TOPICAL REVIEW

New aspects of $\pi$–d interactions in magnetic molecular conductors

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Received 10 October 2008
Accepted for publication 26 January 2009
Published 6 July 2009
Online at stacks.iop.org/STAM/10/024302

Abstract

The 2 : 1 cation radical salts of bent donor molecules of ethylenedithio-tetrathiafulvaleno-quinone-1,3-dithiolemethide (EDT-TTFVO), ethylenedithio-diselenadithiafulvalenothioquinone-1,3-diselenolemethide (EDT-DSDTFVSDS) and ethylenedioxy-tetrathiafulvaleno-quinone-1,3-dithiolemethide (EDO-TTFVODS) with FeX$_4^-$ (X = Cl, Br) ions are prepared by electrocrystallization. The crystal structures of these salts are composed of alternately stacked donor molecule and magnetic anion layers. The band structures of the donor molecule layers are calculated using the overlap integrals between neighboring donor molecules and are compared with the observed electronic transport properties. The magnetic ordering of the Fe(III) $d$ spins of FeX$_4^-$ ions is determined from magnetization and heat capacity measurements. The magnetic ordering temperatures are estimated by considering a combination of a direct $d$–$d$ interaction between the $d$ spins and an indirect $\pi$–$d$ interaction between the conduction $\pi$ electron and the $d$ spins, whose magnitudes are separately calculated from the crystal structures with an extended Hückel molecular orbital method. The occurrence of a $\pi$–$d$ interaction is proved by the negative magnetoresistance, and the magnitude of magnetoresistance reflects the strength of the $\pi$–$d$ interaction. The effect of pressure on the magnetoresistance is studied, and the result indicates that the magnitude of magnetoresistance increases, namely, the $\pi$–$d$ interaction is enhanced with increasing pressure. From these experimental results it is shown that (EDT-TTFVO)$_2$·FeBr$_4$ is a ferromagnetic semiconductor, (EDT-DSDTFVSDS)$_2$·FeBr$_4$ and (EDT-TTFVODS)$_2$·FeBr$_4$·(DCE)$_{0.5}$ (DCE = 1,2-dichloroethane) are genuine antiferromagnetic metals. Among them, the (EDT-TTFVO)$_2$·FeBr$_4$ salt is the first $\pi$–$d$ molecular system where the $d$ spins of FeBr$_4^-$ ions are ferromagnetically ordered through antiferromagnetic interaction with the conduction $\pi$ electrons. Corresponding to this ferromagnetic ordering, an anomalous dielectric slow-down phenomenon toward the ordering temperature is observed. The $\pi$–$d$ interaction in (EDT-DSDTFVSDS)$_2$·FeBr$_4$ is very large and comparable to that in $\lambda$-(BETS)$_2$·FeCl$_4$, which has the highest reported value so far, while the $d$–$d$ interaction is fairly small. Concerning the ratio between the magnitudes of $\pi$–$d$ and $d$–$d$ interactions ($J_{\pi d}/J_{dd}$), this salt is currently the best $\pi$–$d$ molecular system.

Keywords: bent donor molecule, magnetic FeX$_4^-$ ion, cation radical salt, magnetic molecular conductor, crystal structure, band structure, metallic conductivity, ferro-/antiferro-magnetic ordering, $\pi$–$d/d$–$d$ interaction, magnetoresistance

(Some figures in this article are in colour only in the electronic version)
1. Introduction

Ferromagnetism in transition metals such as Fe, Co, and Ni has been explained by a direct exchange interaction between itinerant d electrons. On the other hand, the ferromagnetism in Gd metal originates from an indirect exchange between f electrons mediated by conduction s/p electrons [1–3]. This interaction is also essential for dilute d electron systems such as CuMn alloys, in which the direct exchange interaction is negligible because the distances between d electrons are too large. The unpaired d electrons, which remain in the inner shell of each metal atom, behave as localized electrons with magnetic moments. However, the s/p electrons are subject to strong interaction with those in neighboring atoms to form an electron conduction band where the electrons can move freely within the solid. When a conduction s/p electron approaches a d electron site, significant electron-electron interaction can occur. It is called s–d interaction, and its Hamiltonian, is

\[
\mathcal{H} = -2J_{sd}\delta(r)s \cdot S.
\]

Here \(s\) and \(S\) are the spin operators for a conduction s/p electron and a localized d electron, respectively, \(\delta(r)\) is the \(\delta\) function, \(J_{sd}\) is the coupling constant for the exchange interaction between a conduction s/p electron and a localized d electron, and \(r\) is the distance between the electrons. Since the d site is present at each atom in the solid, the conduction carriers can mediate the interaction between all neighboring localized d electrons to bring about a long-range interaction. The Hamiltonian for d electrons with spins \(S_i, S_j\) at sites \(i\) and \(j\), separated by distance \(R_{ij}\), is given by

\[
\mathcal{H} = \sum_i \sum_j \frac{3N}{16\pi^2} \frac{J_{sd}^2}{E_F} I(R_{ij}) S_i z S_j z.
\]

The exchange interaction between localized d electrons through metallic conduction s/p electrons is generally called the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction [1–3], which can explain the strong ferromagnetism in the Gd metal.

Regarding the magnetic interaction between the itinerant and localized electrons, it is of interest to replace the s/p-electron-based conduction band in ferromagnetic metals by a \(\pi\)-electron-based conduction band in molecular conductors involving localized d electrons. By designing the molecular and crystal structures, a variety of magnetic interactions between \(\pi\) conduction electrons and localized d electrons can be realized in molecular conductors. Many molecular conductors and magnetic conductors have been prepared so far [4]; they are mainly cation radical salts based on \(\pi\)-conjugated donor molecules with nonmagnetic or magnetic anions. The \(\pi\) electrons in cation radical salts usually form one- or two-dimensional band structures. Hence, the electronic transport properties of most salts are subject to insulating states at low temperatures due to the inherent instability of their low-dimensional electronic structures. In addition, it has been recognized that the overlap of \(\pi\) electron orbitals between neighboring donor molecules usually results in a small transfer integral \(t = 0.1–1.0\,\text{eV}\) in contrast to a large \(t\) of several eV in inorganic metals. The value of \(t\) is smaller than or comparable to that of the on-site Coulomb interaction \(U\). Consequently, molecular conductors are characterized as highly correlated electron systems in which \(\pi\) electrons play an important role in the electron transport.

Molecular magnetic conductors based on the cation radical salts of \(\pi\)-conjugated donor molecules with magnetic anions, particularly transition-metal anions with d spins, usually have crystal structures composed of alternately stacked donor and magnetic anion layers, as shown in figure 1. At the interface between each pair of alternate layers, a direct d–d interaction between the neighboring d electrons (spins) of magnetic anions and an indirect \(\pi–d\) interaction between the conduction \(\pi\) electron and the d electron (spin) are formed (figure 2(a)). The \(\pi–d\) interaction has a strong effect on the electron transport on the \(\pi\) conduction layer [5–9]. Upon increasing the
π–d interaction, the scattering time τ of the conduction π electron shortens; accordingly, the electron mobility should be reduced. However, when a magnetic field \( H \) larger than the spin-flop field \( H_{sf} \) is applied to the crystal, the d electrons (spins) are forced to align in the same orientation, namely, to induce ferromagnetic ordering, accompanied with the disruption of the π–d interaction (figure 2(b)). As a result, \( t \) and \( \tau \) increase, enhancing the electron mobility. This is experimentally reflected in the decrease in electrical resistivity \( \rho \) upon applying magnetic field, and the so-called negative magnetoresistance is observed (\( \Delta \rho / \rho < 0: \Delta \rho = \rho (H) - \rho (0) \)). On the other hand, the magnetic ordering of the d electrons (spins) under \( H = 0 \) is achieved by a combination of d-d and π–d interactions. The d–d interaction in the π–d system is usually antiferromagnetic; thus, the ferromagnetic interaction between the d electrons (spins) through the conduction π electrons is necessary to achieve the ferromagnetic ordering of d electrons (spins). In this case the conduction π electrons are spin polarized.

Tetrathiafulvalenes (TTFs) and tetraselenafulvalenes (TSFs), as well as their derivatives known as ‘straight donor molecules’ [10], are conventional donor molecules, whereas FeX\(_2^+\) (\( X = \text{Cl, Br} \)), Fe(ox)\(_3^-\), [MnCr(ox)\(_3\)]\(^-\), CuX\(_2^-\) (\( X = \text{Cl, Br} \)), CoX\(_2^-\) (\( X = \text{Cl, Br} \)), MnBr\(_2^-\), etc, are magnetic anions with d spins. Innovative attempts have been made to prepare cation radical salts based on these donor molecules and anions, and the resulting cation radical salts exhibit many interesting properties. Metallic conductivity together with ferromagnetism or antiferromagnetism has been demonstrated in (BEDT-TTF)\(_2\)•[MnCr(C\(_2\)O\(_4\))] \([\text{BEDT-TTF: bis(ethylenedithio)-tetrathiafulvalenyl}] [11] and \( \kappa \cdot \text{(BETS)}\)_2•FeX\(_4\) (\( X = \text{Cl, Br} \)) [12, 13], respectively. However, the π–d interactions in these cation radical salts are negligible or very weak. In case of magnetic molecular conductors based on straight donor molecules, a strong π–d interaction has only been demonstrated in \( \lambda \cdot \text{(BETS)}\)_2•FeCl\(_4\) [BETS: bis(ethylenedithio)-tetraselenafulvalene] [14], which exhibits a metal-insulator transition at 8.5 K. To realize stronger π–d interaction in other new cation radical salts and to clarify further characteristics of the interaction, we now focus on cation radical salts based on the ‘bent donor molecules’ of ethylenedithio-tetrathiafulvenoquinone-1,3-dithiolomethide (EDT-TTFVO), ethylenedithio-dilenedithiafulvenoquinone-1,3-dithiolomethide (EDT-DSDTFVO), ethylenedithio-dilenedithiafulvenothioquinone-1,3-dithiolomethide (EDT-DSDTFVSDS), ethylenedioxy-tetrathiafulvenoquinone-1,3-dithiolomethide (EDT-TTFVOS), and ethylenedioxy-tetrathiafulvenoquinone-1,3-dithiolomethide (EDT-TTFVOS), whose structures are shown in figure 3. All these new donor molecules have been prepared by the authors [15]. These new donor molecules have the following characteristics: (i) the molecular skeleton is highly planar, (ii) the electron-donating ability is comparable to that of the corresponding straight donor molecule and (iii) most importantly, the highest occupied molecular orbital (HOMO) has a comparatively wide electron distribution, even on the terminal 1,3-dithiole or 1,3-diselenole ring, which increases the strength of the π–d interaction with the d spins of magnetic anions [15]. In this review, we describe 2:1 cation radical salts formed between the above bent donor molecules and FeX\(_4^-\) ions, which exhibit metallic or semiconducting behavior with a small energy gap associated with anti-ferromagnetism or ferrimagnetism. Strong π–d interaction in these salts is proved by magnetoresistance measurements.

2. Bent donor molecules containing an ethylenedithio group: quasi-one-dimensional π electron system with strong π–d interaction

2.1. (EDT-TTFVO)\(_2\)•FeBr\(_4^+\)

The 2:1 salts (EDT-TTFVO)\(_2\)•FeBr\(_4^+\) and (EDT-TTFVO)\(_2\)•GaBr\(_4^-\), formed between EDT-TTFVO and an FeBr\(_4^+\) or GaBr\(_4^-\) ion, are obtained as crystals having needle or plate shapes [16]. The needle-like crystals exhibit π–d interaction and very interesting electrical and magnetic properties [17]. The crystal structures of FeBr\(_4^+\) and GaBr\(_4^-\) salts are isomorphous to each other (figure 4(a) for the FeBr\(_4^+\) salt). In the crystal, EDT-TTFVO molecules adopt head-to-tail
stacking along the $b$-axis to form quasi-uniform columns with slightly different interplanar distances of 3.49 and 3.55 Å. The FeBr$_4^-$ ions are almost straightly aligned parallel to the donor stacking direction.

The intracolumnar intermolecular overlap integrals are approximately uniform owing to the limitation of the calculation method ($(b_1 = b_2 = -17.9 \times 10^{-3}$), and there are four different intercolumnar overlap integrals $a_1 = -3.11 \times 10^{-3}$, $a_2 = -3.17 \times 10^{-3}$, $c_1 = -1.87 \times 10^{-3}$ and $c_2 = -1.85 \times 10^{-3}$ (figure 4(b)). The intracolumnar overlap integrals are much larger than the intercolumnar ones, indicating the one-dimensional electronic structure. Consistent with this, the calculated Fermi surface exhibits a quasi-one-dimensional feature as shown in figure 4(c), which implies that the metallic state cannot be maintained down to low temperatures.

Both FeBr$_4^-$ and GaBr$_4^-$ salts show moderate electrical conductivities $\sigma$ at room temperature. In good agreement with their band structures, weak metallic behavior is observed down to $\sim 170$ K. Below $170$ K, both salts become semiconducting with small activation energies $E_g \sim 10$ meV at 60–$170$ K. The origin of the metal–semiconductor transition at 170 K has not been elucidated yet.

Figure 5 shows dependence of the product of paramagnetic susceptibility $\chi_p$ and temperature ($\chi_pT$) on temperature in the range 5–300 K for the FeBr$_4^-$ salt. The $\chi_pT$ value gradually decreases upon cooling to $\sim 15$ K, but it increases below 15 K. The temperature dependence of $\chi_p$ in the range 15–300 K closely follows the Curie–Weiss law for the antiferromagnetically interacting $d$ spins of the FeBr$_4^-$ ions: $\chi_p = C/(T-\Theta) + \chi_S$ with the Curie constant $C = 4.71$ emu K mol$^{-1}$, Weiss temperature $\Theta = -3.9$ K, and a temperature-independent paramagnetic susceptibility related to the conducting $\pi$ electrons $\chi_S = 2.0 \times 10^{-4}$ emu mol$^{-1}$. This $\Theta$ value is small and negative, indicating that weak antiferromagnetic interaction. Surprisingly, below $\sim 15$ K the spin interaction changes from antiferromagnetic to ferromagnetic. In the plot of $1/(\chi_p-\chi_S)$ versus $T$, the value of $1/(\chi_p-\chi_\pi)$ can be fitted well by the Curie–Weiss law with $\Theta = -3.9$ K in the $T$ range of 25–300 K. However, below $\sim 20$ K the $1/(\chi_p-\chi_\pi)$ value deviates from the Curie–Weiss law; it monotonically decreases upon cooling and crosses the $T$-axis at $+0.87$ K. This intersection point corresponds to $\Theta < 20$ K, indicating that the FeBr$_4^-$ $d$ spins are subject to weak but ferromagnetic interaction. This change in the interaction of the Fe $d$ spins above and below $\sim 15$ K can be considered as follows. Above 15 K, the Fe $d$ spins are subject to direct interaction with each other in a very weak and antiferromagnetic manner, while the conducting $\pi$ electrons preferentially contribute to the metallic conduction. There is no significant interaction between the Fe $d$ spins and the conducting $\pi$ electrons. However, below 15 K the localization of the conducting $\pi$ electrons becomes significant, and the Fe $d$ spins preferentially interact with each other through the $\pi$ spins produced on the donor-stacked column. Remarkably, such an indirect $d$–$\pi$–$d$ spin interaction is ferromagnetic, although its origin is still unclear.

The slope of the $1/(\chi_p-\chi_\pi)$ versus $T$ plot at higher $T(25–300$ K) corresponds to $1/C(C = 4.71)$, while below $\sim 20$ K the slope $(1/C; C = 3.98)$ becomes steeper. Thus, the low-temperature $C$ value is $\sim 15\%$ lower than the high-temperature one. This may be caused by decrease of the spin quantum number $S$ of the Fe(III) $d$ spin from the 5/2 value due to some geometrical change around the Fe atom in the FeBr$_4^-$ ion. Alternatively, there is significant antiferromagnetic interaction with the conducting $\pi$ electrons on the donor-stacked column. The magnetization $M$ curve was measured in the applied field $H \pm 50$ kOe at 1.8 K [18]. A sigmoidal curve without
hysteresis (coercive force < 7 Oe) was obtained with \( M = \pm 25350 \text{ emu mol}^{-1}(\pm 4.39 \mu_B) \) at \( H = \pm 50 \text{ kOe} \). This value increases for higher fields. Numerical simulation predicts that the saturation of occurs at \( H \sim \pm 300 \text{ kOe} \), with \( M = \pm 28900 \text{ emu mol}^{-1}(\pm 5.00 \mu_B) \), which is very close to that obtained from (EDT-TTFVO\(_2\))\(_4\)•FeBr\(_4\) with \( 6 \times 10^{23} \text{ Fe(III)}(S = 5/2) \) spins per mole. This result reveals the Fe(III) d spin value is still 5/2 and it decreases with the antiferromagnetic \( \pi-\delta \) interaction.

The observed \( M \) curve is compared with two related Brillouin functions with \( S = 5/2 \) and \( \Theta = 0 \text{ K} \), and with \( S = 5/2 \) and \( \Theta = +0.87 \text{ K} \) at 1.8 K. For magnetic fields lower than \( \sim \pm 10 \text{ kOe} \) the observed \( M \) values are larger than those in the Brillouin function with \( \Theta = 0 \text{ K} \) at each \( \pm H \). However, the observed \( M \) curve shows a very good fit to the Brillouin function with \( \Theta = +0.87 \text{ K} \) when \( H \) is lower than \( \pm 1 \text{ kOe} \). However, above \( \pm 1 \text{ kOe} \) the curves diverge and saturate more slowly than the Brillouin function. The slower saturation behavior of the observed \( M \) curve and the decreased value of \( C \) at the low \( T \) can be reasonably explained by considering that at low temperature, the conducting \( \pi \) electrons participate by antiferromagnetic interaction with the Fe d spins, eventually bringing about ferromagnetic interaction between the neighboring Fe d spins. It is obvious that in this spin-interacting system, the magnetic moments of the Fe d spins exhibit slower saturation because of the participation of the magnetic moments from the conducting \( \pi \) electrons in the reverse direction. Furthermore, \( M \) is measured down to 0.4 K by an induction method using a pulse magnet system combined with a \(^3\text{He} \) refrigerator. As shown in figure 6(a), the \( M \) curve still reaches saturation faster as \( T \) decreases below 2 K. However, the slope becomes very small, between 1.2 and 0.4 K, suggesting that the \( M \) curve is completely saturated near this temperature range. No hysteresis is observed.

To confirm the presence of this ferrimagnetic ordering due to the interaction between the Fe d spins of FeBr\(_4^–\) ions and the \( \pi \) spins on the donor-stacked column and to determine the transition temperature \( T_C \), the above \( M \) curve data are analyzed using the Arrott method of constructing a \( M^2/H/M \) plot [19]. The Arrott method is suitable for high \( T_C \), but not for a ferrimagnet with low \( T_C \) and a small hysteresis loop. Therefore, a resonant circuit method developed by Noguchi et al is employed, which can sensitively detect the jump in \( M \) in a small hysteresis loop caused by ferromagnetic or ferrimagnetic ordering [20]. As shown in figure 6(b), an oscillation initially appears below 1 K, when \( H \) changes sign, and the magnitude of the oscillation increases as \( T \) decreases. The oscillating behavior is clearer for bare signals induced in the pickup coil. The inset of figure 6(b) shows an example at 0.4 K. When \( H \) crosses zero, a sharp jump in \( M \) occurs in the hysteresis loop, which causes a transient oscillation in the signal, and the frequency corresponding to the jump in \( M \) crosses the resonant frequency of the circuit. Because the initial amplitude of the oscillation is proportional to the jump in \( M \), the amplitude is plotted against \( T \), and a step-like change is observed (figure 6(b)). The transition temperature is estimated as \( T_C \approx 1.02 \text{ K} \) at the midpoint of the step.

The determination of \( T_C \) and the existence of ferromagnetic ordering are also confirmed by measuring heat capacity \( C_{\text{mol}} \). The \( C_{\text{mol}}(T) \) dependence in the range 0.5–20 K shows a clear peak at 0.9 K, which is close to the \( T_C \) value determined from the magnetization measurement. The lattice contribution on the order of 1 mJ K\(^{-2}\) mol\(^{-1}\) is estimated from the linear relation in the \( C_{\text{mol}}/T \) versus \( T^2 \) plot below 8 K. However, under these conditions it is difficult to eliminate the electronic contribution, since the \( \pi-\delta \) interaction may form a strongly correlated electron system. After subtracting the lattice contribution from \( C_{\text{mol}} \), the magnetic heat capacity \( C_{\text{mag}} \) is obtained (figure 7(a)). The shape of \( C_{\text{mag}} \) is not a \( \lambda \)-type anomaly as commonly observed in a second-order transition, but a cusp with a tail that extends to the high-\( T \) region, which is characteristic of the short-range or low-dimensional ordering in Heisenberg spin systems arranged in a two-dimensional square lattice [21]. Accordingly, the Fe d spins of FeBr\(_4^–\) ions and the \( \pi \) spins on the donor-stacked column are in the two-dimensional ferrimagnetic ordering state above \( T_C \), but are converted to a three-dimensional ferrimagnet below \( T_C \). The magnetic entropy \( S_{\text{mag}} \) is calculated by integrating \( C_{\text{mag}}/T \) with respect to \( T \) (figure 7(a)). Compared with \( R \ln 6 \) and \( (R \ln 6 + R \ln 2) \) (\( R \): gas constant), which correspond to \( S_{\text{mag}} \) for Fe d
spins with $S = 5/2$ and the total $S_{\text{mag}}$ for Fe d spins with $S = 5/2$ and donor $\pi$ spins with $S = 1/2$, respectively, the observed value of $S_{\text{mag}}$ is larger than $R \ln 6$ but smaller than $(R \ln 6 + R \ln 2)$ above 2.5 K, suggesting that the d spins coexist with the $\pi$ spins on the donor-stacked columns, which provide an additional contribution to $S_{\text{mag}}$.

The temperature dependence of $C_{\text{mol}}$ at several magnetic fields of 0–10 kOe was also studied (figure 7(b)) [18]. The magnetic field was applied perpendicular to the plane of the FeBr$_4^-$ ion square lattice. $C_{\text{mol}}$ shows strong field dependence, i.e. its maximum gradually shifts to the higher temperatures as $H$ increases. This round peak is due to the magnetic Schottky anomaly caused by the Zeeman splitting of the degenerated ground state in magnetic field. This field dependence is very similar to those in other ferromagnetic and ferrimagnetic materials; it contrasts that of antiferromagnets, which show weak field dependence.

To further clarify the $\pi$–d interaction in this salt, electric resistivity $\rho$ and magnetoresistance measured along the $a$-axis were studied under high magnetic fields applied parallel to the least conducting $c^*$-direction at pressures up to 8.0 GPa [22]. As shown in figure 8(a), $\rho$ and $E_g$ for the insulating state are suppressed by applying pressure $P < 170$ K, while the insulating state is retained below 146 K ($T_{\text{min}}$) even under 8.0 GPa. The conductivity increase indicates that the bandwidth $W$ of the conduction $\pi$ electron band is enhanced by pressure. $T_{\text{min}}$ decreases with increasing $P$ up to 4 GPa, but above 4 GPa, the increase is small. Moreover, $d\rho/dT$ above $T_{\text{min}}$ changes near 4 GPa from positive (metallic behavior) to negative (nonmetallic behavior) with increasing $P$. Accordingly, the pressure dependence of $T_{\text{min}}$ cannot simply be explained by increasing bandwidth. Presumably, the pressure causes a change not only in the bandwidth but also in other parameters involved in the enhancement of the $\pi$–d interaction, which can stabilize the insulating state above 4 GPa.

Figure 8(b) shows magnetoresistance under 4.0 and 6.5 GPa at 4.2 K [22]. The magnetoresistance under 4.0 GPa increases with increasing $H$ until $H^* = 12.5$ kOe, where a maximum appears, and above $H^*$ it decreases. The magnetoresistance under 6.5 GPa also shows similar behavior, but
$H^*$ slightly shifts to a higher $H$ side and the magnitude of the positive magnetoresistance is strongly suppressed. On the assumption that the positive magnetoresistance originates from the orbital effect, i.e. $\Delta \rho / \rho \sim (\mu H)^2$, the marked reduction of magnetoresistance below $H^*$ can be related to the decrease of mobility $\mu = e \tau / m^*$, i.e. a decrease in the scattering time $\tau$ and/or an increase in the effective mass $m^*$. It would be difficult to explain the decrease in $\tau$ with pressure. Therefore, we assume that the reduction of $\mu$ is caused by the increase in $m^*$, which is enhanced by the interaction with the Fe d spins of the FeBr$_4^-$ ion. The enhancement of $m^*$ may be responsible for the stabilization of the insulating state above 4 GPa. When $H$ exceeds $H^*$, it is most probable that the negative magnetoresistance is caused by the alignment of the Fe d spins with $H$, suggesting that the spin fluctuation of the FeBr$_4^-$ ions contributes to the occurrence of the insulating state above 4 GPa as well as the correlation effect. These results indicate that the $\pi$–d interaction is enhanced and that it has a strong effect on the transport properties of this salt above 4 GPa.

Corresponding to the ferromagnetic ordering of Fe(III) d spins through the antiferromagnetic interaction with the conducting $\pi$ electrons in this FeBr$_4^-$ salt, a dielectric slow-down phenomenon toward the ferrimagnetic state is observed [23, 24]. The dielectric constant $\varepsilon(\omega)$ is expressed as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, $\varepsilon_2 = 4\pi\sigma_1/\omega$. Here $\sigma_1$ is conductivity, and $\varepsilon_1$ and $\varepsilon_2(\sigma_1)$ are obtained from the capacitance and conductance measured down to 0.4 K by a three-terminal method, using a capacitance bridge with an excitation frequency $f = \omega/2\pi$ in the range 0.3 Hz–100 kHz. Figures 9(a) and (b) respectively show the temperature dependences of $\sigma_1$ and $\varepsilon_1$ at $f = 14$ Hz–14 kHz and zero dc bias ($E_{\text{bias}} = 0$). With the decrease in $T$ from $\sim$40 K, $\sigma_1$ decreases monotonically, yielding almost the same semiconducting energy gap as that obtained in dc measurement (figure 9(a)). Below $\sim$15 K, $\sigma_1$ becomes highly dispersive with increasing frequency and exhibits frequency-dependent peaks at low temperatures. On the other hand, as shown in figure 9(b), $\varepsilon_1$ exhibits a broad peak around 10–15 K at $f = 14$ Hz. The peak shifts to a higher temperature and weakens with increasing $f$. The magnitude of $\varepsilon_1 \sim 10^4$ is very large. At lower temperatures, a step-like change occurs at the temperature where the peak in $\sigma_1$ appears. Figures 10(a) and (b) show the temperature dependences of $\varepsilon_1$ and $\varepsilon_2$, respectively, measured at 563 Hz at different temperatures below 15 K. The characteristic behaviors around 3 K can be well analyzed using a Debye relaxation mechanism [25] with a single relaxation time $\tau$:

$$
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)
= \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)(\varepsilon_0 - \varepsilon_{\infty})(\omega\tau)}{1 + (\omega\tau)^2} + \frac{1}{1 + (\omega\tau)^2},
$$

where $\varepsilon_\infty$ is the dielectric constant at $\omega = \infty$. When the frequency $\omega$ of electric field becomes close to the relaxation rate $\tau^{-1}$, namely $\omega \tau \sim 1$, the dielectric response $\varepsilon_1$ becomes small, while the dielectric loss $\varepsilon_2$ shows a peak, owing to the time delay in the response.

It is assumed that $\varepsilon_2$ consists of a non-Debye relaxation component $\varepsilon_{2,A}$ and a Debye relaxation component $\varepsilon_{2,B}$. By subtracting $\varepsilon_{2,A}$ from $\varepsilon_2$, $\varepsilon_{2,B}$ is obtained, which exhibits an asymmetric peak centered at $T_p = 3.2$ K (figure 10(b)). Similar treatment of $\varepsilon_1$ is performed for all the other excitation frequencies. Similarly, $\varepsilon_1$ is divided into a non-Debye relaxation component $\varepsilon_{1,A}$ and a Debye relaxation component $\varepsilon_{1,B}$ (figure 10(a)). The self-consistently obtained $\varepsilon_{1,B}$ and $\varepsilon_{2,B}$ have a typical Cole–Cole plot, indicating that the data can be understood in terms of the Debye relaxation with a single relaxation process. This suggests that the physical process of the Debye relaxation here is due to an order-disorder type interconversion between two or more stable states.

Let us analyze $\tau - T_p$ data at $T < 7$ K. The data cannot be reproduced by the Arrhenius plot for an activation-type process as conventionally observed in polar crystals. Alternatively, a satisfactory fit can be obtained using

$$
\tau = T_0 \left( \frac{T_p - T_0}{T_0} \right)^{-n_\tau},
$$

where the characteristic $T_p$, $T_0$, and critical index $n_\tau$ are the fitting parameters. The $\tau^{-1/n_\tau}$–$T_p$ plot shown in figure 11 gives $n_\tau = 6.5$ and $T_0 = (0.75 \pm 0.15)$ K. This result suggests that $\tau$ diverges at $T = T_0$, which is very close to or slightly lower than the cusp at $T = 0.86$ K in the measurement of $C_{\text{mol}}$.

The changes in $\sigma_1$ and $\varepsilon_1$ were studied by applying $E_{\text{bias}}$ at $f = 1$ kHz and $T = 4.2$ K. With increasing $E_{\text{bias}}$, the magnitude of $\sigma_1$ increases by more than one order, while $\varepsilon_1$
remains constant at low $E_{\text{bias}}$, followed by a sharp decrease toward zero. The integration of $\varepsilon_1$ with respect to $E_{\text{bias}}$ gives a ferroelectric-like polarization curve. The $E_{\text{bias}}$ dependence of $\sigma_{\text{diff}}$ ($dJ/dE_{\text{bias}}$, where $J$ is dc current density) also shows similar behavior. That $\sigma_1 \sim \sigma_{\text{diff}}$ at a high $E_{\text{bias}}$ indicates that the conductivity can be exclusively ascribed to the \(\pi\) electron transport, because the dc response originates solely from the conduction of \(\pi\) electrons, which at low $E_{\text{bias}}$ are highly localized, but are forced into current-carrying states at high $E_{\text{bias}}$. At $E_{\text{bias}} \sim 0$, $\sigma_1$ becomes as large as $\sim 100\sigma_{\text{diff}}$, which means that the excess conductivity of $\sigma_1$ may be due to the dielectric loss of some polarizations with a time-varying excitation field. These results demonstrate that the dielectric slowing down intrinsically proceeds toward a ferrimagnetic ordering state in this salt.

2.2. (EDT-DSDTFVO)$_2$•FeBr$_4$

The electronic structure of (EDT-TTFVO)$_2$•FeBr$_4$ is one dimensional, which results in the instability of the metallic states at low temperatures. To increase the dimensionality of the electronic structure, one may consider reinforcing the lateral intermolecular interactions. Therefore, a slight chemical modification of EDT-TTFVO is carried out by replacing two sulfur atoms in the central TTF skeleton with two Se atoms, to form EDT-DSDTFVO, since the size and polarization of selenium atom are larger than those of sulfur. Single crystals of (EDT-DSDTFVO)$_2$•MX$_4$ (M = Fe, Ga; X = Cl, Br) salts are obtained by electrocrystallization. The crystal structure of (EDT-DSDTFVO)$_2$•FeBr$_4$ has been successfully solved [26].

Figure 10. Temperature dependences of (a) $\varepsilon_1$ and (b) $\varepsilon_2$ at $f = 563$ Hz for (EDT-TTFVO)$_2$•FeBr$_4$. (Reproduced with permission from [24].)

Figure 11. Plot of $\tau^{-1/\eta}$ versus $T_p$ for two different samples (● and □) of (EDT-TTFVO)$_2$•FeBr$_4$. The straight line is obtained by substituting $n = 6.5$ and $T_p = (0.75 \pm 0.15)K$ into equation (5). (Reproduced with permission from [24].)

Similar crystal structures were obtained for the other MX$_4^-$ salts, whose crystal structure analyses were insufficient because of the large orientational disorder of the donor molecule. In the crystal structure of the FeBr$_4^-$ salt, the asymmetric unit contains one donor molecule and half of the anion. Figure 12(a) depicts the projection of the salt onto the $ac$-plane. The donor molecules have an approximately planar shape and are uniformly stacked with several $S \cdots S(Se)$ contacts along the $b$-axis. Furthermore, these stacked columns are aligned along the $c$-axis, so that the donor layer has a \(\beta\)-like packing. There are also several close contacts between the S and Se atoms of donor molecules in neighboring columns, suggesting a considerable intercolumnar interaction. On the other hand, the FeBr$_4^-$ ions intervene between the donor layers and are aligned uniformly along the $b$-axis, but have a zigzag arrangement along the $c$-axis. The Br$\cdots$Br distances between neighboring FeBr$_4^-$ ions are 4.16 and 4.27 Å, which are much longer than the van der Waals contact distance (3.91 Å). In contrast, the FeBr$_4^-$ ions are in close contact with neighboring donor molecules, as can be seen from the short Br$\cdots$S distances (3.62–3.83 Å), suggesting a strong \(\pi\cdots\pi\) interaction between the donor molecules and FeBr$_4^-$ ions.

There are three different intermolecular overlap integrals $b = -28.1 \times 10^{-3}$, $p = 4.37 \times 10^{-3}$ and $q = 5.51 \times 10^{-3}$, as shown in figure 12(b). Compared with those in (EDT-TTFVO)$_2$•FeBr$_4$, the intermolecular lateral interactions are enhanced; however, the overlap integral along the stacking direction ($b$) is 5–6 times larger than those along the lateral directions ($p$ and $q$). The calculated band dispersion has a quarter-filled nature because of the 2:1 composition of the donor molecule and FeBr$_4^-$ ion, and the uniform stacking structure of the donor molecules. As shown in figure 12(c), the Fermi surface is two-dimensional but opens along the $k_c$ (lateral) direction, in a similar manner to that of (EDT-TTFVO)$_2$•FeBr$_4$. Furthermore, the Fermi surface is folded in half along the $k_c$ direction because the period of the crystal lattice in this salt is double that in
(EDT-TTFVO)$_2$·FeBr$_4$ along the $k_z$ direction. This increases the dimensionality of the electronic structure and therefore stabilizes the metallic state down to lower temperatures.

The in-plane and out-of-plane resistivities ($\rho_\parallel$ and $\rho_\perp$, respectively) of the plate-like crystals of (EDT-DSDTFVO)$_2$·MX$_4$(M = Fe, Ga; X = Cl, Br) are measured down to 4.2 K. The in-plane resistivities are 0.02–0.12 cm$^2$/V s at room temperature, while the out-of-plane resistivities are $\sim$10 times larger. As shown in figure 13(a), all the salts show metallic behavior in $\rho_\parallel$ down to 30–70 K. Below the corresponding temperatures, slight upturn in $\rho_\parallel$ is observed; however, the increase is very small and the values of $\rho_\parallel$ at 4.2 K are approximately the same as those at room temperature [26]. The estimated activation energies are 1–3 meV; therefore, all the salts are intrinsically metallic down to 4.2 K. The temperature dependences of $\rho_\perp$ in GaCl$_4$ and FeCl$_4$ salts show similar tendencies to those observed in $\rho_\parallel$, and the upturns of $\rho_\perp$ are nearly suppressed by applying pressure $\sim$7 kbar (figures 13(b) and (c)) [27].

The $\chi_\rho$ values of polycrystalline samples of the FeCl$_4$ and FeBr$_4$ salts are measured under field of 1 kOe in the temperature range 1.9–300 K. The temperature dependences of $\chi_\rho$ obey the Curie–Weiss law with $C = 4.52$ emu K mol$^{-1}$ and $\Theta = -0.3$ K above 1.9 K for the FeCl$_4$ salt, and with $C = 4.61$ emu K mol$^{-1}$ and $\Theta = -9.7$ K above 8 K for the FeBr$_4$ salt, indicating that Fe d spins are subject to very weak or comparatively strong antiferromagnetic interaction, respectively. In both salts, no antiferromagnetic ordering was recognized down to 1.9 K.

The magnetoresistance of (EDT-DSDTFVO)$_2$·MCl$_4$ (M = Fe, Ga) was studied in [27]. Magnetic field up to 50 kOe was applied parallel to the conducting $bc$-plane, and $\Delta \rho_\parallel/\rho_\parallel$ was measured at 4.0 K. The GaCl$_4$ salt shows a positive magnetoresistance of 4% under a field of 50 kOe, similar to that observed in nonmagnetic metals. On the other hand, a large negative magnetoresistance is observed for the FeCl$_4$ salt (–14.7% at 50 kOe). This negative magnetoresistance originates from the suppression of spin scattering caused by spin alignment under the applied magnetic field. The difference in magnetoresistance between the GaCl$_4$ and FeCl$_4$ salts provides direct evidence of $\pi$–d interaction in the FeCl$_4$ salt. Furthermore, the negative magnetoresistance in the FeCl$_4$ salt is enhanced under increasing pressure: $\sim$16.3% under 6.5 kbar and $\sim$17.7% under 9.5 kbar at 50 kOe. A slight decrease in the positive magnetoresistance is observed in the GaCl$_4$ salt by applying pressure: 3.5% under 7.7 kbar and 3.3% under 15 kbar at 50 kOe. The magnetoresistances of the GaBr$_4$ and FeBr$_4$ salts are both positive. However, the magnetoresistance in the FeBr$_4$ salt is $\sim$30% of that in the GaBr$_4$ salt: 4.1 and 12.0% at 1.3 K under a field of 50 kOe for FeBr$_4$ and GaBr$_4$ salts, respectively. Probably, the magnetoresistance in the FeBr$_4$ salt involves a negative component in addition to a large and positive component.
2.3. \( (EDT-DSDTFVSDS)_2 \cdot FeBr_4 \)

To further increase the interaction between the donor and anion, a new donor molecule, EDT-DSDTFVSDS, is designed and synthesized. This molecule is derived from EDT-DSDTFVO by replacing the \( C=O \) group and 1,3-dithiole ring with a \( C=S \) group and 1,3-diselenole ring, respectively. It is expected that the short atomic contacts between the donor molecule and anion will be enhanced by the increased size and polarization of the Se atom in this donor molecule compared with the corresponding sulfur atom in EDT-EDSTFVO. The 2:1 salts of EDT-DSDTFVSDS with an \( FeBr_4^- \) or \( GaBr_4^- \) ion are black plate-like crystals \[28\]. The crystal structures of both salts have been successfully solved and are isomorphous to each other.

In the crystal structure, the asymmetric unit contains one donor molecule, which is approximately planar. Figure 14(a) depicts the projection onto the \( ac \)-plane for the \( FeBr_4^- \) salt. The donor molecules show head-to-tail stacking resulting in uniform columns along the \( b \)-axis, and several \( S \cdots \cdots S \) and \( S \cdots \cdots \) contacts are observed along the stacking direction. The terminal 1,3-diselenole rings are outside the stacking columns of the central TTF skeleton, which is different from those in \( (EDT-DSDTFVO)_2 \cdot FeBr_4 \), where the 1,3-dithiole rings are inside the stacking columns. Despite this difference, the donor molecule arrangement of this salt is very similar to that of \( (EDT-DSDTFVO)_2 \cdot FeBr_4 \) and belongs to the \( \beta \)-type packing pattern. Several close \( S \cdots \cdots \)Se contacts are also observed between neighboring columns, suggesting a strong two-dimensional intermolecular interaction. The \( FeBr_4^- \) ions are aligned in a rectangular form in the \( bc \)-plane and are sandwiched by the donor layers. In comparison with \( (EDT-DSDTFVO)_2 \cdot FeBr_4 \), the neighboring \( FeBr_4^- \) ions are separated further from each other due to the staggered 1,3-diselenole rings. Accordingly, the shortest \( Br \cdots \cdots Br \) distance between neighboring \( FeBr_4^- \) ions is 4.47 Å, which is much larger than the van der Waals distance 3.90 Å. In contrast, the \( FeBr_4^- \) ion has very close \( Br \cdots \cdots S (3.75 \text{ Å}) \) and \( Br \cdots \cdots Se (3.91, 3.94, 4.06 \text{ and } 4.13 \text{ Å}) \) contacts with neighboring donor molecules. These structural features suggest that the \( \pi-d \) interaction between the \( FeBr_4^- \) ion and the donor molecule should be much stronger than the \( d-d \) interaction between the \( FeBr_4^- \) ions.

The intermolecular interactions in the donor layer are schematically shown in figure 14(b). The overlap integral along the stacking direction \( (b = -39.71 \times 10^{-3}) \) is four
to six times larger than those along the lateral direction ($p = 9.44 \times 10^{-3}$, $q = 7.11 \times 10^{-3}$ and $r = 1.73 \times 10^{-3}$). The calculated Fermi surface exhibits a two-dimensional feature but opens along the $k_c$-direction, similarly to that of (EDT-DSDTFVO)$_2$•FeBr$_4$ (figure 14(c)).

The conductivities of the FeBr$_4^-$ and GaBr$_4^-$ salts along the $b$-axis are 200–300$\text{S cm}^{-1}$ at 290 K, and the $\rho(T)$ dependences are shown in figure 15. Both FeBr$_4^-$ and GaBr$_4^-$ salts exhibit metallic behavior down to $\sim$30 K. Below this temperature, the slight upturns in $\rho$ are observed while conductivities remain high at $\sim$70 and 100$\text{S cm}^{-1}$ for FeBr$_4^-$ and GaBr$_4^-$ salts, respectively. Below $\sim$10 K, the increase in $\rho$ is more rapid in the FeBr$_4^-$ salt than in the GaBr$_4^-$ salt. Note that a turning point in $\rho$ is observed for the FeBr$_4^-$ salt near 3.3 K, which corresponds to the temperature $T_N$ of antiferromagnetic ordering of the $d$ spins of FeBr$_4^-$ ions as described below.

The magnetization of the FeBr$_4^-$ salt is measured using single crystals under $H = 10\text{kOe}$ applied along each of the lattice axes ($a$-, $b$- and $c$-axes). The temperature dependence of $\chi_p$ is also determined using the polycrystalline sample and can be fitted to the Curie–Weiss law with $C = 4.71\text{emu K mol}^{-1}$ and $\Theta = -10.5\text{K}$, suggesting a relatively strong antiferromagnetic interaction between the $d$ spins of FeBr$_4^-$ ions. As shown in figure 16(a), $\chi_p$ sharply drops below $\sim$5 K only for $H \parallel c$, suggesting an antiferromagnetic ordering along the $c$-axis. The $M$–$H$ curves measured at 1.9 K show a spin-flop around 18$\text{kOe}$ only for $H \parallel c$ (figure 16(b)). Furthermore, the $C_{\text{mol}}$ was measured in the temperature range 0.5–30 K for both FeBr$_4^-$ and GaBr$_4^-$ salts.

Figure 14. (a) Crystal structure of (EDT-DSDTFVSDS)$_2$•FeBr$_4$ projected onto the $ac$-plane, (b) packing pattern of donor molecules with the intermolecular overlap integrals schematically shown, and (c) calculated Fermi surface of donor layers based on the crystal structure at room temperature.

Figure 15. Temperature dependences of $\rho/\rho_r$ in the range 0.6–300 K for the FeBr$_4^-$ and GaBr$_4^-$ salts of EDT-DSDTFVSDS. (Reproduced with permission from [29].)

The $C_{\text{mag}}$ of the $d$ spins in the FeBr$_4^-$ salt is obtained by subtracting $C_{\text{mol}}$ estimated from the GaBr$_4^-$ salt; however, this value of $C_{\text{mag}}$ still contains the electronic contribution of the $\pi$–$d$ interaction. Figure 17 shows the temperature dependence of $C_{\text{mag}}$. A maximum in the $C_{\text{mag}}$ appears at 3.3 K, but the shape is not a $\lambda$-type. Such a shape with a tail extending to the higher temperatures is characteristic of a short-range or low-dimensional ordering in Heisenberg spin systems arranged in a two-dimensional square lattice. The measurements of $M$ and $C_{\text{mol}}$ undoubtedly indicate an...
antiferromagnetic ordering near $T_N = 3.3$ K with the spin easy axis parallel to the c-axis.

As mentioned above, $\rho$ increases more rapidly in the FeBr$_4$ salt than in the GaBr$_4$ salt below 30 K. It is supposed that the stabilization of the insulating state in the FeBr$_4$ salt is most plausibly due to the significant $\pi$–d interaction. To confirm this point, magnetoresistance was measured for both salts under a grease pressure of $\sim 0.2$ kbar. A field of up to 50–140 kOe was applied parallel to either $a$, $b$, or $c$-axis. For the GaBr$_4$ salt, the magnetoresistance is ca. +3% at 50 kOe and 4.2 K. In contrast, the FeBr$_4$ salt shows large negative magnetoresistances of about –20% at 50 kOe, and about –40% at 140 kOe and 4.2 K, irrespective of the direction of the applied field. Figures 18(a)–(c) show the magnetoresistances along $H \parallel a$, $H \parallel b$ and $H \parallel c$ in the FeBr$_4$ salt, respectively. A sharp dip appears near 18 kOe for $H \parallel c$ without hysteresis, but no dip is observed for $H \parallel a$ and $H \parallel b$. This is clear evidence for strong anisotropic $\pi$–d interaction. The saturated behavior under negative magnetoresistance continues beyond 100 kOe, and the magnetoresistance at 149 kOe and 0.7 K amounts to –85%.

![Figure 16](image1.png)

![Figure 17](image2.png)

**Figure 16.** (a) Temperature dependences of $X_\theta$ ($H = 10$ kOe, $T < 20$ K) and (b) field ($H$) dependences of $M$ ($T = 1.9$ K, $H < 50$ kOe) for $H \parallel a$ (red circles), $H \parallel b$ (blue circles), and $H \parallel c$ (green pluses) directions of the single crystal and for the polycrystalline sample (–) of (EDT-DSDTFVSDS)$_2$•FeBr$_4$ (Reproduced with permission from [28].)

The angular dependences of magnetoresistance for the FeBr$_4$ and GaBr$_4$ salts were studied below 8 K. The result for the FeBr$_4$ salt at 8.0 K is very similar to those at 4.2 and 1.4 K for the GaBr$_4$ salt, suggesting that the $\pi$ electronic state of the FeBr$_4$ salt above 8 K is the same as that of the GaBr$_4$ salt. However, below 4.2 K the angular dependence of magnetoresistance for the FeBr$_4$ salt is distinctly different from that for the GaBr$_4$ salt, indicating that the electrical conductivity of the FeBr$_4$ salt is strongly affected by the Fe d spins.

The relation between the antiferromagnetic arrangement of the d spins and the enhancement of the insulating state was theoretically interpreted in [29]. The more rapid increase in $\rho$ in the FeBr$_4$ salt than in the GaBr$_4$ salt below 30 K is assumed as the activation-type gap enhancement caused by the periodic magnetic potential of the d spins under magnetic field, $Q_p(H)$. The magnetoresistance, $\Delta \rho(H)/\rho(0T)$, is expressed as

$$\frac{\Delta \rho(H)}{\rho(0T)} = \frac{R_{Fe}(H) - R_{Fe}(0T)}{R_{Fe}(0T)} = \frac{R_{Ga}}{R_{Fe}} \times \exp \left\{ \frac{2Q_p(H)}{5} \ln \left( \frac{R_{Fe}}{R_{Ga}} \right) \right\} - 1. \quad (6)$$

Here $R_{Fe}(H) = R_{Ga} \exp(\alpha Q_p(H)/k_B T)$; $\alpha$ is a factor intrinsic to the material expressing the strength of the $\pi$–d interaction $\alpha = 2k_B T/5 \ln(R_{Fe}/R_{Ga})$, and $R_{Fe}$ and $R_{Ga}$ are the electrical resistances of the FeBr$_4$ and GaBr$_4$ salts normalized to those at 300 K, respectively. $Q_p(H)$ is given by equations (7) and (8)

$$Q_p(H) = \frac{5}{2} \sin \left\{ \cos^{-1} \left( \frac{2M(H)}{5g} \right) \right\}$$

for $H \parallel b$ and $H \parallel c > H_{SF}$ \quad (7)

$$Q_p(H) = \frac{\sqrt{25 - (10M(H)/g)^2}}{2}$$

for $H \parallel c < H_{SF}$. \quad (8)
Figure 18. Magnetoresistance of (EDT-DSDTFVSDS)$_2$·FeBr$_4$ for (a) $H \parallel a$ at $T = 0.6$, 1.3 and 4.2 K and $H < 50$ kOe, (b) $H \parallel b$ at $T = 0.7$ and 4.2 K and $H < 140$ kOe, (c) $H \parallel c$ at $T = 0.6$, 1.3 and 4.2 K and $H < 50$ kOe, and experimental (—) and calculated (-----) results for (d) $H \parallel b$ at $T = 0.7$ K and for (e) $H \parallel c$ at $T = 1.3$ K. (Reproduced with permission from [29].)

Here $g$ is the Zeeman splitting factor, assumed here as $g = 2$; $H_{SF}$ is the spin-flop field. The calculated results are in good agreement with the observed giant negative magnetoresistance for $H \parallel b$ at 0.7 K (figure 18(d)). Additionally, the dip anomaly in magnetoresistance for $H \parallel c$ at 1.3 K is well reproduced (figure 18(e)). These results support the model of the antiferromagnetic arrangement of the d spins that enhances the insulating state due to the π electrons through the π–d interaction.

The effects of pressure on the $\rho(T)$ dependences and on magnetoresistance were studied for the FeBr$_4^-$ and GaBr$_4^-$ salts [30]. The insulating state of the GaBr$_4^-$ salt is gradually suppressed by pressure, and at 2.0 GPa this salt becomes metallic in the whole temperature range (figure 19(a)). For the FeBr$_4^-$ salt, the insulating state is also gradually suppressed with increasing pressure, and metallic behavior is observed down to 7 K (figure 19(b)). However, even at 2.5 GPa, the insulating state is still retained below 7 K, where the π–d interaction becomes significant. When the applied pressure exceeds 2.5 GPa, the insulating states in both salts are stabilized and the phase transition temperatures increases with pressure. There is almost no change in the magnetoresistance at 4.2 K upon applying a pressure of up to 2.0–2.5 GPa, at which the GaBr$_4^-$ salt exhibits a metallic state, while a slightly insulating state is preserved for the FeBr$_4^-$ salt.
3. Bent donor molecules containing an ethylenedioxy group: two-dimensional π-electron system with strong π–d interaction

The electronic structures of the salts described in chapter 2 are intrinsically one-dimensional that necessarily results in the instability of their metallic state. To realize stable metallic salts involving strong π–d interaction, further chemical modification of the donor molecule is carried out. It has been demonstrated that the TTF derivative containing a bi (ethylenedioxy) group BO has a strong tendency to provide two-dimensional stable metals due to a unique feature of the ethylenedioxy group, which has the ability to form hydrogen bonds (CH•••O) [10]. In this chapter, we focus on the structures and properties of cation radical salts based on bent donor molecules containing an ethylenedioxy group.

3.1. \( \text{(EDO-TTFVO)}_2 \cdot \text{FeCl}_4 \)

EDT-TTFVO is slightly modified by replacing the ethylenedithio group with an ethylenedioxy group, resulting in EDO-TTFVO. The 2:1 salt of EDO-TTFVO with the FeCl\(_4\) ion, \( \text{(EDO-TTFVO)}_2 \cdot \text{FeCl}_4 \), was obtained by electrocrystallization as a black needle-like crystals [31]. Two crystallographically independent donor molecules (A and B) are involved in the crystal, and they are located on the mirror plane, indicating the complete planarity of their molecular structures (figure 20(a)). The donor molecules form an A–B–A–B-type lateral array along the c-axis with several short S•••S(O) contacts, suggesting a strong intermolecular interaction along this direction. In the b-c plane, the donor molecules form two identical diagonal stacks of the form A–A’–B–B’ along the [0 2 1] and [0 2 −1] directions. This donor array resembles the \( \beta '' \)-type packing [32] typical for BO salts. There is a relatively short hydrogen bond (CH•••O, 2.87 Å) between the ethylenedioxy groups along the p1 direction, which might explain this characteristic for BO salts packing. The FeCl\(_4^–\) ions form a two-dimensional rectangular arrangement in the b-c plane with a short Cl•••Cl contact (3.48 Å) along the b-axis. In addition, there is a short Cl•••S contact (3.60 Å) between the 1,3-dithiole ring of the donor molecule and the Cl atom of the FeCl\(_4^–\) ion, suggesting the possibility of a strong π–d interaction by virtue of the characteristic bent donor molecular structure of EDO-TTFVO.

There are two types of overlap integrals (\( b_1 = 7.0 \times 10^{-3} \) and \( b_2 = 10.4 \times 10^{-3} \)) along the lateral direction, and three types of overlap integrals (\( p_1(A-B) = 10.9 \times 10^{-3} \), \( p_2(A-A') = 4.3 \times 10^{-3} \) and \( p_3(B-B') = 3.5 \times 10^{-3} \)) along the diagonal stacking direction (figure 20(b)). The magnitudes of the overlap integrals along the lateral and diagonal directions are comparable to each other, suggesting a two-dimensional interaction in the conducting b-c plane. As a result, the calculated Fermi surface shows a two-dimensional feature and closes along line Y–M but opens along line Z–M, giving rise to one closed ellipse around point Z and two open Fermi surfaces along line M–Y–M (figure 20(c)).

The conductivities parallel and perpendicular to the conducting b-c plane are 8.4 and 0.02 S cm\(^{-1}\) at room temperature, respectively. The temperature dependences of both \( \rho (T \parallel b-c \text{ plane}) \) and \( \rho (T \perp b-c \text{ plane}) \) are understood as stable and metallic down to 0.3 K. This salt is the first stable metal among the cation radical salts based on bent donor molecules. The stabilization of the metallic state originates from the formation of a two-dimensional electronic structure by introducing an ethylenedioxy group.

Susceptibility \( \chi_p \) was measured under an applied field of 1 kOe using the polycrystalline sample in the temperature range 1.9–300 K. The temperature dependence of \( \chi_p \) above 15 K can be well fitted with the Curie–Weiss law with \( C = 4.45 \text{ emu K mol}^{-1} \) and \( \Theta = -9.8 \text{ K} \), suggesting a relatively strong preferential antiferromagnetic interaction between the d spins of FeCl\(_4^–\) ions. Susceptibility \( \chi_p \) was also measured on a single crystal in the temperature range 1.9–20 K along the a-, b- and c-axes. As shown in figure 21, a sudden decrease in \( \chi_p \) is observed below ~3 K when a field is applied along the a-axis. This indicates an antiferromagnetic ordering at \( T_N \approx 3 \text{ K} \) with the spin-easy axis parallel to the a-axis. The \( M \) curve measured at 1.9 K showed a spin-flop at approximately 12 kOe when a field was applied along the a-axis and a very slow increase in \( M \) compared with that of the Brillouin function with \( g = 2.0 \), \( S = 5/2 \) and \( T = 1.9 \text{ K} \). Because the metallic state is maintained even at the antiferromagnetic

![Figure 19](image-url)
ordering, this salt is a new antiferromagnetic molecular metal at ambient pressure.

Figure 22(a) shows the magnetoresistance for magnetic fields of up to 140 kOe at different temperatures between 0.30 and 11.0 K, where the field is applied along the $a$-axis [33]. At 11.0 K, the magnetoresistance increases as $H^2$, which is simply explained in terms of the orbital effect due to the Lorenz force. However, a dip anomaly in magnetoresistance appears at $T_N$ and 60 kOe. The anomaly becomes more prominent and shifts to a higher $H$ with decreasing $T$. At 0.30 K, the dip structure is observed near 80 kOe. In addition, no hysteresis is observed between increasing and decreasing $H$ sweeps, indicating that this phase transition is of second order. The $T_N$ of the FeCl$_4^-$ salt is determined as 3 K from the $\chi_p(T)$ measurements; thus this anomaly in the magnetoresistance near 80 kOe is likely caused by the transition from the antiferromagnetic to the paramagnetic state. For $H$ up to 80 kOe, the field dependence of the magnetoresistance curve gradually changes from concave to convex on cooling. As shown in figure 22(b) for the magnetoresistance plotted versus $H^2$, a large downward deviation from $H^2$ dependence is observed below $T_N$ in the high-field region. Because the alignment of d spins in the FeCl$_4^-$ ions is enhanced with increasing $H$ and the $\pi$–d interaction becomes important below $T_N$, this deviation can be attributed to the suppression of the spin-scattering effect by d spins in the FeCl$_4^-$ ions under the external field.
Figure 22. (a) Magnetic field dependences of resistivity $\rho(H)$ of (EDO-TTFVO)$_2$•FeCl$_4$ in the range of 0–140 kOe at different temperatures and (b) magnetoresistance data in the form of $H^2$ plots in the $H$ range 0–70 kOe. (Reproduced with permission from [31].)

Figure 23. (a) Magnetic field dependences of magnetoresistance for different angles $\theta = 0–90^\circ$ at $T = 0.50$ K and (b) fast Fourier transform (FFT) of Shubnikov–de Haas oscillations for different angles at $T = 0.5$ K for (EDO-TTFVO)$_2$•FeCl$_4$.

3.2. (EDO-TTFVODS)$_2$•FeBr$_4$•(DCE)$_{0.5}$

Another new bent donor molecule EDO-TTFVODS was synthesized, in which the 1,3-dithiole ring in EDO-TTFVO was replaced by a 1,3-diselenole ring, resulting in a stronger $\pi$–d interaction. A single crystal of (EDO-TTFVODS)$_2$•FeBr$_4$•(DCE)$_{0.5}$ was obtained by electrocrystallization in 1,2-dichloroethane (DCE) [34]. The crystal structure is shown in figure 24(a); it is very similar to that of (EDO-TTFVO)$_2$•FeCl$_4$ except for the difference in the anion layer. Each donor layer also has a two-dimensional $\beta''$-type stacking. In the lateral and diagonal 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 intermolecular direction, whereas the intramolecular direction has a regular arrangement of FeBr$_4^-$ ions. Hence the Br•••Br contacts for each pair of FeBr$_4^-$ ions have comparatively short distances of 4.03 and 4.19 Å, whereas the distance is large (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 24. (a) Crystal structure of (EDO-TTFVODS)$_2$·FeBr$_4$·(DCE)$_{0.5}$ projected onto the $bc$-plane, (b) packing pattern of donor molecules with the intermolecular overlap integrals schematically shown, and (c) calculated Fermi surface of donor layers based on the crystal structure at room temperature.

As shown in figure 24(b), there are comparable lateral ($b_1 = -10.6 \times 10^{-3}$ and $b_2 = -5.15 \times 10^{-3}$) and diagonal ($p_1 = -11.1 \times 10^{-3}$, $p_2 = -3.28 \times 10^{-3}$, $p_3 = -2.63 \times 10^{-3}$, $q_1 = -9.79 \times 10^{-3}$, $q_2 = -2.41 \times 10^{-3}$ and $q_3 = -3.36 \times 10^{-3}$) overlap integrals, indicating a two-dimensional interaction between the donor molecules in the conducting $ab$-plane. The Fermi surface obtained by the band structure calculation using the above overlap integrals is also two-dimensional but opens along the $k_b$ and $k_c$ directions because of the low symmetry of the space group $P\bar{1}$ (figure 24(c)). As a result, a rectangular electron pocket surrounds point C, while two different elliptic hole pockets surround points X and Y.

The $\rho$ values of the single crystal in the $ab$-plane ($\rho_{ab}$) and in the $c^*$-direction, perpendicular to the $ab$-plane ($\rho_{c^*}$), are $\sim 0.1$ and $20 \Omega\text{cm}$ at 300 K, respectively. The temperature dependence of $\rho_{ab}$ shows that metallic behavior persists down to 0.45 K in spite of a slight upturn in $\rho_{ab}$ below 5 K. A similar trend is also observed in the $\rho_{c^*}(T)$ dependence. The slight increase in $\rho_{ab}$ and $\rho_{c^*}$ as $T$ decreases below 5 K is most likely caused by the $\pi$–$d$ interaction.

Magnetic susceptibility was measured for both polycrystalline and single-crystal samples of the FeBr$_4^*$ salt in the temperature range 1.9–300 K. The temperature dependence of $\chi_p$ obeys the Curie–Weiss law with $C = 4.48$ emu K mol$^{-1}$ and $\Theta = -18.7$ K above 20 K. However, below 20 K the values of $\chi_p$ become smaller than those predicted by the above Curie–Weiss curve, and a peak appears near 4.5 K suggesting antiferromagnetic ordering. Measurement of $\chi_p$ using the single crystal confirms the value of $T_N$ and the easy axis of the magnetization. Figure 25 shows $\chi_p(T)$ dependences below 15 K when a field of 5 kOe is applied along the $a$-, $b$-, and $c^*$-axes. A distinct decrease in $\chi_p$ is observed near 4 K only along the $c^*$-axis; therefore, $T_N$ is assigned to $\sim 4$ K and the easy axis to the $c^*$-axis. More accurate value $T_N = 4.5$ K was determined from heat capacity measurements.

Figure 26 shows magnetoresistance $\rho_{ab}$ at 0.45 K in fields up to 140 kOe applied perpendicular to the conducting $ab$-plane. The magnetoresistance decreases with $H$ up to 20 kOe, while above 20 kOe magnetoresistance increases with $H$. The minimum value of magnetoresistance is very small (1–2%) and a negative magnetoresistance persists until 70 kOe. Above 70 kOe the magnetoresistance becomes positive and increases up to 260 kOe. Near 160 kOe there is a kink, which appears to be due to the spin-flop, but no Shubnikov–de Haas oscillation is observed until 260 kOe in contrast to the case of (EDO-TTFVODS)$_2$·FeCl$_4$, where the spin-flop occurs at 80 kOe and 0.5 K and the Shubnikov–de Haas oscillation appears at 180 kOe. This probably originates from the much stronger d–d and $\pi$–d interactions for this salt than for (EDO-TTFVODS)$_2$·FeCl$_4$. If the crystal quality is good, the Shubnikov–de Haas oscillation might be observed at fields higher than 260 kOe.
4. Magnitudes of $\pi$–d and d–d interactions in magnetic molecular conductors based on the bent donor molecules

In this chapter, the overall $\pi$–d and d–d interactions as well as their effects on $T_N$ and magnetoresistance in the above five cation radical salts are discussed. The values of $T_N$ are determined by both the magnitudes of direct and indirect interactions between the localized d spins, $J_{dd}$, and those between the conducting $\pi$ electrons and the localized d spins, $J_{\pi d}$. On the other hand, the magnitude of negative magnetoresistance represents the strength of the $\pi$–d interaction. Mori and coworkers developed a method of estimating $J_{dd}$, $J_{\pi d}$, and $T_N$ for $S = 5/2$ spins from an extended Hückel molecular orbital calculation \[35, 36\]. According to this method, $J_{dd}$, $J_{\pi d}$, and $T_N$ are given by

$$J_{dd} = -\frac{2}{25U_{dd}} \sum_{i=1}^{25} t_{i,dd}^2,$$

$$J_{\pi d} = -\frac{2}{5\Delta_{\pi d}} \sum_{i=1}^{5} t_{i,\pi d}^2,$$

$$k_B T_N = \frac{35}{6} J_{dd} + \frac{35}{6} \frac{\chi_d}{\Delta_{\pi d}} - (J_{\pi d})^2.$$

Here $U_{dd}$ is the on-site Coulomb interaction of the donor HOMO, $\Delta_{\pi d}$ is the energy difference between the donor HOMO and the Fe$_X$$^\pi$ d orbitals, $t_{i,dd}$ and $t_{i,\pi d}$ are the transfer integrals between the Fe$_X$$^\pi$ d orbitals and between the donor HOMO and the Fe$_X$$^\pi$ d orbitals, respectively, $k_B$ is the Boltzmann constant, $\chi_d$ is the staggered susceptibility, and $C_\pi$ is the Curie constant due to the $\pi$ spins ($2C_\pi/\chi_d = 500$ K is used in the present calculation).

Using this method, $J_{dd}$, $J_{\pi d}$, and $T_N$ are calculated for the five Fe$_X$ salts together with the other antiferromagnetic molecular metals of $\kappa$-(BETS)$_2$ • FeCl$_4$, $\kappa$-(BETS)$_2$ • FeBr$_4$, and $\lambda$-(BETS)$_2$ • FeCl$_4$ which exhibit the strongest $\pi$–d interactions reported so far. Figure 27 shows a summary of $J_{dd}$ and $J_{\pi d}$ for these eight Fe$X_4$ salts. Among them, the $J_{dd}$ (17.7 K) of $\lambda$-(BETS)$_2$ • FeCl$_4$ is largest, while (EDT-DSDTFVSDS)$_2$ • FeBr$_4$ and (EDO-TTFVODS)$_2$ • FeBr$_4$ (DCE)$_{0.5}$ also have comparable large values of $J_{\pi d}$ (15.6 and 15.4 K, respectively). Remarkably, the $J_{dd} = 0.20$ K of (EDT-DSDTFVSDS)$_2$ • FeBr$_4$ is considerably smaller than that (0.64 K) of $\lambda$-(BETS)$_2$ • FeCl$_4$, whereas (EDO-TTFVODS)$_2$ • FeBr$_4$ (DCE)$_{0.5}$ has a relatively large $J_{dd} = 1.86$ K. Judging from these values of $J_{dd}$ and $J_{\pi d}$ for the three salts, (EDT-DSDTFVSDS)$_2$ • FeBr$_4$ is considered as a superior $\pi$–d system to $\lambda$-(BETS)$_2$ • FeCl$_4$ because of its large $J_{dd}$ and small $J_{\pi d}$, while (EDO-TTFVODS)$_2$ • FeBr$_4$ (DCE)$_{0.5}$ is considered as a novel $\pi$–d system with both large $J_{dd}$ and large $J_{\pi d}$. On the other hand, $J_{dd}$ is moderate for (EDT-TTFVODS)$_2$ • FeBr$_4$ (7.26 K), (EDT-DSDTFVODS)$_2$ • FeBr$_4$ (7.58 K), and $\kappa$-(BETS)$_2$ • FeBr$_4$ (7.93 K), and among them (EDT-TTFVODS)$_2$ • FeBr$_4$ has a relatively large $J_{dd}$ (1.82 K). The FeCl$_4^-$ salts, (EDO-TTFVODS)$_2$ • FeCl$_4$ and $\kappa$-(BETS)$_2$ • FeCl$_4$, have small values of $J_{\pi d}$ (2.91 and 3.12 K), but a comparatively large $J_{dd}$ is observed for (EDO-TTFVODS)$_2$ • FeCl$_4$ (1.17 K). With the exception of (EDT-DSDTFVODS)$_2$ • FeBr$_4$, which exhibits no antiferromagnetic ordering down to 1.9 K, the observed antiferromagnetic ordering temperatures ($T_N$) of the other salts are 4.5 K for (EDO-TTFVODS)$_2$ • FeBr$_4$ (DCE)$_{0.5}$, 3.3 K for (EDT-DSDTFVODS)$_2$ • FeBr$_4$, 3.0 K for (EDO-TTFVODS)$_2$ • FeCl$_4$, 2.5 K for $\kappa$-(BETS)$_2$ • FeBr$_4$, 0.86 K for (EDT-TTFVODS)$_2$ • FeBr$_4$, and 0.45 K for $\kappa$-(BETS)$_2$ • FeCl$_4$. $T_N$ for $\lambda$-(BETS)$_2$ • FeCl$_4$ is rather high (8.5 K), while a metal-to-insulator transition is also observed at the same temperature. According to equation (11), $T_N$ is determined by the sum of $J_{dd}$ and $J_{\pi d}$. Therefore, the high $T_N$ for (EDO-TTFVODS)$_2$ • FeBr$_4$ (DCE)$_{0.5}$ is due to both the large $J_{\pi d}$ and large $J_{dd}$. The comparatively high $T_N$ for (EDO-TTFVODS)$_2$ • FeCl$_4$ originates from the large $J_{dd}$, while $J_{\pi d}$ predominantly contributes to the

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Figure 27. $J_{dd}$ and $J_{ad}$ values of ferrimagnetic or antiferromagnetic molecular semiconductors or metals calculated by the extended Hückel molecular orbital method.

high $T_N$ for (EDT-DSDTFVSODS)$_2$•FeBr$_4$. The moderate $J_{dd}$ and large $J_{ad}$ afford a higher $T_N$ than 0.86 K for (EDT−TTFVO)$_2$•FeBr$_4$, but the unexpectedly low $T_N$ might be due to the antiferromagnetic ordering of the Fe(III) d spins through the antiferromagnetic interaction with the conducting π electrons.

The negative magnetoresistance is caused by the π–d interaction in the FeX$_4$ salts, and its magnitude is dependent on $J_{ad}$. In fact, remarkably large negative magnetoresistances are observed in (EDO-TTFVO)$_2$•FeBr$_4$•(DCE)$_{0.5}$ and particularly in (EDT-DSDTFVSODS)$_2$•FeBr$_4$, both of which have a large $J_{ad}$.

5. Summary

The crystal structures and properties of cation radical salts based on bent donor molecules with FeX$_4$ (X = Cl, Br) anions are reviewed. All salts exhibit comparatively high electrical conductivity at room temperature and have quarter-filled band structures. Among them, the cation radical salts of the bent donor molecules containing an ethylenedioxy group, EDO-TTFVO and EDO-TTFVODS, afford two-dimensional electronic structures, and stable metallic behavior is maintained down to low temperatures. On the other hand, the cation radical salts of the bent donor molecules containing an ethylenedioxithio group, EDT-TTFVO, EDT-DSTTFVO, and EDT-DSTTFVSODS, afford intrinsically one-dimensional band structures, which result in the instability of the metallic state at low temperatures. The resistivity increase with decreasing temperature is more rapid for (EDT-DSTTFVSODS)$_2$•FeBr$_4$ than for the corresponding GaBr$_4$ salt owing to the magnetic π–d interaction, which stabilizes the insulating state.

The Fe(III) ($S = 5/2$) d spins of FeX$_4$ ions are ordered through both direct d–d and indirect π–d interactions, but the ordered states are still two-dimensional as proved by the measurements of $M$ and $C_P$. All salts exhibit antiferromagnetic ordering (the ordering is also achieved at temperatures lower than 1.9 K for (EDT-DSDTFVSODS)$_2$•FeBr$_4$ except for (EDT-TTFVO)$_2$•FeBr$_4$, which exhibits a ferromagnetic ordering near 1 K. For the salts exhibiting antiferromagnetic ordering, the d↑–π(↓)–d↓–π↑ interaction predominantly works together with the antiferromagnetic d–d interaction. In contrast, for (EDT-TTFVO)$_2$•FeBr$_4$, the d(↑)–π(↓)–d(↑) interaction is preferential to the antiferromagnetic d–d interaction, which results in the ferromagnetic ordering of the d spins, while the overall spin system is ferrimagnetic. By virtue of the π–d or d–π–d interaction, the electric dipoles on the donor molecule layers exhibit a dielectric slowing-down phenomenon toward this ferrimagnetic state. The mechanism of this anomalous dielectric phenomenon needs further investigation.

The magnetic exchange interactions, $J_{dd}$ and $J_{ad}$, are obtained by molecular orbital calculations. The $J_{dd}$ values of (EDT-DSDTFVSODS)$_2$•FeBr$_4$ and (EDO-TTFVODS)$_2$•FeBr$_4$•(DCE)$_{0.5}$ are large and comparable to that of $\lambda$-(BETS)$_2$•FeCl$_4$. The $J_{ad}$ of (EDT-DSDTFVSODS)$_2$•FeBr$_4$ is smaller, while the $J_{dd}$ of (EDO-TTFVODS)$_2$•FeBr$_4$•(DCE)$_{0.5}$ is larger than that of $\lambda$-(BETS)$_2$•FeCl$_4$. Corresponding to the strong π–d interaction, (EDT-DSDTFVSODS)$_2$•FeBr$_4$ exhibits a large negative magnetoresistance of 85% at $H = 149$ kOe and $T = 0.7$ K. The relatively high magnetic ordering temperatures are mainly determined by both $J_{dd}$ and $J_{ad}$ for (EDO-TTFVODS)$_2$•FeBr$_4$•(DCE)$_{0.5}$, by $J_{dd}$ for (EDT-DSDTFVSODS)$_2$•FeBr$_4$, and by $J_{ad}$ for (EDO-TTFVODS)$_2$•FeCl$_4$.

In inorganic ferromagnetic metals with a significantly larger $t$ than $U$, the electron transport is not affected even by the strong interaction between the conduction s/p electrons and the localized d electrons/spins. In contrast, in molecular conductors, $t$ is usually smaller than $U$. Accordingly, molecular π–d systems exhibit a variety of types of electron transport resulting from the π–d interactions. In $\lambda$-(BETS)$_2$•FeCl$_4$ the metallic conductivity is destroyed by the strong π–d interaction and is abruptly converted to the insulating state. Also, in (EDT-DSDTFVSODS)$_2$•FeBr$_4$, the insulating state generated in the low-temperature range is stabilized by the strong π–d interaction, whereas in (EDO-TTFVODS)$_2$•FeBr$_4$•(DCE)$_{0.5}$ the strong π–d interaction has no effect on the metallic state. In view of these results, the π–d interactions can provide a variety of types of electron conduction and magnetism depending on the difference in magnitudes between $t$ and $U$ and the π–d interaction. Accordingly, it should be possible to realize an unprecedented ferromagnetic molecular metal with a strong π–d interaction, one of the targets of this study.

Acknowledgments

We are deeply grateful to collaborators, whose names appear in the papers cited in this review, for their valuable cooperation and discussion.
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