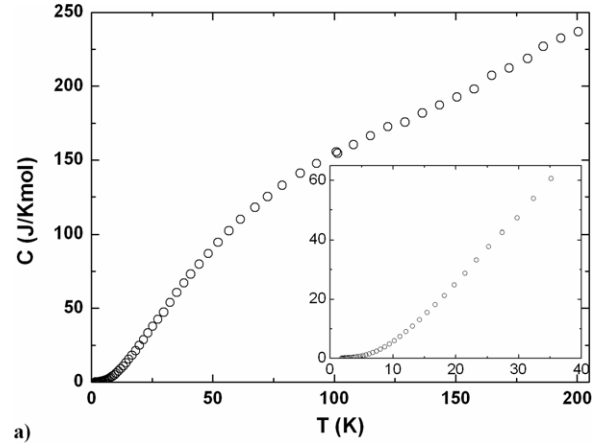
where  $P_1 = 1.9 \mu_B K^{-1}$  and  $P_2 = 34.3$  K. The maximum value of magnetic moment is in this way equal to  $1.9 \mu_B$ , which is very close to that of one unpaired electron, which confirms the suggestion from the crystal structure about the distribution of electron density on TCNQ-radicals.

The temperature dependence of magnetic susceptibility cannot be approximated by the Bonner–Fisher model [23] or the random exchange Heisenberg antiferromagnetic chain (REHAC) model [2, 24]. We compared our experimental data with the one-dimensional Heisenberg antiferromagnetic chain model and two-dimensional Heisenberg antiferromagnetic model, and we did not find a satisfying agreement (figure 6). However, in the whole temperature range the susceptibility can be well described with an empirical formula for spin-ladders proposed by Barnes and Riera in their work [25]:

$$\chi(T) = \frac{c_1}{T} \frac{1}{1 + (\frac{T}{c_2})^{c_3}} \frac{1}{1 + (\frac{c_5}{T})^{c_6}}, \quad (2)$$

with parameters  $c_1 = 3.250$ ;  $c_2 = 0.008$ ;  $c_3 = 1.567$ ;  $c_4 = 0.0003$ ;  $c_5 = 76.83$  and  $c_6 = 1.888$  (figure 6). However, mere analysis of the magnetic susceptibility is not sufficient to select a proper theoretical model. Therefore we also studied the temperature dependence of heat capacity.

The heat capacity was measured in the temperature range from 2 to 300 K (figure 7(a)). The lattice part of the heat capacity is usually evaluated from the heat capacity of a nonmagnetic isomorph. But no adequate isomorphous compound (TCNQ ARS) with a nonmagnetic component has been found. In order to obtain the magnetic contribution to the specific heat, we subtract the lattice part ( $C_{\text{lattice}}$ ) of the specific heat from the total data in the standard way, assuming  $C_{\text{lattice}} \sim T^3$  at low temperatures. The magnetic part ( $C_{\text{mag}}$ ) of the specific heat at low temperatures can be analyzed in terms of the  $S = 1/2$  two-leg Heisenberg spin-ladder model with a



**Figure 7.** (a) Heat capacity of sample (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub>; inset shows the low-temperature part; (b) approximation of low-temperature part of the heat capacity with formula  $C_{\text{exp}} = \alpha T^2 \exp[-\beta T^2] + \gamma T^3$ ,  $\alpha = 4.3275 \times 10^{-2}$ ,  $\beta = 1.1669 \times 10^{-3}$  and  $\gamma = 1.9243 \times 10^{-3}$ . Inset: results of approximation for magnetic part of heat capacity—dashed line, Maxwell function—dotted line.

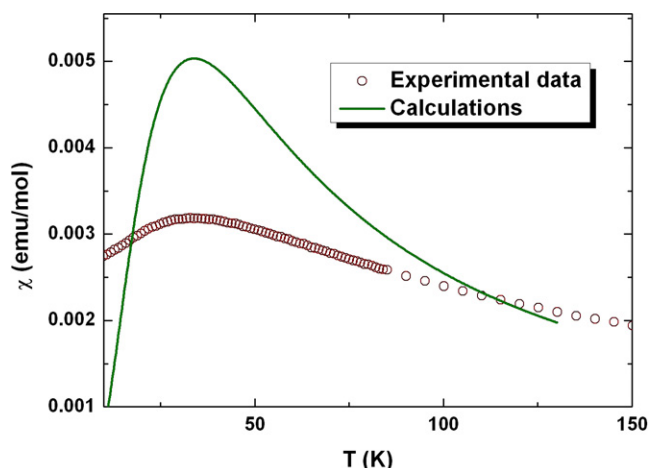
spin Hamiltonian written as

$$H = J_{\text{rung}} \sum_{j=1}^{N/2} S_{1,j} S_{2,j} + J_{\text{leg}} \sum_{i=1}^2 \sum_{j=1}^{N/2} S_{i,j} S_{i,j+1} - h \sum_{i,j} S_{i,j}^z, \quad (3)$$

where  $J_{\text{rung}}$  and  $J_{\text{leg}}$  are the exchange constants along the rung and the leg, respectively,  $S_{ij}$  is the spin on the  $i$ th leg and the  $j$ th rung and  $h$  is the external magnetic field. At low temperatures, up to 20 K, this model can be approximated by the Maxwell function  $C_{\text{mag}} = \alpha T^2 \exp[-\beta T^2]$ . Numerical calculations were done using the temperature-dependent density-matrix-renormalization-group (DMRG) method<sup>6</sup>.

In this procedure, we kept up to five states in the effective state space. The best agreement with experimental data of  $\chi$  and  $C_{\text{mag}}$  is obtained for  $J_{\text{rung}}/k_B = 28$  K,  $J_{\text{rung}}/J_{\text{leg}} = 40$  and  $h/k_B = 50$  (figure 7(b)). The parameters  $J_{\text{rung}}$ ,  $J_{\text{leg}}$  and  $h$  come from optimal correspondence of the calculated magnetic

<sup>6</sup> Software for the magnetic susceptibility and magnetic contribution to the heat capacity enumeration was designed by V Ceranovskij.



**Figure 8.** Experimental data of magnetic susceptibility (open circles). The solid line represents numerical calculation done by the temperature-dependent density-matrix-renormalization-group (DMRG) method for the  $S = 1/2$  two-leg Heisenberg spin-ladder (see footnote 6).

susceptibility and low-temperature heat capacity data (figures 7 and 8).

As can be seen in figures 7 and 8, conformity with the theoretical model is fully satisfactory for the heat capacity, while for the magnetic susceptibility it is only qualitative. So the chosen theoretical model is not fully satisfactory in describing both the heat capacity and magnetic susceptibility behavior of the studied material, probably due to its sophisticated structure. As we mentioned earlier x-ray data show that in this structure three crystallographically non-equivalent TCNQ molecules and two types of stacks are present. For the description of the magnetic behavior of this system a more complex Hamiltonian is needed. However, a larger difference between parameters  $J_{\text{rung}}$  and  $J_{\text{leg}}$  corresponds to the structure of the given ARS: the parameter  $J_{\text{rung}}$  can be assigned to A stacks and parameter  $J_{\text{leg}}$  to BC stacks (see figure 1(b)).

## 5. Conclusion

In this paper we present and discuss the physical properties of the novel (N-Me-2,6-di-Me-Pz)(TCNQ)<sub>2</sub> anion-radical salt; the discussion is based on the crystal structure of the salt. Spectral investigation, performed mainly by the Raman scattering method, permitted us to evaluate the electron distribution on the TCNQ anions and confirm the presence of different anion species. The presence of TCNQ anions with various charges is important for understanding the magnetic ordering of the salt. The magnetization versus temperature in fields up to 5 T, heat capacity and magnetic susceptibility measured in the temperature range from 2 to 300 K permitted us to propose the model of magnetic phenomena of the salt. It was suggested that the magnetic subsystem shows some features of a quasi-one-dimensional spin-ladder type behavior. On the other hand, the studied system can be described as a

quasi-two-dimensional system considering its crystal structure and electrical resistivity.

## Acknowledgments

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