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Ferromagnetic Ordering of Fe(III) d Spins of $FeBr_4^-$ Ions in (Ethylenedithiotetrathiafulvalenothioquinone-ethylenedithio-1,3-dithiolemethide)·$FeBr_4$

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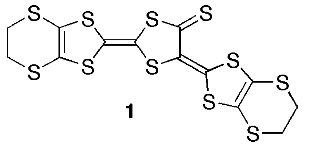
The 1:1 salt of a new donor molecule, ethylenedithiotetrathiafulvalenothioquinone-ethylenedithio-1,3-dithiolemethide (**1**), with $FeBr_4^-$ ion, **1**·$FeBr_4$, was prepared and found to exhibit a room-temperature electrical conductivity of 4×10^{-2} S cm^{-1} and semiconducting behavior with an activation energy of 170 meV. The paramagnetic susceptibility obeyed the Curie–Weiss law with a Curie constant of 4.42 emu K mol^{-1} and a Weiss temperature of +3.4 K, and below 15 K, this short-range ferromagnetic interaction increasingly extended to two- and/or three-dimensional interactions, eventually giving rise to a ferromagnetic ordering, whose temperature (T_C) was determined to be 1.8 ± 0.2 K using a resonant circuit method. The magnetic field dependence of magnetization showed that the saturation of magnetization was accomplished at ca. 60 kOe and the saturated value was ca. 5 μ_B, which is very close to the value obtained only due to Fe(III) ($S = {}^5/_2$) d spins of one $FeBr_4^-$ ion.

Molecular systems with significant interaction between conducting π electrons and localized π, d, or f spins continue to draw much attention from the viewpoint of the development of bifunctional molecular materials,[1–4] in particular, ferromagnetic semiconductors or metals that could be utilized as a component for *molecular-type* spintronics.[5] Very recently, we succeeded in the preparation of a metallic/semiconducting 2:1 salt of ethylenedithiotetrathiafulvalenoquinone-1,3-dithiolemethide (**2**) with $FeBr_4^-$ ion, ($\mathbf{2}_2$·$FeBr_4$), in which the ferrimagnetic ordering due to the Fe(III) d spins of the $FeBr_4^-$ ion is considered to be accomplished by virtue of the localized π spins produced on the donor columns by charge localization.[6,7] Now, we observed a ferromagnetic ordering due to the Fe(III) d spins of the $FeBr_4^-$ ion in the 1:1 salt of a newly synthesized derivative of **2**, ethylenedithiotetrathiafulvalenothioquinone-ethylenedithio-1,3-dithiolemethide (**1**), with the $FeBr_4^-$ ion, **1**·$FeBr_4$, which has such a crystal structure as to surround each $FeBr_4^-$ ion by four **1** molecules in marked contrast to that of 1:1 salt of ethylenedithiotetrathiafulvalenothioquione-1,3-dithiolemethide (**3**) with $FeBr_4^-$ ion (**3**·$FeBr_4$), which has an alternately stacked structure of **3** molecule and the $FeBr_4^-$ ion layers.[8]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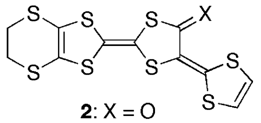
2: X = O
3: X = S

The new donor molecule, **1**, was synthesized in good yield in a similar manner as its related donor molecules obtained so far.[9] When a CS_2 solution of **1** was contacted with a CH_3CN solution of 10 molar equiv of $FeBr_3$ through a CH_3CN solvent at room temperature for ca. 1 week, black needle crystals of **1**·$FeBr_4$ (mp > 300 °C) appeared at the boundary between the upper two phases. The X-ray structure analysis of these crystals was successfully carried out at room temperature using a Rigaku RAXIS−RAPID imaging plate area detector. From the 1:1 composition of **1** and the $FeBr_4^-$

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(9) A black powder (mp 233−235 °C). ^1H NMR ($CS_2/CDCl_3$) d 3.40 (s, 4H), 3.29 (s, 4H). Calcd for **1** ($C_{13}H_8S_{11}$): C, 30.21; H, 1.56. Found: C, 30.31; H, 1.66.

10.1021/ic0482988 CCC: $30.25

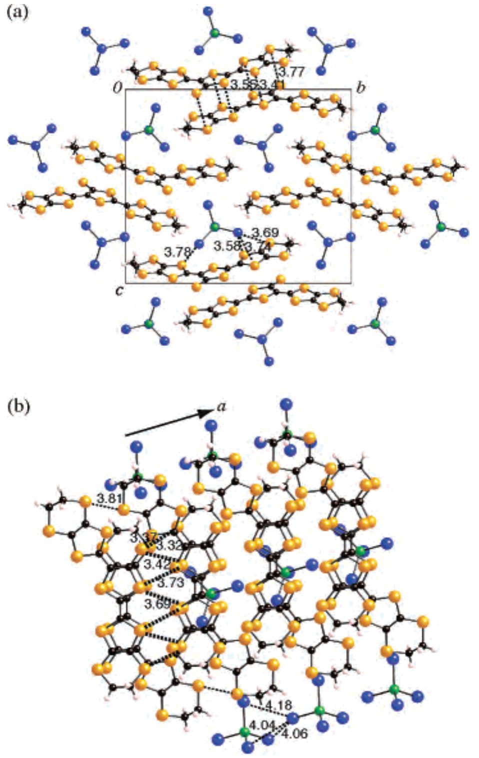

Figure 1. (a) Crystal structure of **1**·$FeBr_4$ projected on the *bc* plane. (b) Arrangement of the donor dimers and the anions along the *a* axis.

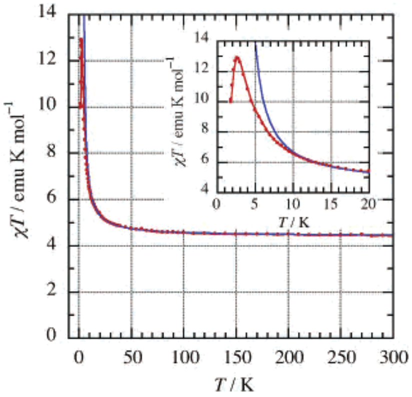

Figure 2. Temperature dependence of χT for **1**·$FeBr_4$. The solid curve is obtained by using $C = 4.42$ and $\theta = +3.4$ in an equation for the Curie–Weiss law [$\chi T = C/(T - \theta)T$]. Inset shows an expansion in the low-temperature region below 20 K.

ion, each **1** molecule is in the radical cation state. Although the tetrathiafulvalene (TTF)-like part of the molecule is highly planar as seen from very small dihedral angles (2.0°, 3.3°, and 5.4°) between the neighboring planes, the additional 1,3-dithiole ring connects to the TTF skeleton with a large torsional angle of 10.7°. On the other hand, each $FeBr_4^-$ ion has a slightly distorted tetrahedral geometry around the Fe atom, given that the Br–Fe–Br angles are different from each other [105.56(5)–112.22(6)°] and very close to those in the other $FeBr_4^-$ salts.[6–8,10] As seen from the projections on the *bc* plane (Figure 1a), the neighboring two donor molecules are strongly dimerized, with a short interplanar distance of 3.51 Å and a number of S···S contacts that are shorter than the sum of van der Waals (vdW) radii of two S atoms (3.70 Å).[11] There is a moderate overlap between the neighboring dimers through several S···S contacts along the side-by-side direction (Figure 1b). Accompanied by this stacking structure of the donor molecules, each $FeBr_4^-$ ion is accommodated in such an open space as to be surrounded by four donor molecules. The neighboring $FeBr_4^-$ ions are separated from each other [even the nearest Br···Br distance is 4.044(2) Å along the *a* axis and longer than the sum of vdW radii of two Br atoms (3.90 Å)[11]] and form a one-dimensional uniform array along the *a* axis as shown in Figure 1b. There are several Br···S contacts with shorter distances (3.58–3.78 Å) than the sum of vdW radii of Br and S atoms (3.80 Å)[11] between S atoms of the donor molecule and Br atoms of the $FeBr_4^-$ ion (see Figure 1a). This unique mixed-layer structure of **1** molecules and $FeBr_4^-$ ions is markedly different from that of **3**·$FeBr_4$, in which two different layers of **3** molecules and $FeBr_4^-$ ions are alternately aligned to each other.[8] Presumably, the steric effect of the ethylenedithio group attached to the 1,3-dithiole ring is a main cause for the different stacking structures between **1**·$FeBr_4$ and **3**·$FeBr_4$.

From the facts that each of the **1** molecules is completely one-electron-oxidized and furthermore forms strong dimerization, the electrical conductivity of **1**·$FeBr_4$ single crystals at room temperature was expected to be very low, but it was actually comparatively high (4×10^{-2} S cm^{-1}). The temperature dependence of the electrical conductivity was semiconducting with a moderate activation energy of 170 meV. The SQUID measurement was carried out using the microcrystals. Figure 2 shows the temperature dependence of paramagnetic susceptibility $\chi_p T$ in the temperature range of 1.9–300 K. The $\chi_p T$ value gradually increased with decreasing temperature from 300 K and reached a maximum near 2.6 K, but below this temperature, it decreased almost linearly with decreasing temperature (see inset in Figure 2). This result strongly suggests preferential occurrence of ferromagnetic interactions between the spins involved in **1**·$FeBr_4$ and furthermore extension to a ferromagnetic ordering. The $\chi_p T$ vs T curve above 15 K well obeyed the Curie–Weiss law expressed by the equation of $\chi_p T = [C/(T - \theta)]T$, where C is the Curie constant and θ is the Weiss temperature. The C and θ values in the best fit were 4.42 emu K mol^{-1} and +3.4 K, respectively. This C value is the same as that of an Fe(III) ($S = {}^5/_2$) spin entity due to one $FeBr_4^-$ ion per formula unit of **1**·$FeBr_4$, suggesting that, for temperatures higher than 15 K, the Fe(III) d spins actually contribute to the magnetic property of **1**·$FeBr_4$ and apparently the localized π spins on the **1** molecules make no contribution. However, below 15 K, the short-range ferromagnetic interaction as mentioned above gradually extended to two- and/or three-dimensional interactions, eventually giving rise to ferromagnetic ordering below 2.6 K. The ferromagnetic ordering temperature (T_C) was determined using a resonant circuit method developed by us very recently, which is quite useful in the case of ferromagnets with very low T_C and very small

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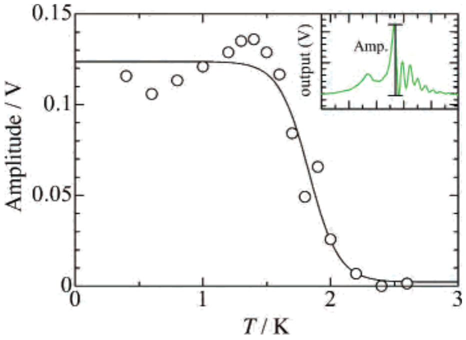

Figure 3. Temperature dependence of the oscillation amplitude. The solid curve is drawn by an empirically filled function. Inset shows an example of the signal voltage (amplitude = 0.12 V) measured at 0.4 K by the resonant circuit method.

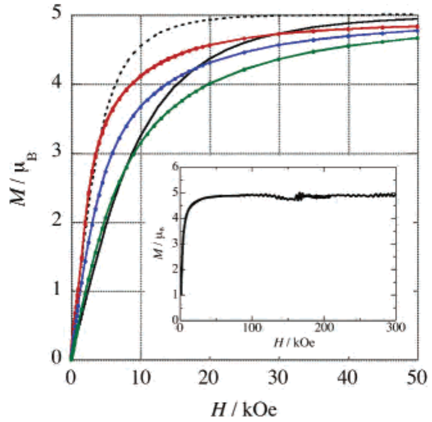

Figure 4. Observed magnetization curves for **1**·$FeBr_4$ at (red) 1.9, (blue) 3.0, and (green) 4.0 K in the H range up to 50 kOe. Also shown are Brillouin functions with $g = 2$, $S = {}^5/_2$, $\theta = 0$ K, and $T = 1.9$ K (black solid line) and with $g = 2$, $S = {}^5/_2$, $\theta = +1.1$ K, and $T = 1.9$ K (black dashed line). Inset shows a magnetization curve at 1.5 K in the H range up to 300 kOe.

hysteresis such as the present ferromagnet.[7,12] Because the initial amplitude of the oscillation induced in the M pickup coil is proportional to the M jump, the amplitude was plotted against temperature, and a steplike change with a start at 2.0 K and a final at 1.6 K was obtained (see Figure 3). If the T_C is defined as the midpoint of the steplike change, the value is determined to be 1.8 K.

The magnetic field (H) dependence of magnetization (M) was investigated at various temperatures of 1.9, 3.0, and 4.0 K up to 50 kOe with a SQUID magnetometer. The high-field magnetization up to 300 kOe at 1.5 K was measured using a homemade pulsed-magnet system. As seen from the M curves at 1.9, 3.0, and 4.0 K up to 50 kOe (Figure 4), the M curves reached saturation faster as the temperature decreased from 4.0 K. However, the saturation was not completed even at 1.9 K and 50 kOe. A hysteresis was not observed in the M loop at 1.9 K (coercive force < 10 Oe). The M curve at 1.9 K increased more sharply than that of the Brillouin function with $g = 2$, $S = {}^5/_2$, and $\theta = 0$ K with increasing H in the lower H range, whereas in the higher H range, the degree of the M increase became smaller as compared with that in the Brillouin function, giving rise to reversal in the magnetizations between the two curves near 30 kOe. The observed curve is well consistent with the Brillouin function with $g = 2$, $S = {}^5/_2$, and $\theta = +1.1$ K for H lower than 3 kOe, but afterward, the two curves largely differed from each other. These results show the ferromagnetic interaction between the Fe(III) d spins. On the other hand, the M value very slightly increased with increasing H from 50 kOe and immediately reached saturation near 60 kOe (see inset of Figure 4). The saturated M was ca. 5 μ_B, which is very close to that due only to the Fe(III) ($S = {}^5/_2$) d spins of one $FeBr_4^-$ ion and largely different from the 4 μ_B value obtained by normal ferrimagnetic ordering[13,14] due to the Fe(III) d spins and the $S = {}^1/_2$ π spin of one **1** molecule. This value was not changed even at 300 kOe, suggesting *apparently* no participation of the localized π spins of **1** molecules in this ferromagnetic ordering.

The ferromagnetic ordering due to d spins of the magnetic counteranions in charge-transfer salt-based molecular magnetic conductors was also recognized in **1**·$FeBr_4$ at $T_C = 1.8 \pm 0.2$ K in addition to **2**$_2$·$FeBr_4$ exhibiting ferrimagnetic ordering at $T_C = 0.8 \pm 0.2$ K.[7] There are points of similarity and difference in electrical conducting and magnetic properties between the two $FeBr_4^-$ salts. **1**·$FeBr_4$ exhibits a substantially lower electrical conductivity and a larger activation energy than **2**$_2$·$FeBr_4$ and is an insulator at low temperatures. From their M curve measurement results, significant ferromagnetic interactions occur between the Fe(III) d spins of the $FeBr_4^-$ ions for both of the salts, eventually giving rise to ferromagnetic or ferrimagnetic ordering of the Fe(III) d spins. However, their saturated M values are remarkably different from each other: ca. 5 μ_B for **1**·$FeBr_4$ and 5.4−5.5 μ_B for **2**$_2$·$FeBr_4$.[15] For **2**$_2$·$FeBr_4$, 0.4−0.5 of one localized π spin per unit of two **2** molecules actually contributes to the ferrimagnetic ordering due to the Fe(III) d spins of the $FeBr_4^-$ ions. In contrast, there is no such contribution of the localized π spin of a **1** molecule for **1**·$FeBr_4$, because the localized π spins of two **1** molecules are considered to be in a strong singlet state at low temperatures because of the strong dimerization (the singlet−triplet energy gap is estimated to be a large value of ca. −170 cm^{-1} from the temperature dependence of the signal intensities by the ESR measurement of the corresponding $GaBr_4^-$ salt). Therefore, it is most probable for **1**·$FeBr_4$ that the Fe(III) d spins of the $FeBr_4^-$ ions are subject to a ferromagnetic superexchange interaction via the singlet dimer of the **1** molecules and eventually to ferromagnetic ordering.

Supporting Information Available: An X-ray crystallographic file for the crystal of **1**·$FeBr_4$, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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