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SHORT COMMUNICATION

Electrical, magnetic and spectroscopic properties of $(TTF)_5Fe(NO_3)_3$

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Abstract

Tetrathiafulvalene, TTF, reacts with $Fe(NO_3)\cdot 9H_2O$ to yield a dark purple charge-transfer compound with the formula $(TTF)_5Fe(NO_3)_3$. The effective magnetic moment at room temperature of 0.6 B. M., the temperature independent paramagnetism in the range 77-300 K, and the absence of an EPR signal attributable to iron, indicates low-spin iron(II), with electron transfer from TTF. The g values of the parallel and perpendicular EPR lines, [(T, $g_{\parallel}$, $g_{\perp}$), (300 K, 2.007, 2.010), (77 K, 2.009, 2.013)], and the line widths indicate that the odd electron resides on, and is delocalized over several TTFs. The conductivity at room temperature is 17 S cm^{-1}, and the temperature dependence of the resistivity indicates semiconducting behavior of a complex nature.

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Introduction

Recently it was found that tetrathiafulvalene, TTF, reacts with the metal halides $FeCl_3$, $FeBr_3$, and the hydrated salts of $RuCl_3$, $RhCl_3$, and $IrCl_4$ to form a series of charge-transfer compounds [1]. The compounds formed with iron(III) chloride and iron(III) bromide with the formulas $(TTF)_2FeCl_3$ and $(TTF)_3FeBr_3$ were especially interesting in view of the results for $(BEDT\text{-}TTF)_2FeCl_4$ (BEDT is bis(ethylenedithio)tetrathiafulvalene) [2]. The compounds with TTF have much higher electrical conductivities than $(BEDT\text{-}TTF)_2FeCl_4$, and the properties of all three compounds differ markedly. The magnetic susceptibility of $(TTF)_3FeBr_3$ is nearly constant in the temperature range 4.2 to 300 K, while that of $(TTF)_2FeCl_3$ increases sharply at low temperature [1]. The room temperature magnetic moments are 4.75 and 5.05 B.M. for $(TTF)_2FeCl_3$ and $(TTF)_3FeBr_3$, respectively. The magnetic moment of $(BEDT\text{-}TTF)_2FeCl_4$ is 6.01 B. M., a value that is consistent with high-spin iron(III) and no detectable contribution from the cation [2]. It was shown earlier, that the stoichiometry of the charge-transfer compound formed by the reaction of TTF with complexes of copper(II) halides, depended on the ligand and the halide coordinated to copper(II) [3]. Variation of the counterion of the metal was the next logical step. This research has been undertaken [4], and the product of the reaction of TTF with $Fe(NO_3)_3 \cdot 9H_2O$ yielded a charge-transfer compound with unusual properties. The preparation and properties of $(TTF)_5Fe(NO_3)_3$ are reported here.

Experimental

The charge-transfer compound $(TTF)_5Fe(NO_3)_3$ was obtained as a dark purple microcrystalline precipitate by adding a solution of $Fe(NO_3)_3 \cdot 9H_2O$ in methanol to a solution of excess TTF in methanol under a nitrogen atmosphere. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Calc.: C 28.21, H 1.60, N 3.30. Found: C 29.11, H 1.61, N 3.60%. Electrical resistivities were measured by the Van der Pauw four-probe d.c. method [5] by using a model 21SC Cyrodine Cryocooler from CTI-Cryogenics in the temperature range 80-300 K. Constant current was applied by using a Keithley model 227 current source and the voltage was measured with a Fluke 8502A multimeter. Magnetic susceptibility measurements were carried out with a Faraday Balance in the temperature range 77 K to room temperature [6]. The data were corrected for temperature independent paramagnetism and the diamagnetism of the constituent atoms using Pascal's constants [7,8]. EPR spectra of powdered samples were obtained with a Varian E-3 X-band spectrometer at 9.5 GHz. The free radical DPPH ($g = 2.0036$) was used as a field marker. Electronic spectra were obtained in the range 200-800 nm by using a Simadzu model UV-240 spectrophotometer and solutions or solid/Nujol mulls of the compound. The samples were mounted between quartz plates. Infrared spectra were obtained by using Nujol mulls on a sodium chloride plate with a Mattson Polaris FT-IR spectrophotometer.

Results and discussion

The electrical resistivity of a powdered sample of $(TTF)_5Fe(NO_3)_3$ was measured from 80 K to 300 K. The resistivity increases with decreasing temperature, but as shown in

Figure 1, the temperature dependence of the logarithm of the resistivity versus 1000/T of a powdered sample, pressed into a pellet, is not linear, but forms a smooth convex curve. The results clearly indicate that $(TTF)_5Fe(NO_3)_3$ exhibits semiconducting behavior of a complex nature.

The data can not be fit by the equation $\rho = \rho_0 exp(E_a/k_BT)$, nor by the mobility model $\rho(t) = A \cdot T^{\alpha} exp(E_a/k_BT)$ [9]. The mobility model accounts for thermal activation of charge carriers and the temperature dependence of the mobility of the charge carriers. The plot of ln ρ vs. 1/T is nearly linear in the temperature range 240 to 300 K, and the activation energy was estimated from this asymptote. Least-square fits of the equation $\rho = \rho_0 exp(E_a/k_BT)$ to the data yield an activation energy $E_a = 0.042$ eV . The low activation energy is consistent with the experimentally measured electrical conductivity at room temperature of 17 S cm^{-1}. This value for σ_{RT} is much greater than the electrical conductivities of $(TTF)_2CuCl_4$ [10] or $(BEDT\text{-}TTF)_2FeCl_4$ [2], and similar to those of $(TTF)_nCuCl_2$(n = 2 or 7/3) [11]. TTF in $(TTF)_2CuCl_4$ is known to be completely ionized, whereas TTF is partially ionized in $(TTF)_nCuCl_2$, and columnar structures are formed in the latter compound. $(BEDT\text{-}TTF)_2FeCl_4$ also consists of stacks of completely ionized BEDT-TTF dimer molecules. The relatively high electrical conductivity in $(TTF)_5Fe(NO_3)_3$ indicates that TTF in the compound is partially ionized and stacked to form chains.

Magnetic and spectroscopic properties of $(TTF)_5Fe(NO_3)_3$ also provide evidence of low-dimensional and partially ionized TTF donor molecules in the compound. Electron paramagnetic resonance spectra of a powdered sample were obtained both at room temperature and at 77 K. The EPR spectra exhibit good resolution of parallel ($g_{\parallel}$) and

perpendicular ($g_\perp$) components with the values (T, $g_\parallel$, $g_\perp$) of (300 K, 2.007, 2.010) and (77 K, 2.009, 2.013). The values are very close to g value of TTF^+ ion in solution [12]. This observation indicates that the odd electrons reside on TTF in $(TTF)_5Fe(NO_3)_3$. The relatively narrow peak-to-peak linewidths in the EPR spectra (6-7 gauss) in $(TTF)_5Fe(NO_3)_3$ also indicates that the interaction along and among TTF stacks are significant [13,14]. A signal attributable to iron metal was not detected, and it may be concluded that the iron ion in $(TTF)_5Fe(NO_3)_3$ is in the diamagnetic low-spin octahedral Fe(II) state.

The experimentally determined magnetic susceptibilities are 1.61×10^{-4} and 1.70×10^{-4} emu/mole at 300 K and at 80 K, respectively. The magnetic susceptibilities are almost temperature independent in the temperature range of the measurements, with the effective magnetic moments being 0.62 and 0.34 B.M. at 300 K and at 80 K, respectively. Small and temperature-independent magnetic susceptibility, Pauli paramagnetism, is well known in low-dimensional semiconductors [15], and the magnetic susceptibility results, together with the EPR results, are consistent with the conclusion that the unpaired electrons are associated with and delocalized over the $(TTF)_5^+$ radicals. The data reflect large interactions between molecular units in stacked columnar chains.

Electronic spectra of $(TTF)_5Fe(NO_3)_3$ show λ_{max} = 584 and 442 nm in DMF solution and λ_{max} at 552, 381, and 317 nm in Nujol mulls. The electronic transitions are comparable to the results found for the charge-transfer compounds TTF-FeX_3, in which TTF is partially ionized [1]. There are bands at 378 and 560 nm in Nujol mulls of $(TTF)_3FeBr_3$, with the corresponding bands occurring at 404 and 552 nm for $(TTF)_2FeCl_3$. There are higher energy bands in the halide salts also, but there is no direct correlation with the band at 317 in the

nitrate salt.

The IR spectrum exhibited a very broad intense band extending from about 1,000 cm^{-1} to 4,000 cm^{-1}. The intense absorption arises from the band structure of these semiconductors and masks many of the vibrational modes of the compound [16]. Three vibrational bands of TTF were observed in the absorption tail; these occur at 729 cm^{-1} (υ_{25}, ring SCC bend), 823 cm^{-1} (υ_{16}, CS stretch), and at 1240 cm^{-1} (υ_{23}, CCH bend). The bands were assigned by making comparison with those reported for other one-dimensional TTF compounds [17]. The υ_{16} absorption band (823 cm^{-1}) is intermediate between that of TTF^0 (781 cm^{-1}) and TTF^+ (836 cm^{-1}), signaling fractional-charge occupation of TTF in $(TTF)_5Fe(NO_3)_3$ [11].

There is no straight-forward explanation for the low-spin electronic configuration of the iron(II) ion. Coordination by nitrate ions alone would not be expected to lead to low-spin iron(II). This forces the conclusion that the iron(II) ions are associated with sulfur atoms in the TTF stacks. It is possible that the iron(II) ions are bound to sulfur atoms in adjacent stacks, thereby providing a pathway for inter-stack interactions. Such inter-stack interactions are indicated by the narrow EPR line widths. Tomkiewicz and Taranko [14] have shown that in TTF-halides, the EPR line widths run parallel to the inter-stack interactions with narrow line widths indicating stronger interactions and broader line widths indicating weaker inter-stack interactions. Evidence for this final suggestion for coordination of the iron could be obtained from a structural determination by X-ray crystallography. We have not yet obtained crystals of this quality from our experiments.

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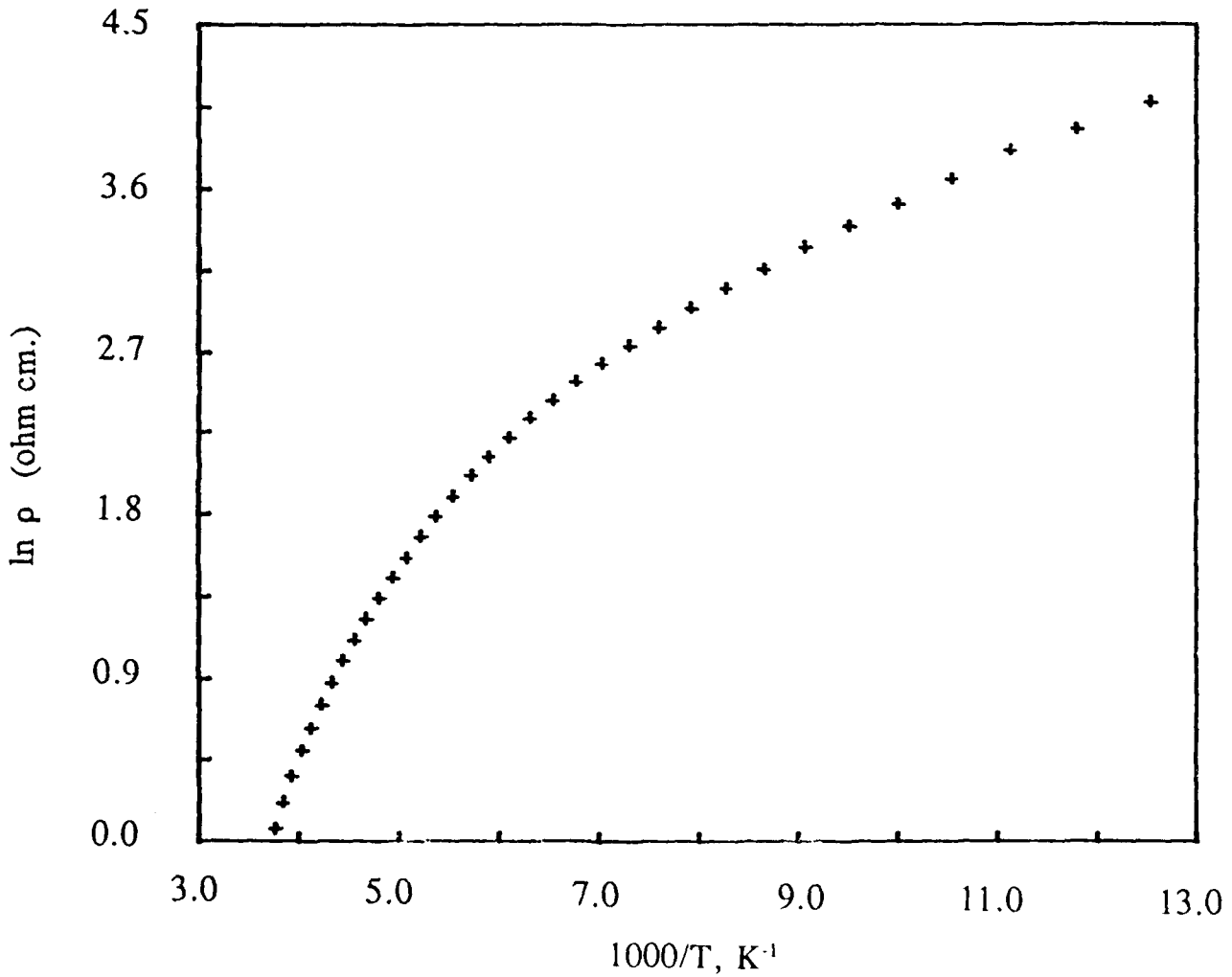
Figure Caption

Figure 1. A plot of ln ρ versus 1000/T (T in units of K) for $(TTF)_5Fe(NO_3)_3$.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