J|A|C|S
COMMUNICATIONS

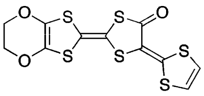
A Metallic (EDT-DSDTFVSDS)$_2$·FeBr$_4$ Salt: Antiferromagnetic Ordering of *d* Spins of FeBr$_4^-$ Ions and Anomalous Magnetoresistance Due to Preferential *π*−*d* Interaction

Toshiki Hayashi,[†] Xunwen Xiao,[†,§] Hideki Fujiwara,*[,†,§] Toyonari Sugimoto,*[,†,§] Hiroyuki Nakazumi,[‡]
Satoru Noguchi,[‡,§] Tsutomu Fujimoto,[||] Syuma Yasuzuka,[||] Harukazu Yoshino,[||] Keizo Murata,*[,||]
Takehiko Mori,*[,⊥] and Hiroko Aruga-Katori[#]

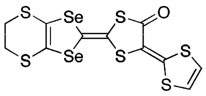
Graduate School of Science, Osaka Prefecture University, Osaka 599-8570, Japan, CREST, Japan Science and Technology Agency, Saitama 332-0012, Japan, Graduate School of Engineering, Osaka Prefecture University, Osaka 599-8531, Japan, Graduate School of Science, Osaka City University, Osaka 558-8585, Japan, Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo 152-8552, Japan, and RIKEN (The Institute of Physical and Chemical Research), Saitama 351-0198, Japan

Received June 19, 2006; E-mail: hfuji@c.s.osakafu-u.ac.jp; toyonari@c.s.osakafu-u.ac.jp; takehiko@o.cc.titech.ac.jp; muratak@sci.osaka-cu.ac.jp.

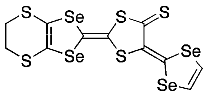
The crystals of cation radical salts of π donor molecules with magnetic transition metal counteranions usually form alternate stacking structures of the donor and counteranion layers, which are responsible for electrical conductivities and magnetisms of the crystals, respectively.[1,2] Current interest is directed toward the coexistence of metallic conductivity and ferromagnetism by virtue of a significant π−*d* or π−*f* interaction between the metal-conducting π electrons on the donor layers and the localized *d* or *f* spins on the counteranion layers. Such conducting π electrons are spin-polarized by the magnetic layers, and can be utilized as a key component for developing a new type of molecular electronics, called "spin electronics or spintronics". In the past decade, considerable efforts have been devoted to the development of a ferromagnetic molecular metal with the π−*d* interaction, but it has not been obtained yet. Although metallic conductivities have been realized in κ-(BETS)$_2$·FeX$_4$ [BETS = bis(ethylenedithio)tetraselenafulvalene, X = Cl, Br],[3] (EDO-TTFVO, **1**)$_2$·FeCl$_4$,[4] and (EDT-DSDTFVO, **2**)$_2$·FeX$_4$ (X = Cl, Br),[5] the Fe(III) *d* spins of these FeX$_4^-$ salts were antiferromagnetically ordered except for **2**$_2$·FeX$_4$. The main origin of the antiferromagnetic ordering in these salts is due to a *d*−*d* interaction between the FeX$_4^-$ ions in the anion layer in preference to a π−*d* interaction between the donor molecules and FeX$_4^-$ ions. Because such a *d*−*d* interaction is usually antiferromagnetic, the antiferromagnetic ordering cannot be avoided as far as it is dominant compared with the π−*d* interaction. In contrast, there is a possibility that the π−*d* interaction brings about the ferromagnetic ordering, which will be discussed here. For the first time, we could find out a preferential π−*d* interaction in the 2:1 salt of a newly prepared donor molecule, EDT-DSDTFVSDS (**3**) with a magnetic FeBr$_4^-$ ion, **3**$_2$·FeBr$_4$, which is essentially metallic down to 4.2 K despite a small upturn in resistivity below ca. 30 K and shows an antiferromagnetic ordering of the *d*-spins at T_N = 3.3 K.



1: EDO-TTFVO



2: EDT-DSDTFVO



3: EDT-DSDTFVSDS

According to a method similar to that used to synthesize **2**,[5] **3** was obtained from 4,5-ethylenedithio-4′,5′-bis(cyanoethylthio)-diselenadithiafulvalene and 2-methylseleno-1,3-diselenolium tetrafluoroborate.[6] MO calculations suggest that the HOMO of **3** has large atomic coefficients on the Se atoms of the terminal 1,3-diselenole ring. The increased coefficients on the Se atoms can play an important role to produce the preferential π−*d* interaction through the Se···halogen contacts together with the bulkiness of the 1,3-diselenole ring which might weaken the *d*−*d* interaction.

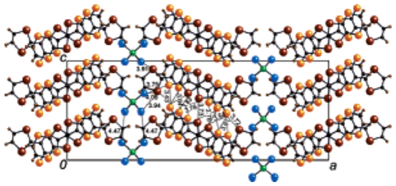


Figure 1. Crystal structure of **3**$_2$·FeBr$_4$ projected down to the *ac*-plane.

A solution of **3** and 10 equiv of *n*-Bu$_4$N·MBr$_4$ (M = Fe, Ga) in chlorobenzene/ethanol (9:1, *v*/*v*) was electrochemically oxidized with a constant current of 0.1 μA at 45 °C. Black platelike crystals were grown on the anode after several weeks. The crystal structures of **3**$_2$·FeBr$_4$ and **3**$_2$·GaBr$_4$ were successfully solved and isostructural to each other.[7] Each crystal involved one crystallographically independent donor molecule with an almost planar molecular structure. As seen from the projection down to the *ac*-plane (Figure 1), the donor molecules form uniformed stacking columns with an equal interplanar distance of 3.75 Å and several S···S and S···Se contacts along the *b*-axis, making each terminal 1,3-diselenole ring projected into the outside. Furthermore, these stacking columns are aligned along the *c*-axis, and the donor layer has a β-like packing motif. Several close S···Se contacts are also observed between neighboring columns, suggesting a strong two-dimensional intercolumnar interaction. On the other hand, the FeBr$_4^-$ ions intervene between the donor layers and are aligned in a rectangular form in the *bc*-plane, but neighboring FeBr$_4^-$ ions are largely separated from each other by the projected 1,3-diselenole rings. Accordingly, the shortest Br···Br distances between neighboring FeBr$_4^-$ ions is 4.47 Å, which is very much longer than van der Waals distance (3.90 Å). In contrast, the FeBr$_4^-$ ion has very close Br···S (3.75 Å) and Br···Se (3.91, 3.94, 4.06, and 4.13 Å) contacts with neighboring donor molecules. These structural features suggest a stronger π−*d* interaction between the FeBr$_4^-$ ions and the donor molecules than the *d*−*d* interaction.

The band calculation of **3**$_2$·FeBr$_4$ was performed by a tight-binding method based on the extended Hückel approximation. The overlap integral along the stacking direction ($b = -39.71 \times 10^{-3}$) is four to six times larger than those along the side-by-side direction ($p =$

[†] Graduate School of Science, Osaka Prefecture University.
[§] Japan Science and Technology Agency.
[‡] Graduate School of Engineering, Osaka Prefecture University.
[||] Graduate School of Science, Osaka City University.
[⊥] Tokyo Institute of Technology.
[#] RIKEN.

10.1021/ja064307v CCC: $33.50

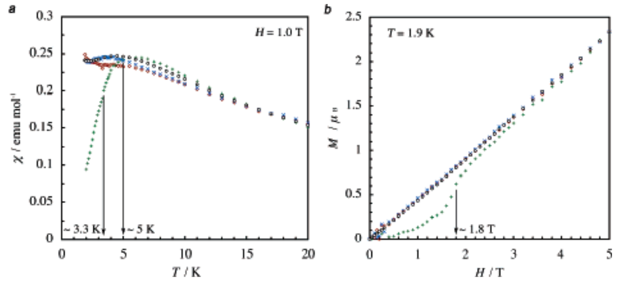


Figure 2. (a) χ vs T ($H = 1.0$ T, $T < 20$ K) and (b) M vs H ($T = 1.9$ K, $H < 5$ T) for H//a (red diamond), H//b (blue cross) and H//c (green plus) directions of the single crystal and for the polycrystalline sample (open circles) of $\mathbf{3}_2$•FeBr$_4$.

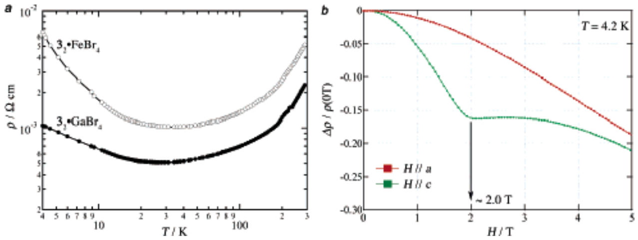


Figure 3. (a) Temperature dependences of ρ values in the temperature range of 4.2 to 290 K for $\mathbf{3}_2$•FeBr$_4$ (open circles) and $\mathbf{3}_2$•GaBr$_4$ (closed circles); (b) MR effect [$\Delta\rho/\rho$(0 T)] for $\mathbf{3}_2$•FeBr$_4$ in the H//a (red) and H//c (green) directions in the H range of <5 T at 4.2 K.

9.44×10^{-3} and $q = 7.11 \times 10^{-3}$), suggesting a quasi-one-dimensional electronic structure. The calculated Fermi surface has a two-dimensionality, but opens along the k_C-direction similar to that of $\mathbf{2}_2$•FeBr$_4$.[5]

Magnetizations (M) of $\mathbf{3}_2$•FeBr$_4$ were measured on a single crystal using a SQUID magnetometer under $H = 1.0$ T applied along the three crystallographic axes (a-, b-, and c-axes). The temperature dependence of magnetic susceptibilities (χ) measured on a polycrystalline sample can be fitted to the Curie−Weiss law with a Curie constant of 4.71 emu K mol^{-1} and a Weiss temperature of −10.5 K, suggesting a relatively strong antiferromagnetic interaction between the d spins of the FeBr$_4^-$ ions. As shown in Figure 2a, χ sharply decreased below ca. 5 K only for H//c, suggesting an antiferromagnetic ordering. The accurate Néel temperature (T_N) was determined to be 3.3 K by a heat capacity measurement. The M−H curves measured at 1.9 K showed a spin-flop around 1.8 T for H//c (see Figure 2b). These results indicate an antiferromagnetic ordering at 3.3 K with an easy axis parallel to the c-axis.

Electrical resistivities (ρ) of the single crystals of $\mathbf{3}_2$•FeBr$_4$ and $\mathbf{3}_2$•GaBr$_4$ were measured down to 4.2 K. The electrical conductivities of $\mathbf{3}_2$•FeBr$_4$ and $\mathbf{3}_2$•GaBr$_4$ measured along the b-axis are 200−300 S cm^{-1} at 290 K. As shown in Figure 3a, essentially metallic behaviors are observed despite small upturns in ρ below ca. 30 K, and the σ values at 4.2 K are still very high (ca. 170 and 1000 S cm^{-1}, respectively). Below ca. 30 K, the increasing degree in ρ is larger for the FeBr$_4^-$ salt than for the GaBr$_4^-$ salt. The magnetoresistance (MR) effect [$\Delta\rho/\rho$(0 T)] was investigated under $H \perp b$ (H//ac-plane). For the GaBr$_4^-$ salt, a very small positive MR effect (ca. 3% at 5 T) was observed at 4.2 K. In contrast, the FeBr$_4^-$ salt exhibited a large and negative MR effect (ca. 20% at 5 T) as shown in Figure 3b. Very interestingly, an anomalous MR with a broad dip appeared at ca. 2.0 T for H//c without hysteresis, but was not observed for H//a.[8] This dip is clearly responsible for the spin-flop transition of the d spins of the FeBr$_4^-$ ion which occurs at almost the same H in the c-direction (easy axis) and gives a definite evidence for the strong π−d interaction.

The magnitudes of the d−d (J_{dd}) and π−d ($J_{\pi d}$) interactions in $\mathbf{3}_2$•FeBr$_4$ were estimated to be 0.20 and 15.6 K, respectively, by the MO calculations.[9] Figure 4 shows the comparison of these J_{dd} and $J_{\pi d}$ values with those in molecular metallic conductors with FeX$_4^-$ (X = Cl, Br) ions so far known, $\mathbf{1}_2$•FeCl$_4$,[4] $\mathbf{2}_2$•FeBr$_4$,[5] κ-(BETS)$_2$•FeCl$_4$, κ-(BETS)$_2$•FeBr$_4$, and λ-(BETS)$_2$•FeCl$_4$.[9] The $J_{\pi d}$ in $\mathbf{3}_2$•FeBr$_4$ is very large and comparable to that in λ-(BETS)$_2$•FeCl$_4$, which exhibited novel conducting and magnetic behaviors such as a field-induced superconductivity as a result of a strong π−d interaction,[10] while the J_{dd} is very small in comparison to that in λ-(BETS)$_2$•FeCl$_4$, suggesting that the π−d interaction is dominant in $\mathbf{3}_2$•FeBr$_4$. Accordingly, $\mathbf{3}_2$•FeBr$_4$ is expected to be the most reliable π−d system to produce a ferromagnetic ordering of the d spins of the FeBr$_4^-$ ions through the strong π−d interaction with metal-conducting π electrons. However, the antiferromagnetic ordering was achieved at $T_N = 3.3$ K. Nevertheless, the present result encourages us to develop a novel ferromagnetic molecular metal with a significant π−d interaction by use of new derivatives of **3**.

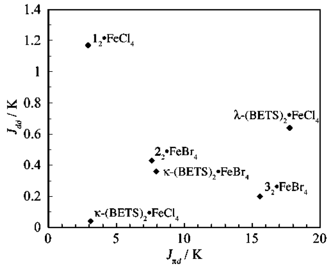


Figure 4. Calculated J_{dd} and $J_{\pi d}$ values for $\mathbf{1}_2$•FeCl$_4$, $\mathbf{2}_2$•FeBr$_4$, $\mathbf{3}_2$•FeBr$_4$, κ-(BETS)$_2$•FeCl$_4$, κ-(BETS)$_2$•FeBr$_4$, and λ-(BETS)$_2$•FeCl$_4$.

Acknowledgment. This work is financially supported in part by a Grant-in-Aid for Scientific Research on Priority Areas of Molecular Conductors (Grant Nos. 16038222 and 15073220) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: An X-ray crystallographic file for $\mathbf{3}_2$•FeBr$_4$ and $\mathbf{3}_2$•GaBr$_4$ in the CIF format, as well as the results of HOMO of **2** and **3**, crystal structure, band structure, and estimation of J values of $\mathbf{3}_2$•FeBr$_4$ in the PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Ouahab, L.; Enoki, T. *Eur. J. Inorg. Chem.* **2004**, 933−941.
(2) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Laukhin, V. N. *Nature* **2000**, *408*, 447−449.
(3) (a) Ojima, E.; Fujiwara, H.; Kato, K.; Kobayashi, H.; Tanaka, H.; Kobayashi, A.; Tokumoto, M.; Cassoux, P. *J. Am. Chem. Soc*. **1999**, *121*, 5581−5582. (b) Otsuka, T.; Kobayashi, A.; Miyamoto, Y.; Kiuchi, J.; Wada, N.; Ojima, E.; Fujiwara, H.; Kobayashi, H. *Chem. Lett.* **2000**, 732−733.
(4) Fujiwara, H.; Wada, K.; Hiraoka, T.; Hayashi, T.; Sugimoto, T.; Nakazumi, H.; Yokogawa, K.; Teramura, M.; Yasuzuka, S.; Murata, K.; Mori, T. *J. Am. Chem. Soc.* **2005**, *127*, 14166−14167.
(5) Fujiwara, H.; Hayashi, T.; Sugimoto, T.; Nakazumi, H.; Noguchi, S.; Li, L.; Yokogawa, K.; Yasuzuka, S.; Murata, K.; Mori, T. *Inorg. Chem.* **2006**, *45*, 5712−5714.
(6) Compound **3**: a purplish black microcrystals; mp 199−200 °C (dec). ^{1}H NMR (400 MHz, d_6-acetone): δ 8.07 (d, $J = 6.8$ Hz, 1H), 7.98 (d, $J = 6.8$ Hz, 1H), 3.32 (s, 4H). Anal. Calcd for $C_{11}H_6S_5Se_4$: C, 21.51; H, 0.98. Found: C, 21.33; H, 1.05%. MS (EI) m/z: 614 (M$^+$).
(7) Crystal data for $\mathbf{3}_2$•FeBr$_4$: $C_{11}H_6Br_2Fe_{0.5}S_5Se_4$, $M_r = 802.04$, orthorhombic, $a = 37.64(4)$, $b = 7.498(6)$, and $c = 14.03(1)$ Å, $V = 3960(6)$ Å^3, $T = 296$ K, space group $Pccn$, $Z = 8$, μ(Mo Kα) = 12.333 cm^{-1}, 48066 reflections measured ($R_{\text{int}} = 0.100$), 4305 unique, of which 1968 were used in all calculations [$F^2 > 1.00\sigma(F^2)$]. The final R and Rw were 0.057 and 0.095, respectively. Crystal data for $\mathbf{3}_2$•GaBr$_4$: $C_{11}H_6Br_2Ga_{0.5}S_5Se_4$, $M_r = 808.98$, orthorhombic, $a = 37.766(6)$, $b = 7.5021(11)$, $c = 14.043(2)$ Å, $V = 3978.7(10)$ Å^3, $T = 293$ K, space group $Pccn$, $Z = 8$, μ(Mo Kα) = 12.586 cm^{-1}, 53826 reflections measured ($R_{\text{int}} = 0.048$), 5124 unique, of which 2677 were used in all calculations [$F^2 > 3.00\sigma(F^2)$]. The final R and Rw were 0.054 and 0.066, respectively.
(8) Nishijo, J.; Miyazaki, A.; Enoki, T.; Watanabe, R.; Kuwatani, Y.; Iyoda, M. *Inorg. Chem.* **2005**, *44*, 2493−2506.
(9) Mori, T.; Katsuhara, M. *J. Phys. Soc. Jpn.* **2002**, *71*, 826−844.
(10) Uji, S.; Shinagawa, H.; Terashima, T.; Yakabe, T.; Terai. Y.; Tokumoto, M.; Kobayashi, A.; Tanaka, H.; Kobayashi, H. *Nature* **2001**, *410*, 908−910.

JA064307V