

**A Novel BEDT-TTF-based Purely Organic Magnetic Conductor,
 α -(BEDT-TTF)₂(TEMPO-N(CH₃)COCH₂SO₃)·3H₂O**

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Abstract

A new BEDT-TTF-based salt with an organic free radical TEMPO has been prepared. The salt consists of alternate layers of conducting and magnetic sheets, between which are short S(BEDT-TTF)...O(TEMPO) contacts. The magnetic susceptibility is well modelled by the combination of a Curie-Weiss and a 2-D Heisenberg models with $J = -89$ K and $\theta = +0.05$ K.

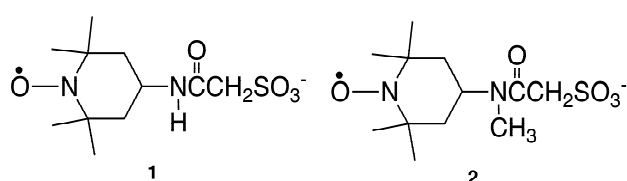
1. Introduction

Over the past decade, molecule-based magnetic conductors have attracted great interest due to the discovery of their unique physical properties. For example, paramagnetic superconductivity [1-3], a paramagnetic metallic state [3], metallic antiferromagnetism [3,4], metallic ferromagnetism [3,5], a field induced metallic/superconducting state [6], etc. have been reported. Their interesting properties emerge from interactions between magnetic centres incorporated into conducting lattices. In many cases, the magnetic source is a transition metal compound. However, magnetic interactions in these salts are usually very small. This is because the transition metals are usually surrounded by ligands such as Cl⁻, Br⁻, C₂O₄²⁻, CN⁻, etc., through which the metals must interact indirectly with one other.

An alternative source of localized spins are stable organic free radicals. The spin is localized on one or a few atoms, which are not completely surrounded by other atoms.

In other words, the spin is located on a ‘bare’ orbital, which can potentially overlap directly with another orbital which contains a localized spin or conduction electron. Therefore many researchers have introduced organic radicals in organic conducting salts. For example, charge-transfer (CT) salts of free radical substituted organochalcogen donors [7-16], CT complexes of free radicals and acceptors [17-18], CT salts of free radical substituted cations and acceptors [19-23], have been reported. For more than five years, we have focused on preparing new organic magnetic anions that include the organic free radical tetramethylpiperidine-1-oxyl (TEMPO) with sulfonate ($-\text{SO}_3^-$) for use as a counterion in (donor)_n(anion)-type organic conductors [24-31]. Recently, we prepared a sulfo derivative of TEMPO, TEMPO-NHCOCH₂SO₃⁻ (**1**). **1** forms a CT salt of the donor, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with stoichiometry $\alpha\text{-(BEDT-TTF)}_3(\text{TEMPO-NHCOCH}_2\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$ [31]. This salt is a semiconductor and has a TEMPO \cdots TEMPO interaction to form a 1-D ferromagnetic chain. Its temperature-dependent magnetic susceptibility is well described by a 1-D ferromagnetic Heisenberg model with $J = +0.42$ K.

In this paper, we report the structures and physical properties of the N-methyl derivative of **1**, TEMPO-N(CH₃)COCH₂SO₃⁻ (**2**) prepared as a tetraphenylphosphonium (PPh₄) salt (**3**) and its electrochemically synthesized salt with BEDT-TTF, $\alpha\text{-(BEDT-TTF)}_2(\text{2}) \cdot 3\text{H}_2\text{O}$ (**4**). We also report the temperature dependence of electrical resistivity of **4** under high pressure.



2. Experimental

4-methylamino-TEMPO was prepared according to the literature method [32] (yield 66%). The acidic TEMPO-N(CH₃)COCH₂SO₃H was prepared by reacting 4-methylamino-TEMPO (1.5 g, 7.8 mmol) with sulfoacetic acid (1.3 g, 9.4 mmol) in the presence of **dicyclohexylcarbodiimide (DCC)**, 3.9 g, 19 mmol) and **dimethylaminopyridine (DMAP)**, 2.3 g, 19 mmol) in 30 mL of CH₂Cl₂ at room

temperature with stirring overnight. Metathesis of the acid **1** with $\text{PPh}_4\cdot\text{Br}$ gave **3** as orange crystals, which were then recrystallized from acetone (yield 23%). X-ray diffraction data of **1** were collected on a Rigaku AFC-5R 4-circle diffractometer at room temperature. Plate-shaped crystals of **4** were obtained by the controlled-current electrocrystallization method [33-34] in *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ (15 mL) with 10 mg of BEDT-TTF and 70 mg of **3**. Single crystal X-ray diffraction data of **4** were collected with a Quantum CCD area detector on a Rigaku AFC-7R diffractometer, at room temperature. The electrical resistivity was measured by a standard four-probe method. The temperature-dependent electrical resistivity under static pressure was measured using a clamp-type pressure cell. The magnetic susceptibility of a polycrystalline sample from 2-300 K was measured using a Quantum Design MPMS-5S SQUID magnetometer.

3. Results and discussion

The crystal data of the PPh_4 salt (**3**) are as follows: 299 K, Triclinic $P\bar{1}$, $a = 12.074(2)$, $b = 13.910(3)$, $c = 10.616(5)$ Å, $\alpha = 98.05(3)$, $\beta = 98.49(3)$, $\gamma = 100.05(2)^\circ$, $V = 1711(1)$ Å³, $R = 0.065$, $R_w = 0.068$. One PPh_4 cation and one anion of **2** are crystallographically independent. In the crystal, there is a TEMPO spin dimer about the center of symmetry with a short O...O contact of 4.775(5) Å. Actually, the temperature-dependent magnetic susceptibility is well explained by a Singlet-Triplet model [35] with $C = 0.378$ emu·K/mol and $J = -5.78$ K.

The crystal data of the BEDT-TTF salt (**4**) are as follows: 297 K, Triclinic $P1$, $a = 8.4178(4)$, $b = 11.678(1)$, $c = 24.028(2)$ Å, $\alpha = 98.178(4)$, $\beta = 100.7030(7)$, $\gamma = 89.3580(9)^\circ$, $V = 2297.1(3)$ Å³, $R = 0.055$, $R_w = 0.043$. Fig. 1 shows the crystal structure of **4**. There are four cations [**A**, **B**, **C**, and **D** in Fig. 2(a)], two anions, and six water molecules in the unit cell. Since the space group is $P1$, all of the molecules in the unit cell are crystallographically independent. A donor to anion ratio of 2:1 indicates that each BEDT-TTF molecule has a formula charge of +1/2. The crystal consists of alternating layers of the donors and the anions, with water molecules in the anionic layer. The packing arrangement of the donor layer is shown in Fig. 2(a). Along the *a*-axis, there are two independent BEDT-TTF stacks, **ABAB** and **CDCD**, which interact with each other alternately along the *b*-axis, giving an α -type 2-D conducting sheet. There are many short S...S contacts between the columns. On the other hand there are no

short intra-column contacts and relatively long plane-plane distances in the range of 3.80-3.90 Å [Fig. 2(a)], suggesting that the intra-column interactions are weaker than the inter-column interactions. The central C=C distances of **A**, **B**, **C**, and **D** are 1.37(1), 1.35(1), 1.358(9), and 1.382(9) Å, respectively. We have used bond lengths to estimate the charge on each BEDT-TTF molecule [36], which gives charges for **A**, **B**, **C**, and **D** of +0.85, +0.11, +0.36, and +0.80, respectively. This suggests that the positive charge is not equally distributed over the BEDT-TTF molecules but not completely localized as in charge disproportionation. Fig. 2(b) shows the crystal structure of the anionic layer. All of the orange- and red-colored $-\text{SO}_3^-$ groups are directed approximately in the $[-1\ 1\ 0]$ direction, indicating the crystal is polar. This is consistent with its chiral space group, $P1$. Also an N-O distance of 1.277(7) Å in the TEMPO moiety is observed, which is within the range reported for neutral TEMPO radicals (1.27-1.30 Å) [37]. It is noteworthy that the crystal has short S...O contacts between BEDT-TTF and TEMPO as shown in Fig. 1. The distances are as long as the van der Waals distance (3.37 Å). This suggests that the material may display a new phenomenon where the interplay between conduction and localized electrons plays a crucial role.

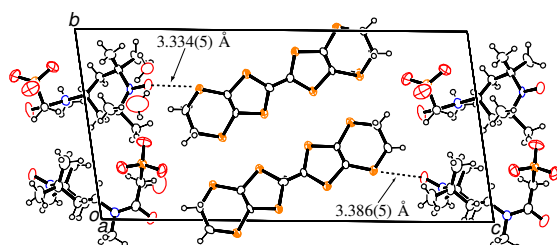
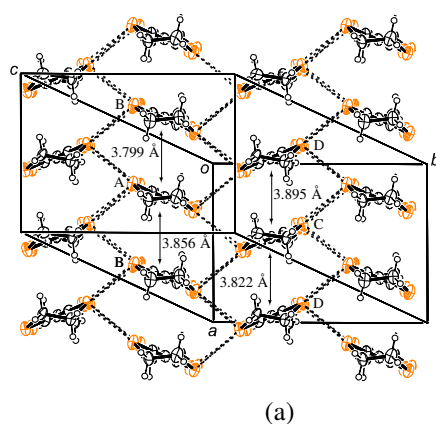


Fig. 1. A projection of the crystal structure of **4** along the a -axis.



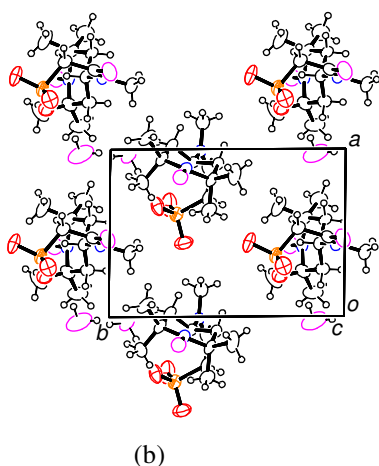


Fig. 2. (a) Packing arrangement of the donor layer in **4**. Dashed lines indicate S...S contacts shorter than the van der Waals distance (< 3.7 Å). (b) Crystal structure of the anionic layer.

Fig. 3 shows the Arrhenius plot of the electrical resistivity of **4**. The salt is a semiconductor with a room temperature resistivity of 5.4 Ω·cm. The activation energy (E_a) from 300-250 K is 0.65 eV. At 250 K the resistivity curve bends and below this point E_a becomes smaller, 0.22 eV. It is somewhat strange that the activation energy is smaller at lower temperatures and we discuss this below.

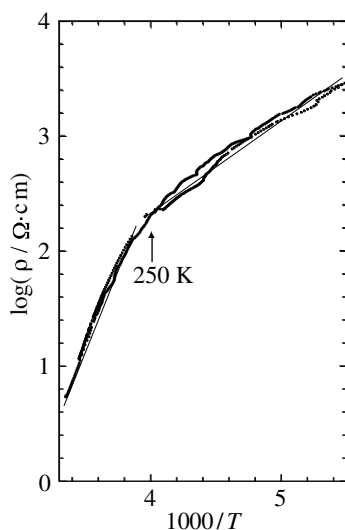


Fig. 3. Electrical resistivity versus $1000/T$ plot of **4**. Solid lines are guide for eyes.

Fig. 4 shows the temperature dependence of the electrical resistivity of **4** under static pressure up to 15 kbar. The results clearly indicate that there is a

semiconductor-to-semiconductor transition and the transition temperature decreases with increasing pressure. This suggests that the ambient pressure activation energy below 250 K is smaller than that above 250 K because the state from 250-300 K is located on a phase boundary. The high temperature state might be observed above room temperature. The sample does not show metallic behavior up to 15 kbar at which the lowest activation energy is 0.041 eV.

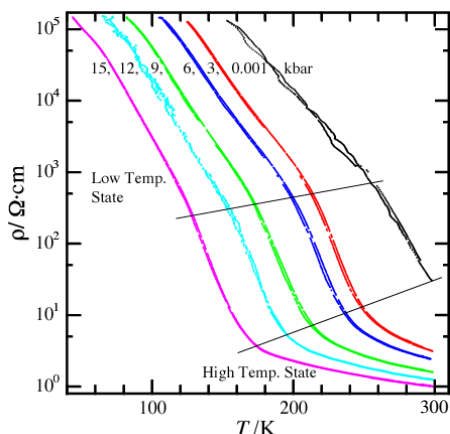
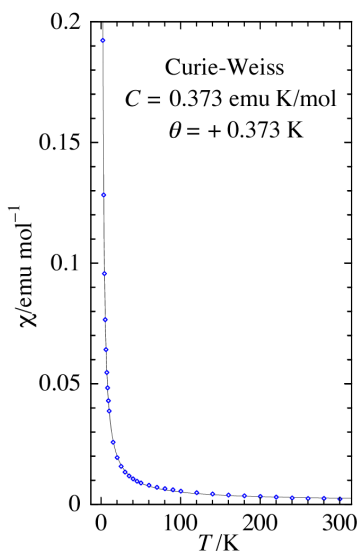


Fig. 4. Temperature dependences of electrical resistivity of **4** under static pressure up to 15 kbar.

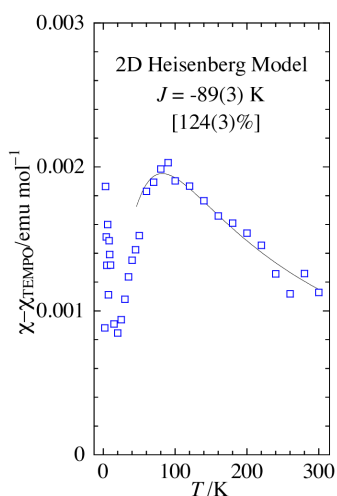
Fig. 5(a) shows the χ - T plot of **4**. The result can be modelled by a Curie-Weiss law with $C = 0.373$ emu·K/mol and $\theta = +0.05$ K with a residual paramagnetic term that does not obey the Curie-Weiss law. The Curie constant is close to the value predicted for TEMPO (0.375 emu·K/mol), suggesting that this moiety dominates the Curie term. On the other hand, the additional paramagnetic term may be a contribution from the BEDT-TTF cations. To obtain the temperature dependence of the paramagnetic term, we subtracted the Curie term from the total data. The resultant magnetic susceptibility curve is shown in Fig. 5(b). The susceptibility in the range of 0.8 - 2.0×10^{-3} emu/mol is much larger than that of the usual organic metallic conductors (2 - 6×10^{-4} emu/mol) or band insulators ($< 1 \times 10^{-4}$ emu/mol), suggesting that the electrons are localized on the BEDT-TTF molecules. The curve has a broad maximum around 100 K, which is a signature of a low-dimensional Heisenberg antiferromagnet. Indeed, the curve can be modelled well by a 2-D antiferromagnetic Heisenberg model [38]. The best fit [overlaid line in Fig. 5(b)] is found with $J = -89(3)$ K (124(3)% of spin concentration). The result suggests that the system has charge disproportionation, which is also indicated at room temperature by the X-ray diffraction data. However, the X-ray diffraction was measured

at 297 K, at which point the system is located on the low temperature edge of the high temperature state (see Fig. 3 and 4) where the **charge is not fully disproportionated**. Lowering the temperature and so moving into the low temperature state then promotes **more** charge disproportionation. The occurrence of the charge disproportionation is likely to be the driving force for the phase transition. **In addition, the donor arrangement has a dihedral angle (θ) between donor columns of 131.8-132.6° which is quite similar to that of θ -(BEDT-TTF)₂Cu₂(CN)[N(CN)₂]₂ ($\theta = 132^\circ$), also a 2-D antiferromagnet with a charge-order transition at 220 K [39-40].**

Although this salt has significant short contacts between O atoms of TEMPO and S atoms of BEDT-TTF as shown in Fig. 1, there is no evidence of an interaction between localized spins and the conduction electrons. Usually, such interaction becomes apparent in the magnetic or transport data at very low temperature. The observation of the significant magnetic interaction via the donor layer would likely require the layer being metallic or magnetic at low temperatures. However, here the spins localized on a BEDT-TTF molecule strongly interact antiferromagnetically with each other and so become non-magnetic at low temperature where the salt is also an insulator. This may also be the reason why the Weiss constant of this salt is almost zero. Preparation of metallic or magnetic salts including a TEMPO anion is now in progress.



(a)



(b)

Fig. 5. (a) χ - T plots for salt **4** where χ is the magnetic susceptibility per half of the unit cell [(BEDT-TTF)₂(**2**)·3H₂O]. The solid line is calculated on the basis of a Curie-Weiss expression. (b) χ - T plots after subtracting the Curie term ($\chi_{\text{Curie-Weiss}} = 0.373/(T-0.05)$) from the total susceptibility. The solid line is calculated on the basis of a 2-D Heisenberg model.

In conclusion, we have found a novel BEDT-TTF-based charge transfer salt that includes the organic magnetic anion, TEMPO-N(CH₃)COCH₂SO₃⁻. The salt has a semiconductor-to-semiconductor transition just below room temperature. The transition temperature decreases with increasing static pressure. The magnetic susceptibility is explained by the combination of a Curie-Weiss and 2-D Heisenberg models with $J = -89$ K and $\theta = +0.05$ K.

Acknowledgements

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