New BEDT-TTF-based Organic Conductor Including an Organic Anion Derived from the TEMPO Radical, α-(BEDT-TTF)$_3$(TEMPO–NHCOCH$_2$SO$_3$)$_2$·6H$_2$O

Hiroki Akutsu,* Jun-ichi Yamada, and Shin'ichi Nakatsuji
Department of Material Science, Graduate School of Science, Himeji Institute of Technology,
3-2-1, Kouto, Kamigori-cho, Ako-gun, Hyogo 678-1297

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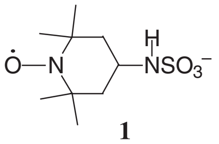
We report the genuine-organic magnetic conductor including organic free radical as a part of a counter anion, α-(BEDT-TTF)$_3$(TEMPO–NHCOCH$_2$SO$_3$)$_2$·6H$_2$O, which consists of the conducting layers of the BEDT-TTF cations arranged in the α-packing mode and the magnetic layers of the TEMPO–NHCOCH$_2$SO$_3$ anions with water molecules alternatively along the *c* axis. In the magnetic layer, TEMPO groups gather to form a 1-D ferromagnetic network. The salt is semiconductive ($\rho_{RT} = 5.1\ \Omega$·cm and $E_a = 0.050$ eV) and its temperature-dependent susceptibility obeys the 1-D ferromagnetic Heisenberg model ($C = 0.380$ emu/mol K and $J = +0.42$ K).

Numerous organic magnetic conductors, which include inorganic transition metals as a magnetic source, have been prepared. The goal is to discover new physical phenomena where the interplay between the conduction π electrons and the localized d spins plays a crucial role.[1] Another source of localized spins, stable organic free radicals has also been extensively used. For example, charge-transfer (CT) salts of free radical substituted organocalcogen donors,[2] CT complexes between free radicals and acceptors,[3] CT salts of free radical substituted cations and acceptors,[4] were previously reported. However, genuine-organic magnetic CT salts of common organocalcogen donors such as tetramethyltetraselenafulvalene (TMTSF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are not available. This is because of a lack of suitable anionic organic free-radical derivative components to form the CT salts. We have investigated the preparation and characterization of free radical substituted anions for use as the counter ion in CT salts. In our previous papers,[5,6] we reported anions **1** and **2** and their tetrathiafulvalene (TTF) salts obtained by metathesis of their tetraphenylphosphonium (PPh$_4$) salts with (TTF)$_3$(BF$_4$)$_2$. However, we could not obtain other organocalcogen donor salts by electrocrystallization because of electrochemical decomposition of the –NHSO$_3$ and –OSO$_3$ parts of anions.[6] Therefore, a more electrochemically stable anion has been desired. In this paper, we report the structures and physical properties of a tetramethylpiperidine-1-oxyl (TEMPO) based new anion, TEMPO–NHCOCH$_2$SO$_3$ (**3**) prepared as a tetraphenylphosphonium (PPh$_4$) salt and its electrochemically synthesized salt with BEDT-TTF (**4**), α-(**4**)$_3$(**3**)$_2$·6H$_2$O.



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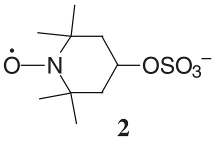

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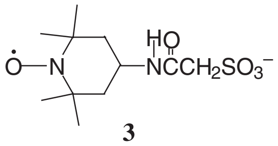

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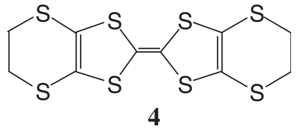

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The acidic TEMPO–NHCOCH$_2$SO$_3$H was prepared by reacting 4-amino-TEMPO (1.0 g, 5.8 mmol) with sulfoacetic acid (HOOCCH$_2$SO$_3$H) (1.0 g, 7.0 mmol) in the presence of dicyclohexylcarbodiimide (DCC, 2.9 g, 14.0 mmol) and dimethylaminopyridine (DMAP, 0.9 g, 7.0 mmol) in 30 mL of CH$_2$Cl$_2$ at room temperature with stirring overnight. Exchange of the counter cation with PPh$_4$·Br gave the PPh$_4$ salt of **3**, as orange block-like crystals, recrystallized from acetone (yield 58%). X-ray diffraction data were collected on a Rigaku AFC-5R 4-circle diffractometer at room temperature.[7] In the crystal, one PPh$_4$ cation and an anion of **3** are independent. The observed N–O distance of 1.288(3) Å is within the range of those of reported neutral TEMPO radicals (1.27–1.30 Å).[8] The magnetic susceptibility of a polycrystalline sample from 2–300 K using a Quantum Design MPMS-5S SQUID magnetometer has a Curie-like behavior with $C = 0.373$ emu mol^{-1} K^{-1}.

Crystals of α-(**4**)$_3$(**3**)$_2$·6H$_2$O were obtained by the controlled-current electrocrystallization method[9] in PhCl (15 mL) with 15 mg of **4** and 70 mg of PPh$_4$·**3**. Poorer quality crystals were also obtained by the conventional constant-current method (0.2–0.3 μA) in PhCl. Single-crystal X-ray diffraction data were recorded using a Quantum CCD area detector on a Rigaku AFC-7R diffractometer at room temperature.[10] The crystal structure of the salt is shown in Figure 1. In the asymmetric unit, there are one (**A**) and a half (**B**) cations, one anion, and three water molecules (Figure 1). The donor forms a trimer (A–B–A′) about a center of symmetry without lateral shifts. It stacks along the *a* axis with a lateral shift of ca. 2.8 Å along the molecular long axis. In the stack, the mean intratrimer (A–B) and intertrimer (A–A′) plane–plane distances are 3.74 and 3.71 Å, respectively (Figure 2). Furthermore, the stack interacts with each other along the *b* axis (side-by-side direction), giving the α-type 2-D conducting sheet. The central C=C bond lengths of molecules **A** and **B** are similar, 1.360(4) and 1.372(6) Å, respectively, which indicates each cation has the almost same charge, the average

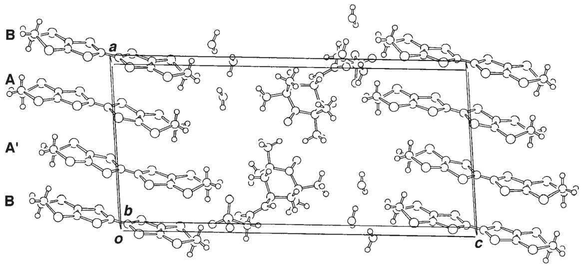

Figure 1. Crystal structure of α-(**4**)$_3$(**3**)$_2$·6H$_2$O.

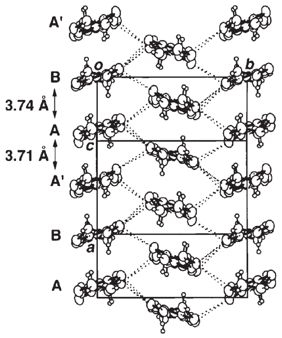

Figure 2. Packing arrangement of **4** in α-$(\mathbf{4})_3(\mathbf{3})_2{\cdot}6H_2O$. Dashed lines indicate S···S contacts shorter than the sum of the van der Waals distances (<3.70 Å).

charge of +2/3 on each BEDT-TTF molecule. Therefore, there is no significant charge separation in the salt. However, an average charge of +2 per trimer suggests that the salt is a band insulator. Actually, the electrical resistivity, as measurement down to liquid nitrogen temperature, shows semiconductive behavior with $\rho_{RT} = 5.1\,\Omega{\cdot}cm$ and $E_a = 0.050\,eV$.

The magnetic layer includes three independent water molecules, which form a 1-D hydrogen-bond chain along the *a* axis and the chain has many hydrogen bonds to the other oxygen atoms apart from the oxygen atom of the spin center (O5). O5 interacts with the N1 (2.865(4) Å) and C20 (3.383(4) Å) of the nearest TEMPO to form a 1-D magnetic network along the *b* axis (Figure 3). According to the McConnell's theory,[11] both contacts can mediate the ferromagnetic interaction. The SQUID measurement of the salt was performed from 2 to 300 K. The temperature-dependent magnetic susceptibility is well explained by the 1-D ferromagnetic Heisenberg model with $C = 0.380$ emu/mol K and $J = +0.42$ K (Figure 4). The *C* value indicates the presence of one spin per the asymmetric unit, which appears to be located on the TEMPO moiety because usually there is no spin on the divalent trimer of BEDT-TTF. Furthermore, the donor layer plays no significant part in the magnetic interaction because there are no short contacts between BEDT-TTF and TEMPO. In addition, the N–O distance of the TEMPO part is 1.284(3) Å, within the range for neutral TEMPO derivatives (1.27–1.30 Å),[8] indicating no oxidation from TEMPO part of **1** in the title salt.

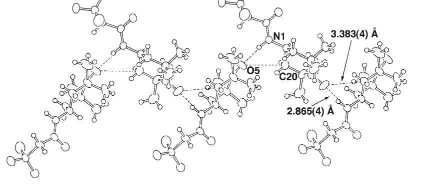

Figure 3. Magnetic networks in the anion layer of α-$(\mathbf{4})_3(\mathbf{3})_2{\cdot}6H_2O$. Dashed lines indicate short contacts within 3.6 Å from O5.

In conclusion we have found a new type of BEDT-TTF-based charge transfer salt that includes the organic magnetic anion, TEMPO–$NHCOCH_2SO_3$. The salt is a semiconductor with a rather low room temperature resistivity ($\rho_{RT} = 5.1\,\Omega{\cdot}cm$) and shows a 1-D Heisenberg-like behavior with a weak ferromagnetic interaction ($J = +0.42$ K). Since the salt was obtained by electrocrystallization without decomposition of the anion, the formation of CT salts with other organocalcogen donors is expected to be successful and is now in progress.

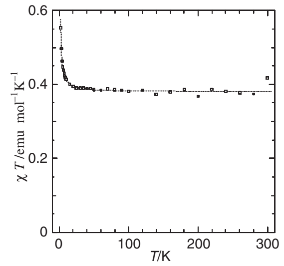

Figure 4. χT–T plots for the α-$(\mathbf{4})_3(\mathbf{3})_2{\cdot}6H_2O$ salt where χ is the magnetic susceptibility per the asymmetric unit $[(\mathbf{4})_{1.5}(\mathbf{3}){\cdot}3H_2O]$. Dashed line is calculated on the basis of a 1-D Heisenberg expression.

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References and Notes

1 H. Kobayashi, A. Kobayashi, and P. Cassoux, *Chem. Soc. Rev.*, **29**, 325 (2000); S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, and H. Kobayashi, *Nature*, **410**, 908 (2001).

2 T. Sugano, T. Fukasaka, and M. Kinoshita, *Synth. Met.*, **41–43**, 3281 (1991); H. Fujiwara and H. Kobayashi, *Chem. Commun.*, **1999**, 2417; H. Fujiwara, E. Fujiwara, and H. Kobayashi, *Chem. Lett.*, **2002**, 1048; H. Fujiwara, H.-J. Lee, H. Kobayashi, E. Fujiwara, and A. Kobayashi, *Chem. Lett.*, **32**, 482 (2003); J. Nakazaki, M. M. Matsushita, A. Izuoka, and T. Sugawara, *Tetrahedron Lett.*, **40**, 5027 (1999); J. Nakazaki, Y. Ishikawa, A. Izuoka, T. Sugawara, and Y. Kawada, *Chem. Phys. Lett.*, **319**, 385 (2000); T. Sugimoto, S. Yamaga, M. Nakai, K. Ohmori, M. Tsujii, H. Nakatsuji, and H. Hosoito, *Chem. Lett.*, **1993**, 1361.

3 K. A. Hutchison, G. Srdanov, R. Menon, J.-C. P. Gabriel, B. Knight, and F. Wudl, *J. Am. Chem. Soc.*, **118**, 13081 (1996); S. Nakatsuji and H. Anzai, *J. Mater. Chem.*, **7**, 2161 (1997).

4 Y. Nakamura, N. Koga, and H. Iwamura, *Chem. Lett.*, **1991**, 69; K. Mukai, S. Jinno, Y. Shimobe, N. Azuma, Y. Hosokoshi, K. Inoue, M. Taniguchi, Y. Misaki, and K. Tanaka, *Polyhedron*, **20**, 1537 (2001); S. Aonuma, H. Casellas, C. Faulmann, B. Garreau de Bonneval, I. Malfant, P. Cassoux, P. G. Lacroix, Y. Hosokoshi, and K. Inoue, *J. Mater. Chem.*, **11**, 337 (2001).

5 H. Akutsu, J. Yamada, and S. Nakatsuji, *Chem. Lett.*, **2001**, 208.

6 H. Akutsu, J. Yamada, and S. Nakatsuji, *Synth. Met.*, **120**, 871 (2001).

7 Crystal data for $PPh_4{\cdot}\mathbf{3}$: $C_{35}H_{40}O_5N_2PS$, $M_r = 631.75$, triclinic, space group $P\bar{1}$, $a = 11.997(1)$, $b = 13.410(1)$, $c = 10.827(1)$ Å, $\alpha = 97.074(9)$, $\beta = 103.137(9)$, $\gamma = 81.331(9)^\circ$, $V = 1669.7(3)$ Å^3, $T = 298$ K, $Z = 2$, μ(Mo Kα) $= 0.188\,mm^{-1}$, $D_{calcd} = 1.256\,g/cm^3$, 8182 reflections measured, 7671 independent ($R_{int} = 0.032$). 4163 reflections ($I > 3\sigma(I)$), $R = 0.052$ and $R_w = 0.056$ (CCDC-217185).

8 R. N. Shibaeva, *Zh. Strukt. Khim.*, **16**, 330 (1975).

9 H. Anzai, J. M. Delrieu, S. Takahashi, S. Nakatsuji, and J. Yamada, *J. Cryst. Growth*, **154**, 145 (1995); H. Nishikawa, T. Sato, T. Kodama, I. Ikemoto, K. Kikuchi, H. Anzai, and J. Yamada, *J. Mater. Chem.*, **9**, 693 (1999).

10 Crystal data for $(\mathbf{4})_3(\mathbf{3})_2{\cdot}6H_2O$: $C_{52}H_{76}O_{16}N_4S_{26}$, $M_r = 1846.74$, monoclinic, space group $P2_1/a$, $a = 12.4910(8)$, $b = 11.625(1)$, $c = 26.4670(7)$ Å, $\beta = 94.1770(6)$, $V = 3833.0(4)$ Å^3, $T = 298$ K, $Z = 2$, μ(Mo Kα) $= 0.786\,mm^{-1}$, $D_{calcd} = 1.600\,g/cm^3$, 33217 reflections measured, 8511 independent ($R_{int} = 0.0002$). 5967 reflections ($I > 3\sigma(I)$), $R = 0.067$ and $R_w = 0.055$ (CCDC-21786).

11 H. M. McConnell, *J. Chem. Phys.*, **39**, 1910 (1963).

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