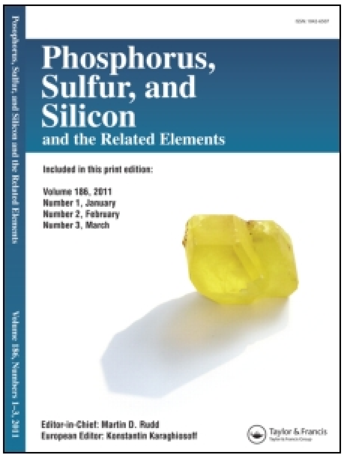

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π-*d* Interaction-Based Molecular Magnets: Role of Sulfur-to-Selenium Substitution

Akira Miyazaki[a]; Kazuki Okabe[a]; Kengo Enomoto[a]; Toshiaki Enoki[a]
[a] Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan

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π-*d* Interaction-Based Molecular Magnets: Role of Sulfur-to-Selenium Substitution

Akira Miyazaki
Kazuki Okabe
Kengo Enomoto
Toshiaki Enoki
Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan

The crystal structure and physical properties of the three conducting molecular magnets are discussed. (DMET)$_2$FeBr$_4$ is composed of alternating stacks of quasi-one-dimensional donor sheets and square lattice magnetic anion sheets. This salt undergoes an spin density wave (SDW) transition of the donor layer at 40 K and an antiferromagnetic transition of Fe^{3+} spins on the anion layer at 3.7 K. The one-to-one correspondence of the anomalies appearing on the magnetization curves with those on the magnetoresistance supports the presence of the π-d *interaction. The all-sulfur analog (EDTDM)$_2$FeBr$_4$ shows, besides similar behaviors as the DMET salt, insulator-to-metal transition of the ground state by applying the pressure, accompanied with a large negative magnetoresistance. (EDS-TTF)$_2$FeBr$_4$ shows little* π-d *interaction despite the presence of close Se—Br contacts, showing the importance of the intermolecular orbital overlap between the* π*- and* d*-components.*

Keywords Molecular conductor; molecular magnet; π-*d* interaction

INTRODUCTION

Physical properties of molecular metals and superconductors are one of the central interests in the current field of solid-state physics and chemistry. Most of such molecular conductors are built with organic donor molecule tetrathiafulvalene (TTF) (Figure 1) and its derivative from the following reasons. As these molecules have high planarity with π-conjugated system, the molecular conductors have inherent low-dimensionality in their electronic nature that attracts the physicist. The

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Address correspondence to Akira Miyazaki, Tokyo Institute of Technology, Department of Chemistry, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan. E-mail: miyazaki@chem.titech.ac.jp

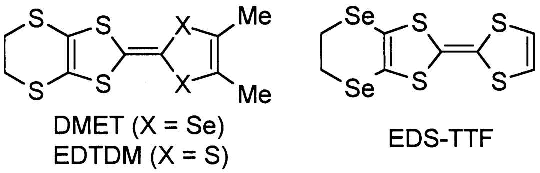

FIGURE 1 Molecular structures of DMET, EDTDM and EDS-TTF.

TTF-moiety itself also has a possibility of producing various derivatives by introducing substituents and/or exchanging chalcogen atoms, hence synthetic chemists working especially on the heterocyclic compounds can greatly contribute to enlarge the field of the novel electronic system.

If the magnetic ions such as transition metal halides are introduced into molecular conductors having such a variety of electronic structures, the localized moments of *d*-electrons can interact with the aid of π-electrons in various ways. Molecular magnets based on organic complexes therefore have a possibility of realizing novel magnetic systems. One of the most successful result is the magnetic field-induced superconductivity produced in λ-(BETS)$_2$FeCl$_4$ (BETS = bis(ethylenedithio)tetraselenafulvalene).[1] Here we discuss interplay between the electron transport of the π-electrons and the magnetism of *d*-electron spins for (DMET)$_2$FeBr$_4$, (EDTDM)$_2$FeBr$_4$, and (EDS-TTF)$_2$FeBr$_4$, with focusing on the effect of sulfur-to-selenium substitution effect.[2]

RESULTS AND DISCUSSION

The crystal structure of the three radical ion salts, (DMET)$_2$FeBr$_4$,[3] (EDTDM)$_2$FeBr$_4$,[4] and (EDS-TTF)$_2$FeBr$_4$,[5] are close to each other. Figure 2 shows the crystal structure of (DMET)$_2$FeBr$_4$. The organic donor molecules form quasi-one-dimensional columns elongated along the $a + b$ and $a - b$ directions, while tetrahedral FeBr$_4^-$ anions form a distorted square lattice formed by Br$\cdots$Br contacts. Between the donor columns and magnetic anion close S(Se)$\cdots$Br contacts are observed, whose intermolecular distances are summarized in Table I. The Se$\cdots$Br distance (3.49 Å) in the EDS-TTF salt remarkably is shorter than the sum of van der Waals (vdW) radii for Se and Br atom (3.75 Å), whereas the corresponding Br$\cdots$S distance in the DMET (3.76 Å) or EDTDM (3.79 Å) salt are similar to the vdW distance (3.70 Å). As for the counter anion system, the Br$\cdots$Br distances of these three materials are longer than the vdW distance (3.70 Å).

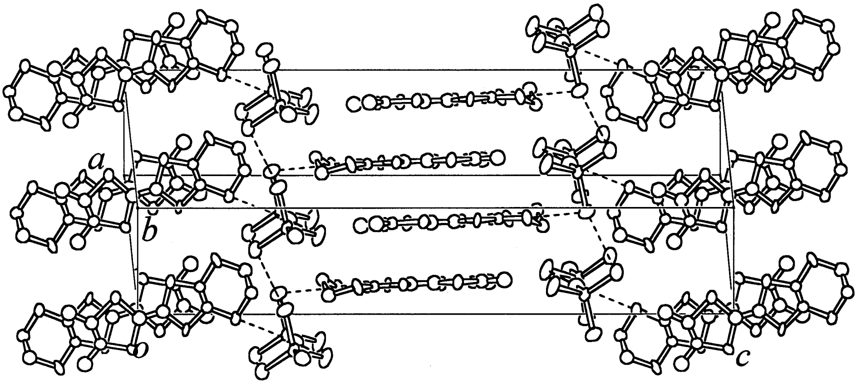

FIGURE 2 Crystal structure of $(DMET)_2FeBr_4$ projected on the $1\bar{1}0$ plane. Dashed lines are close intermolecular contacts.

The electrical conductivities of the DMET and EDTDM salts are metallic down to $T_{MI} \sim 40$ and 15 K, respectively, where metal-insulator transitions take place. These transitions also are confirmed from the magnetic susceptibilities of $DMET_2GaBr_4$ and $(EDTDM)_2GaBr_4$, where the susceptibilities come only from the π-electron part. Above T_{MI} the susceptibilities show small temperature dependence ascribed to the Pauli paramagnetism, whereas below T_{MI} it shows steep decrease showing the disappearance of the conduction electrons. From these results the ground state of the π-electron system for these salts cannot be ascribed to the charge-ordered state nor Mott insulator state. From the solid-state NMR data measured for ^{13}C-enriched $(EDTDM)_2GaBr_4$, the ground state of these salts is suggested as a SDW state.[6] In other words, in the ground states of these salts the π-electrons are not localized on donor molecules but delocalized accompanied with a spin polarization in the donor columns. For the EDS-TTF salt, although the conductivity at the room temperature is high (400 Scm^{-1}), it undergoes a gradual metal-insulator transition at ca. 250 K. Below this temperature it

TABLE I Intermolecular Distances in the Crystals of D_2FeBr_4

D	S(Se)· · ·Br/Å	Br· · ·Br/Å
DMET	3.76	3.88
EDTDM	3.79	3.88
EDS-TTF	3.49	3.86

TABLE II Magnetic Properties of D_2FeBr_4

D	C/emu K mol^{-1}	Θ/K	T_N/K	B_{SF}/T	B_1/T	B_2/T
DMET	4.4	−5.7	3.7	2.0	3.5	5.0
EDTDM	4.7	−2.8	3.0	1.8	2.9	4.5
EDS-TTF	4.58	−0.93	—	—	—	—

behaves as a semiconductor with the activation energy $E_A = 380$ K. The result of the band structure calculation shows that the EDS-TTF salt has stronger 1D character than the DMET and EDTDM salts. This one-dimensionality and/or dimerization of the donor columns can be responsible for the metal-insulator transition.

The magnetic properties of the DMET, EDTDM, and EDS-TTF salts are summarized in Table II. In a high-temperature region, the susceptibilities of all three salts obey the Curie-Weiss law. The Curie constant C is in good agreement with the calculated value of the $S = 5/2$ magnetic anion contribution. For the DMET and EDTDM salts, antiferromagnetic transitions are observed at $T_N = 3.7$ K and 3.0 K, respectively (Figure 3(a)). Since little short range order hump is observed in the susceptibility above T_N, these salts can be treated as three-dimensional

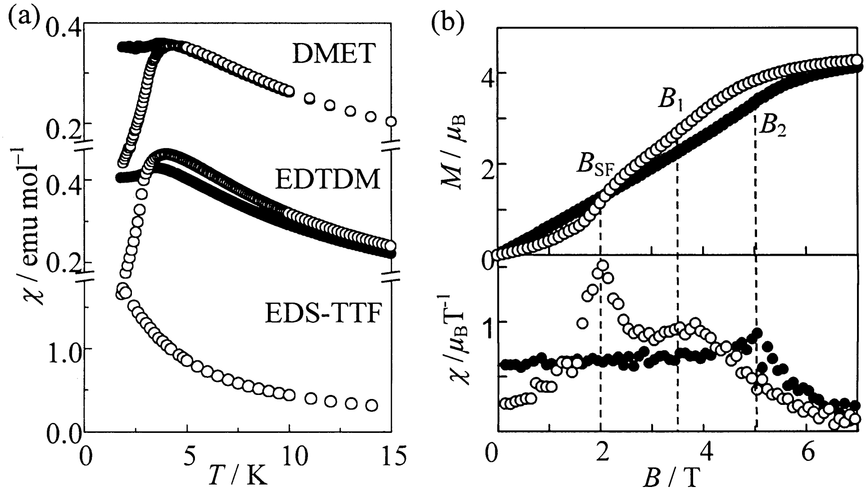

FIGURE 3 (a) Temperature dependence of the magnetic susceptibility of $(DMET)_2FeBr_4$, $(EDTDM)_2FeBr_4$, and $(EDS\text{-}TTF)_2FeBr_4$. O: B // a, ●: // b. (b) Magnetization curves of $(DMET)_2FeBr_4$ at 1.8 K. O: B // a, ●: // b. Magnetic susceptibilities ($\chi = dM/dB$) also are plotted as a function of the field.

(3D) magnetic systems, where donor π-electrons bridging anion quasi-square lattice work to give inter-layer exchange paths. The magnetization curve at 1.8 K (Figure 3(b)) shows a spin-flop transition at B_{SF} when the external field is applied parallel to the *a* axis. It should be noted that the easy-axis magnetization curve is beyond the hard-axis magnetization curve above the spin flop field B_{SF}, and has a shoulder around B_1. Similar shoulder also is observed for the *b*-axis magnetization curve around B_2. When the donor molecule is substituted from DMET into EDTDM, the spin-flop field B_{SF} almost is unchanged whereas the anomalies at B_1 and B_2 appear at the lower field. This suggests that the anomalies at B_1 and B_2 are related to the participation of the donor in the magnetism. Actually, π-electron in the SDW state has a localized spin with a small localized magnetic moment, which interacts with the magnetic counter anion to produce these complicated magnetic behaviors. In fact, the anomalies at B_2 are assigned to the spin-flop transition of the π-electron spin in the SDW state. For the EDS-TTF salt, despite the presence of the close Br$\cdots$Se contacts between the anion and donor layers, the exchange interaction between the magnetic anions are negligible, and no magnetic phase transition is observed down to 1.8 K. The magnetization curve at 2 K is well fitted with the Brillouin curve for $S = 5/2$ spins, showing the little exchange interaction between the localized spins on the anions.

The correlation of the donor π-electron system and anion *d*-electron system is clearly evidenced in the magnetoresistance. Figure 4 presents the field dependence of the magnetoresistance of $\mathrm{DMET_2FeBr_4}$ measured at 1.6 K ($<T_{\mathrm{N}}$). The in-plane magnetoresistance ($\rho_{//}$) takes a broad minimum around 6-7 T where the magnetization of the *d*-electron system is saturated. Moreover, when the external magnetic field is applied along the easy-axis direction, a discontinuous change appears at B_{SF} for the easy axis direction (// *a* axis). The inter-plane resistance, which is inversely proportion to hopping frequency, has a steep decrease at B_{SF} for $B \,//\, a$, and a discontinuous increase at B_2 for $B \,//\, b$. These one-to-one correspondences between the magnetoresistance and magnetization directly evidence the presence of the π-*d* interaction.

The magnetization curves and the field dependence of the magnetoresistance is semiquantitatively reproduced by a molecular-field model[3] with two *d*-electron sublattices and two π-electron sublattices, assuming that the π-electrons in the SDW state produce small, localized magnetic moments on the donor molecules. By fitting this model to the magnetization curves, the exchange interaction between donor-donor ($J_{\pi\pi}$), anion-anion (J_{dd}), and donor-anion ($J_{\pi d}$) pairs are estimated at $J_{\pi\pi} = -13.5$ K, $J_{\pi d} = -0.2$ K, and $J_{dd} = -0.2$ K. These parameters are about one-tenth of the values calculated using the extended Hückel

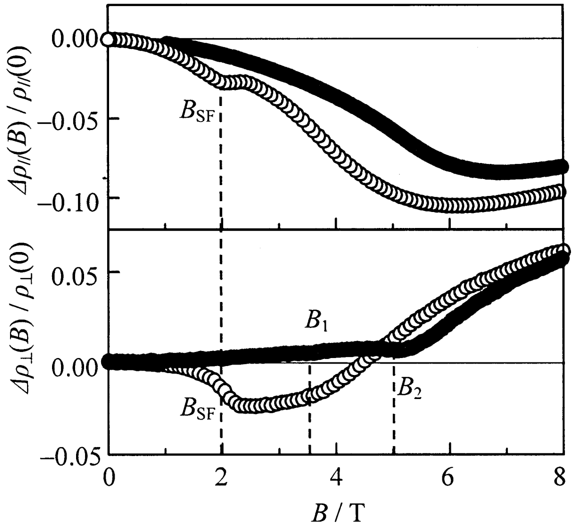

FIGURE 4 Field dependence of the magnetoresistance of $(DMET)_2FeBr_4$ measured at 1.6 K for the in-plane ($\Delta\rho_{//}(B)/\rho_{//}(0)$) and out-of-plane ($\Delta\rho_{\perp}(B)/\rho_{\perp}(0)$) directions. O: B // a, ●: B // b.

Hamiltonian,[6] presumably due to the roughness of the models. The intra- and inter-plane electron transport is subjected to the activation process over the SDW gap and inter-layer hopping process, respectively. The field dependence of the magnetoresistance is therefore obtained from the spin structure of the donors and anions. The result of the calculation semiqualitatively reproduces the experimental results, proving that the inter-plane interaction between the conduction p-electron carriers and the localized magnetic d-electrons plays an important role in the magneto-transport properties and the magnetism.

The correlation in the anomalies between the magnetization and the magnetoresistance is also observed for $(EDTDM)_2FeBr_4$ at ambient pressure. This all-sulfur analog also shows remarkable phenomena under pressure. By applying a pressure, a clear transition from insulator to metallic state takes place at 0.9 GPa. In this marginal region, the resistivity shows an anomaly around the Néel temperature T_N, and a large negative magnetoresistance ($\Delta\rho(B)/\rho(0) = -0.6$) also is observed (Figure 5). These results are explained in terms of the effect of the magnetic ordering of the localized d-electrons to the conducting π-electrons. As the π-electrons lies between the SDW and metallic states, they are sensitive to the external perturbation caused by the magnetic d-electron system. For the selenium-substituted $(DMET)_2FeBr_4$

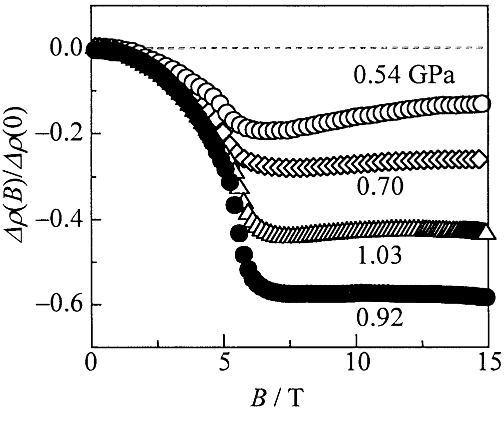

FIGURE 5 Magnetoresistance of $(EDTDM)_2FeBr_4$ measured at 1.8 K.

system, these pressure-induced phenomena are hardly observed. In this case the selenium-substitution increases the intermolecular transfer integral t and reduces the on-site Coulomb repulsion U, hence the SDW state is less stabilized than $(EDTDM)_2FeBr_4$.

The effect of the sulfur-to-selenium substitution on the outer six-membered ring negatively works despite the presence of the remarkably close Se···Br contacts between donors and anions. The semiempirical molecular orbital calculation using PM3 Hamiltonian[7] reveals that the Se 4*p* orbital hardly contributes to the HOMO of the EDS-TTF molecule (atomic orbital coefficient = 0.09). Nevertheless, the outer sulfur atoms of DMET or EDTDM molecules have larger contribution to their HOMOs (atomic orbital coefficient ~0.15). Since the magnitude of the π-dinteraction roughly is proportional to the square of atomic orbital coefficient at the intermolecular contact site, the π-d interaction in the EDS-TTF salt becomes small compared to the DMET or EDTDM salt, in spite of the presence of considerable close contacts between donors and anions. It also should be mentioned that the intermolecular Br···Br distance between $FeBr_4$ anions is almost same among the EDS-TTF, DMET and EDTDM salts, whereas EDS-TTF salt shows no antiferromagnetic transition at least down to 1.8 K. The presence of the π-d interaction in the DMET and EDTDM salts therefore is proved to be essential for the long-range magnetic ordering.

SUMMARY

We have developed conducting molecular magnets based on TTF-type donors and magnetic counter anions: $(DMET)_2FeBr_4$ and related salts.

$(DMET)_2FeBr_4$ shows metallic behavior down to ca 40 K, where the SDW transition takes place. The magnetic anions undergo an antiferromagnetic transition, whose three-dimensionality shows the presence of magnetic interaction through the donor layer. The magnetization curves in the antiferromagnetic phase have a complexity, suggesting the contribution of the localized π-electrons on the donor layers. The interplay of the π-electrons on the donor side and the d-electrons on the anion side directly is proven by the coincidence of the anomalies on the magnetoresistance and magnetization curves, whose behavior is clarified with molecular-field model. The results on the related salts support this conclusion. $(EDTDM)_2FeBr_4$ elucidates the role of π-electrons in the physical properties, whereas the lack of the π-d interaction in $(EDS\text{-}TTF)_2FeBr_4$ indicates the importance of the intermolecular overlap for the establishment of the π-d interaction.

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