Communication

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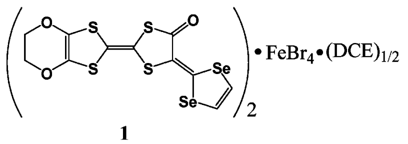

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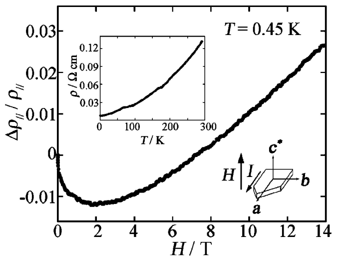

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An Antiferromagnetic Molecular Metal Based on a New Bent-Donor Molecule

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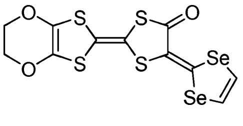
Spintronic devices have generated much recent interest because they can simultaneously store and manipulate data by using both the charge and spin of an electron. A functioning spintronic device based on a tunneling magnetoresistance effect has been built in a heterojunction structure, composed of a crystalline MgO insulator and two thin ferromagnetic metallic layers (Fe, Co, Ni, etc.).[1] The anticipated development of molecular-based spintronics is contingent on the discovery of a ferromagnetic molecular metal.

A number of charge-transfer (CT) salts composed of several π donor molecules and magnetic metal anions with d or f spins have been prepared with this goal in mind. So far only four magnetic molecular conductors display metallic conductivity down to low temperatures and antiferromagnetic ordering of localized d spins of the magnetic $FeCl_4^-$ or $FeBr_4^-$ ions by significant π−d interaction with the conducting π electrons: κ-[bis(ethylenedithio)tetraselenafulvalene, **BETS**]$_2$•$FeCl_4$,[2] κ-(**BETS**)$_2$•$FeBr_4$,[3] (ethylenedioxytetrathiafulvalenoquinone-1,3-dithiolemethide, **EDO-TTFVO**)$_2$•$FeCl_4$[4] and (ethylenedithiodiselenadithiafulvalenothioquinone-1,3-diselenolemethide, **EDT-DSDTFVSDS**)$_2$•$FeBr_4$.[5] While the antiferromagnetic ordering temperature has increased in the new magnetic molecular conductors, the highest temperature remains near 3 K. However, the required ferromagnetic ordering has not yet been achieved, although a molecular metal of [bis(ethylenedithio)tetrathiafulvalene]$_2$•[MnCr(C_2O_4)$_3$] exhibited ferromagnetic order with a very weak π−d interaction.[6] This situation prompts us to investigate a new donor molecule, ethylenedioxytetrathiafulvalenoquinone-1,3-diselenolemethide (**EDO-TTFVODS**, **1**), which offers two key advantages: an ethylenedioxy group that stabilizes the metallic conductivity in (**EDO-TTFVO**)$_2$•$FeCl_4$[4], and a 1,3-diselenole group contributing to a strong π−d interaction between the conducting π electrons and the localized d spins in (**EDT-DSDTFVSDS**)$_2$•$FeBr_4$.[5] In this Communication we report the synthesis of a 2:1 CT salt of **1** with an $FeBr_4^-$ ion, which exhibited a metallic conductivity down to 0.45 K and an antiferromagnetic ordering at the highest temperature (4.5 K) obtained so far in antiferromagnetic molecular metals.



EDO-TTFVODS, **1**

The **1** molecule was prepared using the procedure described previously.[4] The redox potentials of **1** measured in benzonitrile at 0 °C were +0.61 and +0.91 V versus Ag/AgCl, almost the same as those of **EDO-TTFVO** (+0.60 and +0.89 V).[4] We performed electrochemical oxidation of **1** in 1,2-dichloroethane (DCE) containing a supporting electrolyte, NBu_4•$FeBr_4$, with a constant electrical current of 0.1−0.2 μA. After several weeks, we isolated black platelike crystals with a molecular formula of $\mathbf{1}_2$•$FeBr_4$•(DCE)$_{1/2}$. The crystal structure is shown in Figure 1.[7] The crystal contains **1** molecules alternating with ($FeBr_4^-$ ion + DCE molecule) layers. Each donor layer has a two-dimensional β''-type stacking motif. As seen from the diagonal and side-by-side donor arrays, there are comparatively close S⋯S, S⋯Se and Se⋯Se contacts. In each anion layer two $FeBr_4^-$ ions and one DCE molecule are alternately arranged along the intercolumnar direction, while the intracolumnar direction has a regular arrangement of the $FeBr_4^-$ ions. Hence the Br⋯Br contacts for each pair of the $FeBr_4^-$ ions have comparatively short distances of 4.03 and 4.19 Å, while the distance is long (4.55 Å) between the Br atoms of the neighboring $FeBr_4^-$ ions separated by one DCE molecule. On the other hand, the Br⋯Br contact distance along the intracolumnar direction is 3.74 Å, which is shorter than the van der Waals distance (3.90 Å). There are also close contacts between the Se atoms of the donor molecule and the Br atoms of the $FeBr_4^-$ ion.

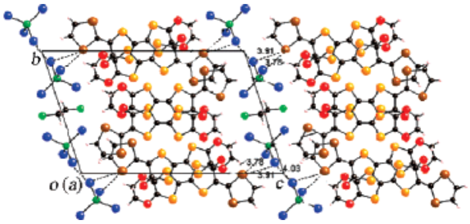


Figure 1. Crystal structure projected down to the *bc*-plane.

With the X-ray structure data described above, we calculated the band structure of the **1** molecule layer using a tight-binding method based on an extended Hückel approximation. The overlap integrals suggest that there are two different overlaps ($b1 = -10.6 \times 10^{-3}$; $b2 = -5.15 \times 10^{-3}$) in the side-by-side direction. We also find six relatively large overlap integrals along the diagonal stacking ($p1 = -11.1 \times 10^{-3}$; $p2 = -3.28 \times 10^{-3}$; $p3 = -2.63 \times 10^{-3}$; $q1 = -9.79 \times 10^{-3}$; $q2 = -2.41 \times 10^{-3}$; $q3 = -3.36 \times 10^{-3}$), indicating a two-dimensional interaction in the conducting *ab*-plane. The calculated Fermi surface is two-dimensional, but opens along the k_a and k_c directions because of the low symmetry of the space group ($P\bar{1}$). As a result, a rectangular electron pocket surrounds the **C** point, while two different elliptic hole pockets surround the **X** and **Y** points, respectively (Figure 2a).

We measured the electrical resistance (ρ) of the single crystal by a four-probe method. The ρ values in the *ab*-plane ($\rho_{\|}$) and in

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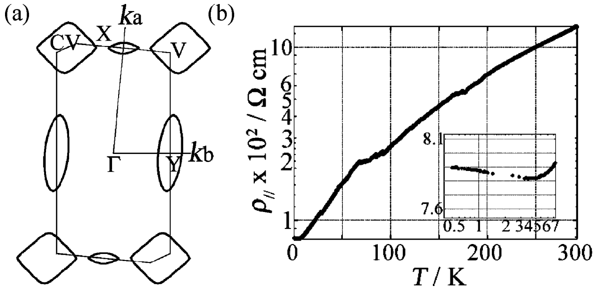

Figure 2. (a) Fermi surface and (b) T-dependence of $\rho_{||}$ between 0.45 and 300 K (below 7 K in the inset).

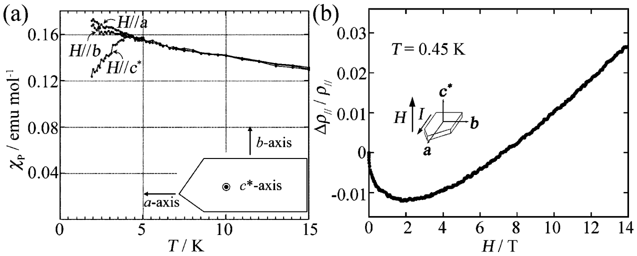

Figure 3. (a) T-dependence of χ_p along $H||a$, $H||b$, and $H||c^*$ below $T = 15$ K and (b) magnetoresistance ($\Delta\rho_{||}/\rho_{||}$) with H applied perpendicular to the conducting ab-plane.

the c^*-direction, perpendicular to the plane ($\rho_\perp$), are ca. 1×10^{-1} and 20 Ω cm at 300 K, respectively. As shown by the temperature-dependence of $\rho_{||}$ in Figure 2b, metallic behavior persists down to 0.45 K in spite of a very slight upturn in $\rho_{||}$ below 5 K. We observe a similar trend in the $\rho_\perp - T$ measurement. The slight increase of the $\rho_{||}$ and $\rho_\perp$ values as the temperature decreases below ca. 4 K is most likely caused by the π−d interaction.

We carried out SQUID measurements on the polycrystalline sample under a magnetic field $H = 1$ kOe at temperatures between 1.9 and 300 K. The temperature-dependence of the paramagnetic susceptibility (χ_p) obeys a Curie−Weiss law [$\chi_p = C/(T - \Theta)$, where C is the Curie constant and Θ is the Weiss temperature] at high temperatures. Our fits give $C = 4.48$ emu K mol^{-1} and $\Theta = -18.7$ K. Below 20 K the χ_p values become smaller than those predicted by the Curie−Weiss equations with the C and Θ values given above, and a peak appears near 4.5 K, suggesting antiferromagnetic ordering. We repeated the SQUID measurements using the single crystals to confirm the antiferromagnetic ordering, and to determine the ordering temperature (T_N) and the easy axis of the magnetization. Figure 3a shows $\chi_p - T$ plots below 15 K when $H = 5$ kOe is applied along the a-, b-, and c^*-axes, respectively. Antiferromagnetic order appears near 4 K with an easy magnetization along the c^*-axis. Heat capacity measurements provide a more accurate value of $T_N = 4.5$ K. This T_N is considerably larger than those previously observed in antiferromagnetic molecular metals, that is, 0.45 K for κ-(**BETS**)$_2$•FeCl$_4$,[2] 2.5 K for κ-(**BETS**)$_2$•FeBr$_4$,[3] 3.0 K for (**EDO-TTFVO**)$_2$•FeCl$_4$[4] and 3.3 K for (**EDT-DSDTFVSDS**)$_2$•FeBr$_4$.[5] The order of T_N in these materials is consistent with the spin exchange integrals for d−d and π−d interactions (J_{dd} and $J_{\pi d}$) obtained from molecular orbital calculations.[8] The J_{dd} and $J_{\pi d}$ values of the present FeBr$_4^-$ salt are 1.86 and 14.5 K, respectively. This is the largest J_{dd} of all the antiferromagnetic molecular metals, while $J_{\pi d}$ is comparable to that of (**EDT-DSDTFVSDS**)$_2$•FeBr$_4$ (15.6 K), and noticeably larger than those of the others.

We investigated the magnetoresistance (MR) of $\rho_{||}$ at 0.45 K by applying a magnetic field perpendicular to the conducting ab-plane, with H ranging to 14 T. The H-dependence of $\Delta\rho_{||}/\rho_{||}$ [$\Delta\rho_{||} = \rho_{||}(H) - \rho_{||}(0)$] in Figure 3b shows a small negative MR (1−2%) for weak H, which reaches a maximum near 2 T. Above 7 T the MR becomes positive. Because the Fe(III) d spins are antiferromagnetically ordered below $T_N = 4.5$ K and no disorder is present in the crystal structure, we attribute this negative MR to the suppression of d spin scattering caused by spin alignment with the applied field. This result undoubtedly reflects the presence of the π−d interaction; however, the π−d interaction need not be weak because the MR is small. Large negative MRs were previously observed in our magnetic molecular conductors that were in semiconducting states with significant π−d interactions,[5,9] whereas this FeBr$_4^-$ salt is metallic.

We have reported electron transport and magnetic measurements which demonstrate that the $\mathbf{1}_2$•FeBr$_4$•(DCE)$_{1/2}$ salt is a genuine molecular metal with stronger π−d interactions than (**EDO-TTFVO**)$_2$•FeCl$_4$. The small negative MR indicates that the metallic conduction is not strongly influenced by the localized d spins. We also observe that the antiferromagnetic ordering temperature is high compared to those of the antiferromagnetic molecular metals known so far, but lower than the large J_{dd} and $J_{\pi d}$ values would suggest. This information may prove useful in the development of ferromagnetic molecular metals or semiconductors with significant π−d interactions.

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Supporting Information Available: An X-ray crystallographic file for the crystal of $\mathbf{1}_2$•FeBr$_4$•(DCE)$_{1/2}$ in CIF format, the T-dependence of $\rho_\perp$ between 0.45 and 300 K, the T-dependence of heat capacity, and the H-dependence of $\Delta\rho_\perp/\rho_\perp$ up to $H = 14$ T at $T = 0.45$ K. This material is available free of charge via the Internet at http://pubs.acs.org.

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