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Structure and properties of a BEDT-TTF-based organic conductor with a ferrocene-based magnetic anion octamethylferrocenedisulfonate

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Abstract: The structure and properties of a new semiconducting BEDT-TTF-based charge-transfer salt containing the magnetic monoanion octamethylferrocenedisulfonate ($^-\text{O}_3\text{S-C}_5(\text{CH}_3)_4\text{Fe}^+\text{C}_5(\text{CH}_3)_4\text{-SO}_3^-$ (ofds)), $\alpha\text{-(BEDT-TTF)}_5(\text{ofds})_2$ is described (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene). The salt is a semiconductor with $\rho_{\text{RT}} = 5.6 \times 10^3 \Omega\cdot\text{cm}$ and $E_g = 0.11 \text{ eV}$. There are two types of spins not only on the ferrocenyl parts but also the 2D donor layers. The former and latter spins obey Curie-Weiss ($C = 0.721 \text{ emu K mol}^{-1}$ and $\theta = -5.5 \text{ K}$) and 2D Heisenberg ($J_{2\text{DH}} = -80.3 \text{ K}$) models, respectively.

Introduction

Ferrocene is one of the most widely used molecules in functional materials for sensors,^[1] solar cells,^[2] magnets,^[3] and so on. The utility of ferrocene and its derivatives is, in part, because it shows stable redox behaviour with respect to chemical and physical environments, which is therefore useful for sensors and dye sensitized solar cells. The neutral ferrocenyl moiety is diamagnetic, whilst the cationic form has a magnetic moment, which has been widely used as a magnetic source in molecular magnetism. One of the most well-known compounds is a ferromagnet, the complex of decamethylferrocene with tetracyanoethylene (TCNE) with $T_C = 4.8 \text{ K}$.^[4]

Organic conductors that have both electrical conducting and magnetic properties have received great attention due to reports of unique physical phenomena that emerge from an interplay between the itinerant and localized electrons.^[5-7] For this reason, ferrocene derivatives have also been introduced into organic conductors.^[8-11] However, these salts show poor conductivity. This is probably because the bulky ferrocenyl components prevent significant intermolecular interactions between the conjugated dithiolene rings of the conductive component. The latter is necessary for appreciable conductivity. Moreover, the ferrocenyl parts of the salts are neutral and therefore diamagnetic. We have also prepared several tetrathiafulvalene (TTF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts with

sulfonates of the ferrocene derivatives,^[12-18] one of which showed metallic conductivity but the ferrocenyl part (Fc) was neutral and diamagnetic.^[14]

Recently, we reported a new derivative octamethylferrocenedisulfonate (ofds).^[18] This anion has such a low oxidation potential of -0.08 V versus SCE that we were able to obtain tetraphenylphosphonium salts of both the yellow dianion where Fc was neutral and the green monoanion where Fc was cationic and paramagnetic. The latter salt was obtained without any treatments with oxidizing agents. The yellow and green salts subsequently gave the same TTF salt, $(\text{TTF})\text{ofds} \cdot 3.5\text{H}_2\text{O}$, in which ofds was monoanionic therefore magnetic. Thus, this was the first TTF-based salt that contained a magnetic ferrocenyl-based counter-ion. However, it had an ambient temperature resistivity of more than $10^6 \Omega\cdot\text{cm}$, and was therefore a poor conductor. Here we report the BEDT-TTF-based salt of ofds, which has both a magnetic anion and appreciable conductivity.

Results and Discussion

Crystal Structure

Electrocrystallisation of BEDT-TTF with $(\text{PPh}_4)_2\text{ofds}$ (yellow) and $(\text{PPh}_4)\text{ofds} \cdot 0.4\text{H}_2\text{O}$ (green) gave the same black plate-like crystals of $\alpha\text{-(BEDT-TTF)}_5(\text{ofds})_2$ (**1**).^[19] The crystal structure is shown in Figure 1a. The structure consists of alternating layers of BEDT-TTF cations arranged in an α -type packing motif (Fig. 1b) and layers containing the ofds anions. There are four (A, B, D and E in Figure 1b) and two halves (C and F) of BEDT-TTF and two ofds molecules (ofds1 and ofds2 in Figure 1c) in the asymmetric unit.

The charges on each crystallographically independent BEDT-TTF donor were estimated according to the literature method.^[20] The calculated charges are shown in Table 1. The data indicates that C and F are approximately monocationic, B and E are neutral whereas A and D carry partial half charges. The donor layer consists of $\dots\text{ABCBAABCBA}\dots$ and $\dots\text{DEFEDDEFED}\dots$ stacks as shown in Figure 1b. Therefore, A and D form face-to-face dimers (AA and DD) highlighted by a blue border in Figure 1b, each dimer has an approximate +1

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overall charge and is sandwiched by the neutral molecules of B and E. This suggests that AA⁺ and DD⁺ monocations are isolated. Each C and F monocation, within a red border in Figure 1b, is also sandwiched by the neutral B and E molecules, suggesting that the C and F monocations are also isolated. This implies that the BEDT-TTF layer has spins on the AA⁺ and DD⁺ dimers and on C⁺ and F⁺ monomers, which is further discussed below, in relation to the physical properties.

(d)

Figure 1. (a) Crystal structure, (b) BEDT-TTF packing motif, (c) ofds arrangement and (d) interactions between sulfonate groups and donor molecules in α -(BEDT-TTF)₅(ofds)₂ (**1**), where dotted lines in (b) and (d) indicate short S...S (< 3.7 Å) and S...O (< 3.34 Å) contacts, respectively.

Table 1. Approximation of charge (Q) on the BEDT-TTF molecules^[20]

Donor	Q	Normalized Q ^[a]
A	+0.621	+0.51
B	+0.231	+0.19
C	+0.921	+0.75
D	+0.573	+0.47
E	+0.125	+0.10
F	+0.869	+0.71

[a] Normalized by the total number of holes in the unit cell.

Figure 1c shows the arrangement of ofds in the anionic layer. Previously we reported^[18] the distances between Fe and the cyclopentadienyl ring (Cp) of neutral and monocationic ferrocene parts of ofds as 1.66–1.67 and 1.71–1.73 Å, respectively. The Fe...Cp distances in **1** are 1.717 and 1.715 Å for ofds1 and 1.716 and 1.709 Å for ofds2, indicating that both Fc parts are cationic, therefore the ofds molecules are monoanionic. The positive charges on the Fc moieties are repelled by the positive BEDT-TTF donor layers, and the negatively charged sulfonates are attracted to the donor layers. Therefore, as shown in Figure 1a, the sulfonate groups protrude marginally into the donor layers and the Fc parts sit away from the donor layers. Figure 1d shows S...O contacts between BEDT-TTF and –SO₃ shorter than the van der Waals distance of 3.37 Å. In our previously reported sulfonate salts that are in the charge disproportionation state, the donor having the shortest S...O contact has the largest positive charge probably because the state has the largest Madelung potential.^[21–23] However, this salt does not conform to the same charge distribution. There are only two short S...O contacts with the almost neutral B and E molecules. Indeed, the almost cationic molecules, C and F, have no short contacts with sulfonates. Because the ofds monoanion has both anionic sulfonate groups and cationic Fc groups, we speculate that the neutral B and E molecules feel both a Coulombic attraction with the sulfonates and also a repulsive interaction with the Fc group. The Coulombic attraction or repulsion energies are so large that the B and E donors may become almost neutral to avoid the repulsion with Fc. For example, the interaction between two electric dipoles of one debye, at the same distance is 2,700 K. We therefore think that it is reasonable to assume that the relatively distant Fc⁺ part affects the molecular charge within the BEDT-TTF layer. The ofds1 and ofds2 have polarities.^[24] However, the polarities are cancelled in each anion layer because of the existence of inversion centres.

Physical Properties

Usually organic conductors with charge disproportionation in the donor layers are semiconductors or insulators. Indeed, temperature-dependent electrical resistivity measurements of **1** indicates that the salt is a semiconductor with $\rho_{RT} = 5.6 \times 10^3 \Omega\text{-cm}$ and $E_a = 0.11 \text{ eV}$.

For the magnetic properties, χT - T plots are shown in Figure 2a. The room temperature χT value of $0.990 \text{ emu K mol}^{-1}$ per (BEDT-TTF)_{2.5}(ofds) is close to the sum of the Curie constants for an ofds monoanion (0.721)^[18] and an $S = 1/2$ spin (0.375) of $1.096 \text{ emu K mol}^{-1}$, suggesting that the stable radical parts and also the BEDT-TTF layers possess spins. Since the observed χT value is approximately $0.1 \text{ emu K mol}^{-1}$ smaller than the expected value, this implies that there are strong antiferromagnetic interactions, which are usually observed between spins on BEDT-TTF layers.^[17, 21-23] These results support the hypothesis that spins are located on the BEDT-TTF layers. The magnetic data can be fitted by the combination of a Curie-Weiss ($C = 0.721 \text{ emu K mol}^{-1}$) and 2D Heisenberg (2DH) models^[25] with $\theta = -5.5 \text{ K}$ and $J_{2DH} = -80.3 \text{ K}$. This suggests that the spins of the Fc moieties and BEDT-TTF layers obey 2D Heisenberg and Curie-Weiss models, respectively. The J_{2DH} value of -80.3 K caused by the interaction between spins on the BEDT-TTF layers almost corresponds to those observed in other salts having 2D magnetic BEDT-TTF layers.^[17, 21-23] The spins seem to form a square lattice and to interact each other along the a and b directions (see Figure 1b). In contrast, the θ value of -5.5 K , caused by the Fc...Fc interaction, is larger than those observed in (PPh₄)ofds ($\theta = -0.18 \text{ K}$)^[18] and (TTF)ofds·3.5H₂O ($\theta = -0.30 \text{ K}$)^[18]. An unpaired spin on Fc⁺ is localized in an orbital directed along the Cp...Fe...Cp axis. Therefore, the Cp...Cp face-to-face contacts are likely to correlate with stronger magnetic interactions than the face-to-side or side-to-side interactions. As shown in Figure 1c, all the Cp...Fe...Cp axes of all ofds anions in **1** point along the a axis. The alignment with short intermolecular Cp...Cp interactions shown in Figure 1d leads to the relatively large Weiss constant, θ .

Figure 2. (a) $\chi_{\text{total}} T$ - T plots of **1** where χ_{total} is the molar magnetic susceptibility per (BEDT-TTF)_{2.5}(ofds). The red solid line is calculated by combining a Curie-Weiss and 2D Heisenberg models. (b) $\chi_{\text{BEDT-TTF}} T$ - T plots of **1** where $\chi_{\text{BEDT-TTF}} = \chi_{\text{total}} - \chi_{\text{ofds}}$ and $\chi_{\text{ofds}} = 0.721/(T + 5.5)$. The blue solid line is calculated by a 2D Heisenberg model. See text for explanation.

In order to obtain the magnetic contribution of the BEDT-TTF layers ($\chi_{\text{BEDT-TTF}}$) we subtracted the Curie-Weiss term (χ_{ofds}

$= 0.721/(T + 5.5)$) from the total magnetic susceptibility (χ_{total}). The resultant curve is shown in Figure 2b. $\chi_{\text{BEDT-TTF}}$ becomes almost zero at the lowest temperature, suggesting formation of spin dimers. The BEDT-TTF layer has five-fold periodicity and each of pentamers has two holes, suggesting that the salt is a band insulator. Therefore the formation of spin dimers at the lowest temperature is natural. In addition, it is claimed^[25] that the 2DH model ceases to be quantitative below $T = 0.9JS(S+1)$ ($= 54.2 \text{ K}$ in this case ($J_{2DH} = -80.3 \text{ K}$)) and we use the data from 60–300 K for the curve fitting. The spins on BEDT-TTF layers are Heisenberg spins therefore spin moments can rotate freely. On the other hand the spins on the Fc parts are Ising spins^[26] so that the spin directions are restricted to the Cp-Fe-Cp directions. As mentioned above, the Fc parts of all ofds anions are aligned in the same direction, almost along the a axis. In addition, we did not mention the interaction between spins on Fc (Ising) and BEDT-TTF (Heisenberg) above because the interaction appeared to be very small ($\ll 2 \text{ K}$), therefore the curve fitting of magnetic susceptibility as mentioned above works well without taking account of the contribution of the interaction. However, the interaction between the Heisenberg and Ising systems may provide a unique magnetic order at a very low temperature, the investigation of which is now in progress.

Conclusions

α -(BEDT-TTF)₅(octamethylferrocenedisulfonate)₂ has been prepared, in which octamethylferrocenedisulfonate (ofds) is monoanionic and the ferrocenyl part is cationic so that magnetic. This semiconductor is the first BEDT-TTF-based salt that contains a magnetically active ferrocenyl-based counter-anion.

Experimental Section

Synthesis

Black plate-like crystals of **1** were synthesised from both yellow diamagnetic (PPh₄)₂ofds and green paramagnetic (PPh₄)ofds·0.4H₂O salts by the constant-current electrocrystallisation method. The former was prepared in a 14:1 v:v mixture of *o*-C₆H₄Cl₂ and CH₃CN with 20 mg of BEDT-TTF and 60 mg of (PPh₄)₂ofds by applying $0.9 \mu\text{A}$ for 34 days. The latter was prepared in a 9:1 v:v mixture of C₆H₅Cl and CH₃CN with 20 mg of BEDT-TTF and 60 mg of (PPh₄)ofds·0.4H₂O by applying $2.9 \mu\text{A}$ for 113 days.

X-ray Analysis

X-ray data of **1** were collected at 150 K with a Rigaku Rapid II imaging plate system with MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated MoK α radiation. The structure was solved by direct methods using SIR92. The atomic parameters were refined by full matrix least-square techniques based on F^2 using SHELX2017. All non-hydrogen atoms were refined with anisotropic temperature factors.

Physical Measurements

Electrical resistivity was measured by a standard four-probe method using a HUSO HECS-994C multi-channel conductometer. Magnetic susceptibility of polycrystalline samples from 2-300 K was measured using a Quantum Design MPMS-5S magnetometer. The measurement was not corrected for sample holder (aluminium foil) nor for the Pascal diamagnetism. However the sum of these contributions was taken into consideration as a temperature independent term obtained from the curve fitting, which was used as a correction.

Keywords: Sulfur heterocycles • BEDT-TTF • Magnetic properties • Electrical properties • Ferrocene

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Organic Conductors

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The first conducting BEDT-TTF-based salt that contains a magnetically active ferrocenyl-based counter-monoanion, which consists of two monoanionic sulfonate groups and one monocationic ferrocenyl group. The salt is a semiconductor. There are two types of spins not only on the ferrocenyl parts but also the 2D donor layers. The former and latter spins obey Curie-Weiss ($C = 0.721 \text{ emu K mol}^{-1}$ and $\theta = -5.5 \text{ K}$) and 2D Heisenberg ($J_{2\text{DH}} = -80.3 \text{ K}$) models, respectively.

*one or two words that highlight the emphasis of the paper or the field of the study