

# 1:1 Composition Organic Metal Including a Magnetic Counteranion, (TTM–TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>

Mao Katsuhara,<sup>†</sup> Masanobu Aragaki,<sup>†</sup> Takehiko Mori,<sup>\*,†</sup> Yohji Misaki,<sup>‡</sup> and Kazuyoshi Tanaka<sup>‡</sup>

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8552, Japan, and Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-8501, Japan

Received May 17, 2000. Revised Manuscript Received August 17, 2000

An organic donor, TTM–TTP (TTM–TTP = 2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene), forms 1:1 donor/anion salts with FeCl<sub>4</sub><sup>−</sup> and FeBr<sub>4</sub><sup>−</sup>, (TTM–TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub> (X = Cl, Br), which have one-dimensional dimerized columns and are insulators even at room temperature. In contrast, the salt with an alloyed anion, (TTM–TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>, shows high electrical conductivity of about 1000 S cm<sup>−1</sup> at room temperature and remains metallic down to 160 K. This salt has uniform, one-dimensional, donor columns. This is the first 1:1 donor/anion composition organic metal with a magnetic counteranion. These compounds exhibit weak magnetic interactions; the Weiss temperatures are around 1–3 K.

## Introduction

It has been widely believed that organic conductors with a 1:1 composition of donors and anions should be insulators because the Coulomb interaction in these conductors is of essential importance in localizing the conduction electrons. Nevertheless, recently a few exceptions to this general rule have been reported. The first metallic organic conductor with a 1:1 donor/anion composition, (TTM–TTP)I<sub>3</sub> (TTM–TTP = 2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene),<sup>1</sup> together with the subsequently found (DMTSA)BF<sub>4</sub> (DMTSA = 2,3-dimethyltetraselenoanthracene)<sup>2</sup> shows metallic conduction down to about 160 K. It has also been found that (TTM–TTP)[C(CN)<sub>3</sub>] retains metallic behavior down to as low as 70 K.<sup>3</sup> These materials have one-dimensional uniform donor columns. In addition, 1:1 organic conductors with dimerized columns such as (TTM–TTP)AuI<sub>2</sub> and (TTM–TTP)AuBr<sub>2</sub> have been reported to be moderately conductive ( $\sigma_{\text{rt}} \sim 10 \text{ S cm}^{-1}$ ), but the temperature dependence of the conductivity is semiconductive even at room temperature.<sup>4</sup>

On the other hand, organic conductors with inorganic magnetic counteranions have attracted a great deal of attention because of their intriguing physical proper-

ties.<sup>5–7</sup>  $\lambda$ -(BETS)<sub>2</sub>FeCl<sub>4</sub> (BETS = bis(ethylenedithio)-tetraselenafulvalene) undergoes a metal–insulator transition at 8 K accompanied by the antiferromagnetic ordering of the Fe spins, but this transition is suppressed by applying a magnetic field of 11 T; this high-field phase is called a field-restored highly conducting state (FRHCS).<sup>6</sup> When the magnetic field changes the antiferromagnetic alignment of the Fe spins to a ferromagnetic alignment, the spin-density-wave (SDW) states on BETS induced by the antiferromagnetic order of the Fe spins are destroyed, restoring metallic conductivity in the BETS sheets. Furthermore,  $\kappa$ -(BETS)<sub>2</sub>FeBr<sub>4</sub> shows an anomalous resistivity anomaly at around 2.5 K, originating in the antiferromagnetic transition of the Fe spins, whereas a superconducting transition is observed at about 1.0 K.<sup>7</sup> In this case the antiferromagnetic ordering of the Fe spins does not destroy the metallic conduction, and the magnetic order coexists with the superconductivity.

From this viewpoint, new interesting properties are expected if an inorganic magnetic anion is introduced to organic conductors with a 1:1 composition. We have therefore attempted to prepare 1:1 composition organic conductors containing magnetic anions. In this report we discuss the structures and physical properties of 1:1 composition organic conductors containing iron halides: (TTM–TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub> (X = Cl, Br; PhCl = chlorobenzene) and a mixed anion salt (TTM–TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>. The salts with pure anions, (TTM–TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub>, have dimerized structures, which lead to half-filled band insulators. Interestingly, when we used a mixed electrolyte of FeCl<sub>4</sub><sup>−</sup> and FeBr<sub>4</sub><sup>−</sup>,

\* To whom correspondence should be addressed.

<sup>†</sup> Tokyo Institute of Technology.

<sup>‡</sup> Kyoto University.

(1) Mori, T.; Inokuchi, H.; Misaki, Y.; Yamabe, T.; Mori, H.; Tanaka, S. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 661–667.

(2) Takimiya, K.; Ohnishi, A.; Aso, Y.; Otsubo, T.; Ogura, F.; Kawabata, K.; Tanaka, K.; Mizutani, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 766–772.

(3) Mori, T.; Kawamoto, T.; Iida, K.; Yamaura, J.; Enoki, T.; Misaki, Y.; Yamabe, T.; Mori, H.; Tanaka, S. *Synth. Met.* **1999**, *103*, 1885–1886.

(4) Kawamoto, T.; Aragaki, M.; Mori, T.; Misaki, Y.; Yamabe, T. *J. Mater. Chem.* **1998**, *8*, 285–288.

(5) Day, P.; Kurmoo, M. *J. Mater. Chem.* **1987**, *8*, 1291–1295.

(6) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368–377.

(7) Ojima, E.; Fujiwara, H.; Kato, K.; Kobayashi, H. *J. Am. Chem. Soc.* **1999**, *121*, 5581–5582.

**Table 1. Crystallographic Data of (TTM-TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub> and (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>**

	(TTM-TTP) FeCl <sub>4</sub> (PhCl) <sub>0.5</sub>	(TTM-TTP)FeBr <sub>4</sub> (PhCl) <sub>0.5</sub>	(TTM-TTP)FeBr <sub>1.8</sub> Cl <sub>2.2</sub>
chemical formula	C <sub>17</sub> H <sub>14.5</sub> S <sub>12</sub> FeCl <sub>4.5</sub>	C <sub>17</sub> H <sub>14.5</sub> S <sub>12</sub> FeBr <sub>4</sub> Cl <sub>0.5</sub>	C <sub>14</sub> H <sub>12</sub> S <sub>12</sub> FeBr <sub>1.8</sub> Cl <sub>2.2</sub>
formula weight	818.91	996.71	842.64
shape	black needle	black needle	black block
crystal system	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C2/c</i>
<i>a</i> /Å	13.76(2)	14.29(2)	23.975(5)
<i>b</i> /Å	14.21(2)	14.47(2)	5.874(1)
<i>c</i> /Å	8.62(2)	8.522(5)	22.772(4)
$\alpha$ /deg	106.8(2)	105.21(4)	90
$\beta$ /deg	95.0(1)	93.33(8)	118.24(1)
$\gamma$ /deg	78.65(9)	75.7(1)	90
<i>V</i> /Å <sup>3</sup>	1581(4)	1647(3)	2825(1)
<i>Z</i>	2	2	4
temperature/K	293	253	293
$\lambda$ /Å	0.7107	0.7107	0.7107
reflections used	317/1399	316/2396	143/2207
<i>R</i> / <i>R</i> <sub>w</sub> <sup>a</sup>	0.185/0.208	0.090/0.120	0.034/0.034

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}; w = 1/\sigma^2.$$

we obtained a different phase, (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>, which has uniform donor columns showing a high electric conductivity of 1000 S cm<sup>-1</sup> at room temperature and exhibiting metallic conductivity down to about 160 K.

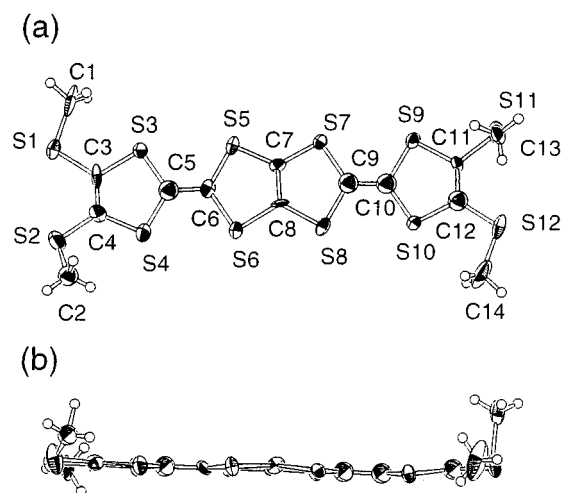
### Experimental Section

**Preparation.** TTM-TTP was prepared as described in ref 8. Crystals were grown by electrochemical oxidation in chlorobenzene in the presence of the donor and the tetrabutylammonium salts of the corresponding anions under a constant current of 0.5  $\mu$ A at 26 °C using H-shaped cells with Pt electrodes. In the presence of pure FeCl<sub>4</sub><sup>-</sup> or FeBr<sub>4</sub><sup>-</sup>, single crystals of the form of black needles were obtained. When FeCl<sub>4</sub><sup>-</sup> and FeBr<sub>4</sub><sup>-</sup> were mixed in chlorobenzene, we obtained large single crystals that were obviously different from the former two in shape; these crystals were in the shape of black blocks or plates with metallic luster.

**Structure Determination.** The crystal structures of the three compounds were determined from single-crystal X-ray diffraction. Intensity data of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> were measured by the  $\omega$  scan technique on a Rigaku automated four-circle diffractometer AFC-7R with graphite monochromatized Mo K $\alpha$  radiation ( $2\theta < 60^\circ$ ). In the case of (TTM-TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub>, measurements were made on a Rigaku Raxis II area detector with graphite monochromatized Mo K $\alpha$  radiation. The structures were solved by the direct method (SHELX86 for (TTM-TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub> and SIR97 for (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>).<sup>9,10</sup> The structures were refined by the full-matrix least-squares procedure by applying anisotropic temperature factors for all non-hydrogen atoms.

**Electronic Band Structure.** The overlap integrals of the highest occupied molecular orbital (HOMO) of TTM-TTP were estimated on the basis of the extended Hückel method.<sup>11</sup> The electronic band structures were calculated in the tight-binding approximation.

**Transport Properties.** Electric resistivity was measured for single crystals by the four-probe method using a low-frequency ac current (usually 10  $\mu$ A). Electrical contacts to the crystals were made with 15- $\mu$ m gold wire and gold paint. The crystals were held in a cryostat, and the temperature was



**Figure 1.** (a) ORTEP drawing and atomic numbering scheme of the donor molecule of (TTM-TTP)FeBr<sub>4</sub>(PhCl)<sub>0.5</sub> and (b) the side view.

monitored by a Cu-Constantan thermocouple and a carbon resistor sensor for above and below about 50 K, respectively. Thermoelectric power measurements were carried out by making two-probe electrical contacts attached to two heat sinks with gold foil and gold paint. All measurements of transport properties are performed along the donor columns.

**Magnetic Susceptibility.** Measurements were performed using a Quantum Design SQUID magnetometer MPMS-7. A single crystal was used for (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>, and a polycrystalline sample was used for (TTM-TTP)FeCl<sub>4</sub>(PhCl)<sub>0.5</sub> and (TTM-TTP)FeBr<sub>4</sub>(PhCl)<sub>0.5</sub>. Magnetization data were taken by changing the applied field at 2 K, and the temperature dependence was measured from 2 to 300 K under the applied field of 10 000 G. The Pascal diamagnetic contribution ( $-302.74 \times 10^{-6}$  emu/mol for TTM-TTP and  $-114.0$ ,  $-154.0$ , and  $-134.0 \times 10^{-6}$  emu/mol for FeCl<sub>4</sub><sup>-</sup>, FeBr<sub>4</sub><sup>-</sup>, and FeBr<sub>1.8</sub>Cl<sub>2.2</sub><sup>-</sup>) has been subtracted from the observed susceptibility.

### Results and Discussion

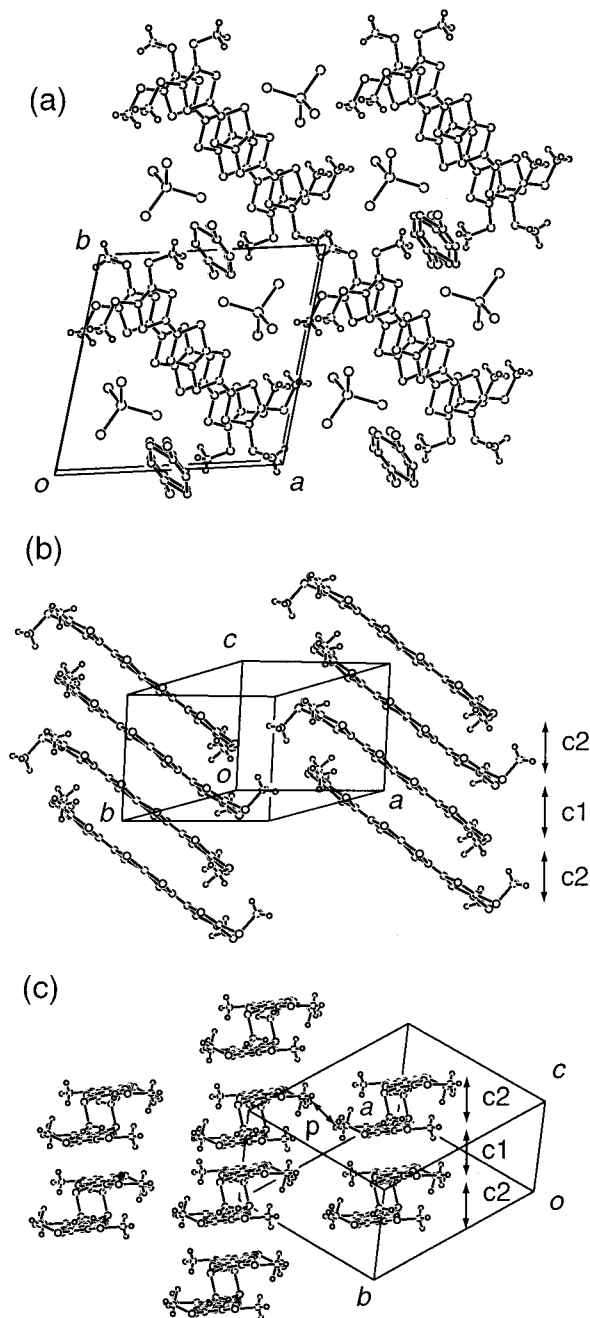
**Crystal Structures.** Crystallographic data for the three compounds are listed in Table 1 and the atomic numbering scheme is shown in Figure 1. The FeCl<sub>4</sub><sup>-</sup> and FeBr<sub>4</sub><sup>-</sup> salts are isostructural (Figure 2). The unit cell contains two TTM-TTP molecules, two FeX<sub>4</sub><sup>-</sup> molecules, and a PhCl molecule; the resulting composition is 1:1:0.5. The PhCl molecule is incorporated from the solvent used for the crystal growth. The donors are

(8) Misaki, Y.; Nishikawa, H.; Kawakami, K.; Koyanagi, S.; Yamabe, T.; Siro, M. *Chem. Lett.* **1992**, 2321. Mori, T.; Kawamoto, T.; Misaki, Y.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1998**, 71, 1321-1326. Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Synthesis* **1994**, 809. Binet, L.; Fabre, J. M.; Montginoul, C.; Simonsen, K. B.; Becher, J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 783.

(9) Sheldrick, G. M.; Kruger, C.; Goddard, R. *Crystallographic Computing 3*; Sheldrick, G. M., Ed.; Oxford University Press: Oxford, 1985; pp 175-189.

(10) Altomare, A.; Cascrano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, 26, 343.

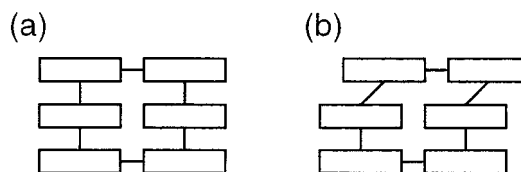
(11) Mori, T. *Bull. Chem. Soc. Jpn.* **1998**, 71, 2509-2526.



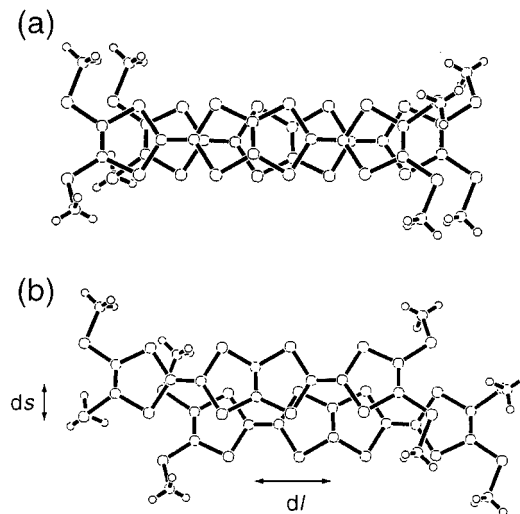
**Figure 2.** Crystal structure of  $(\text{TTM-TTP})\text{FeBr}_4(\text{PhCl})_{0.5}$ . (a) Projection along the  $c$  axis, (b) view along the molecular short axis, and (c) view along the molecular long axis.

located at general positions and construct a dimerized column along the  $c$  axis.

This structure is similar to  $(\text{TTM-TTP})\text{AuI}_2$  and  $(\text{TTM-TTP})\text{AuBr}_2$ .<sup>4</sup> The columns of the  $\text{AuI}_2$  and the  $\text{AuBr}_2$  salts are composed of the usual ring-over-bond overlaps of the donor molecules (Figure 3a). This corresponds to the  $\beta$ -type structure in the BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) salts.<sup>11</sup> Figure 4 shows the overlap modes of the present salts. Because the donor molecules dimerize along the stacking direction, there are two overlap modes,  $c1$  and  $c2$ . The interplanar spacing and the displacements of the donors are listed in Table 2. The columns of the present salts are made up of an alternating stack of ring-over-bond and "ring-over-atom" overlaps (namely, slid along the molecular short axis) (Figure 3b).<sup>11</sup> This is known as the  $\beta'$ -type



**Figure 3.** Schematic view of the (a)  $\beta$ - and (b)  $\beta'$ -type donor stacking (view along the molecular long axis).



**Figure 4.** Overlap modes of intrastack interactions in  $(\text{TTM-TTP})\text{FeBr}_4(\text{PhCl})_{0.5}$ .

**Table 2. Interplanar Spacing and the Displacement of the  $(\text{TTM-TTP})\text{FeX}_4(\text{PhCl})_{0.5}$  ( $c1$ , Intradimer;  $c2$ , Interdimer)**

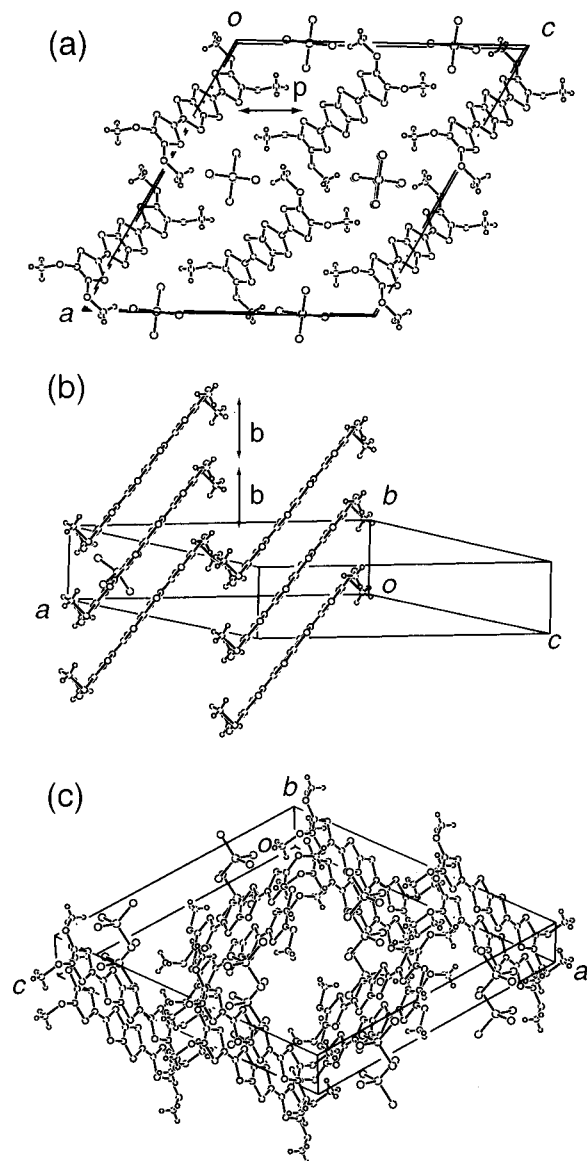
	$d/$	$ds$	interplanar spacing	$d/$	$ds$	interplanar spacing
	$(\text{TTM-TTP})\text{FeCl}_4(\text{PhCl})_{0.5}$			$(\text{TTM-TTP})\text{FeBr}_4(\text{PhCl})_{0.5}$		
$c1$	1.60	0.12	3.41	$c1$	1.58	0.10
$c2$	3.35	1.87	3.42 Å	$c2$	3.28	1.88
						3.42 Å

structure in the BEDT-TTF salts. There are short S-S contacts between the donors in the same column, but those of the neighboring columns are only between outer thiomethyl groups.

The  $\text{FeX}_4^-$  ions are located at general positions and have a tetrahedral shape. There are short contacts between the sulfur atoms of the donors and Cl or Br in the anions. The PhCl molecules are on inversion centers, so the position of Cl is disordered, and the Cl atom is refined with 50% occupancy. There is no vacancy in the PhCl molecule, while the shape of PhCl is distorted to some extent. The PhCl molecules enhance the volume of the "anion sheet", which stabilizes the dimerized structure of the donor columns. Because these anion and solvent molecules exist between the donor chains, there are practically no interactions between the donor chains. Hence, this system is regarded as highly one-dimensional.

The structure of  $(\text{TTM-TTP})\text{FeBr}_{1.8}\text{Cl}_{2.2}$  is entirely different from the pure salts (Figure 5). The donors are located at inversion centers and the  $\text{FeBr}_{1.8}\text{Cl}_{2.2}^-$  ions (alloyed ions) are located on 2-fold axes. The donors form a uniform stack along the  $b$  axis. This is isostructural to  $(\text{TTM-TTP})[\text{C}(\text{CN})_3]$  but the cell volume of the present compound is larger than that of  $(\text{TTM-TTP})[\text{C}(\text{CN})_3]$  ( $2592 \text{ \AA}^3$ ).<sup>3</sup> The interplanar spacing of the donors is 3.42



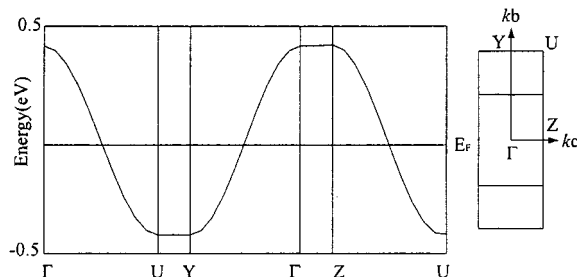


**Figure 5.** Crystal structure of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>. (a) Projection along the *b* axis, (b) structure of the columns, and (c) inclination of the donor molecules.

Å and the displacement along the molecular long axis is 4.77 Å. These values are the same as those in (TTM-TTP)I<sub>3</sub>,<sup>1</sup> and the structure of the donor column is practically the same. In (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>, however, the columns are tilted in two different directions. In Figure 5a, the donors at *z* = 0 are so inclined that the upper half of the molecule extends above the projection plane, but the donors at *z* = 1/2 are inclined inversely (Figure 5c). Because the alloyed anions are located on the 2-fold axes, two pairs of halogens are equivalent. From the population analysis, these two halogen sites are occupied by 19.8 and 71.6% of Br, resulting in the composition of FeBr<sub>1.8</sub>Cl<sub>2.2</sub><sup>-</sup>. On the other hand, the EDS analysis shows composition of FeBr<sub>1.6</sub>Cl<sub>2.4</sub><sup>-</sup>, and this is almost consistent with the result of the X-ray analysis. Thus, although these estimations are semiquantitative, the actual content of Cl may be slightly larger than that of Br. Because electrocrystallization starting from different nominal FeCl<sub>4</sub><sup>-</sup>/FeBr<sub>4</sub><sup>-</sup> ratios resulted in crystals with practically the same composition, determined from the EDS meas-

**Table 3.** Intermolecular Overlap Integrals, *S* ( $\times 10^{-3}$ ) of the HOMO in (TTM-TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub> and (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>

(TTM-TTP)- FeCl <sub>4</sub> (PhCl) <sub>0.5</sub>		(TTM-TTP)- FeBr <sub>4</sub> (PhCl) <sub>0.5</sub>		(TTM-TTP)- FeBr <sub>1.8</sub> Cl <sub>2.2</sub>	
c1	20.5	c1	20.3	b	-20.9
c2	-1.90	c2	-6.81	p1	0.12
p1	-0.11	p1	0.00	p2	0.01
				p3	0.13



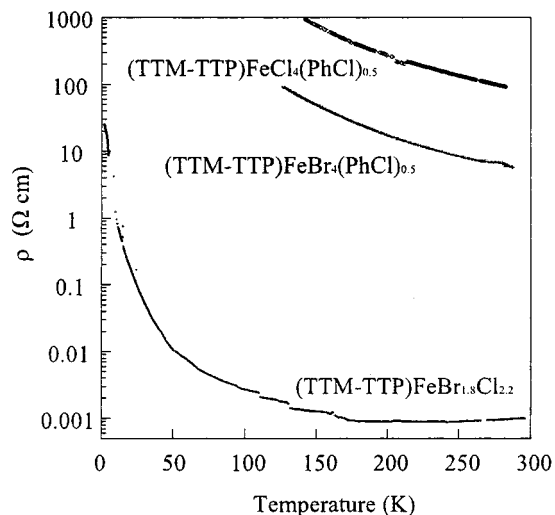
**Figure 6.** Tight-binding energy band structure and Fermi surface (right) of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>, calculated from the overlap of the HOMO obtained on the basis of the extended Hückel molecular orbital calculation.

urements and X-ray analysis, the phase with this definite composition is considered to be stable.

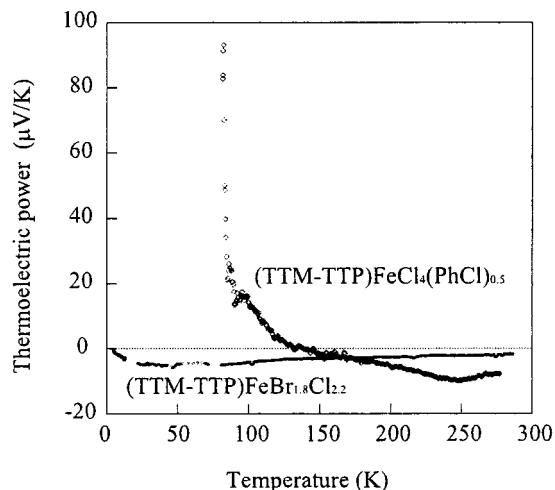
**Energy Band Calculation.** Calculated intermolecular overlap integrals for the HOMOs of the donor molecules are listed in Table 3. In the present compound, the intrastack overlaps are significantly larger than the interstack ones. The donor molecules cannot approach each other closely because of the steric hindrance of the terminal methyl groups and the nonconducting anion and solvent layers between the donor chains. Thus, the interchain interaction is very small. Consequently, the electronic structures of the present materials are regarded as highly one-dimensional.

In the case of the pure FeX<sub>4</sub><sup>-</sup> salts, because a unit cell contains two donor molecules, there are two energy bands, between which the Fermi energy is located as a result of the 1:1 composition. Accordingly, a Fermi surface does not exist. This band structure predicts that these salts are band insulators. The difference between *c*1 and *c*2 designates the degree of dimerization along the stack. The ratios of *c*1 and *c*2 are about 10:1 and 3:1 for the X = Cl and Br salts, and these ratios are larger than that of (TTM-TTP)AuI<sub>2</sub> and (TTM-TTP)AuBr<sub>2</sub> (about 3:2),<sup>4</sup> leading to stronger dimerization. This corresponds to the β'-type donor arrangement.

Figure 6 shows the calculated energy band structure and Fermi surface of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub>. In contrast to the above two compounds, the mixed anion salt has uniform donor columns. Despite the 1:1 composition, a one-dimensional Fermi surface exists. The ratio of the calculated intrastack (*b*) and interstack (*p*) overlap integrals is about 200:1, indicating a highly one-dimensional system. The value of the overlap integral along the stacking direction (about  $20 \times 10^{-3}$ ) and the resulting bandwidth (0.8 eV) are the same as those of (TTM-TTP)I<sub>3</sub> and (TTM-TTP)[C(CN)<sub>3</sub>].<sup>1,3</sup> Because the space group is *C2/c* and only one independent donor exists, the energy levels are degenerate, though four donor molecules are in the unit cell. The Fermi surface of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> is almost the same as that



**Figure 7.** Electric conductivity of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> and (TTM-TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub>.



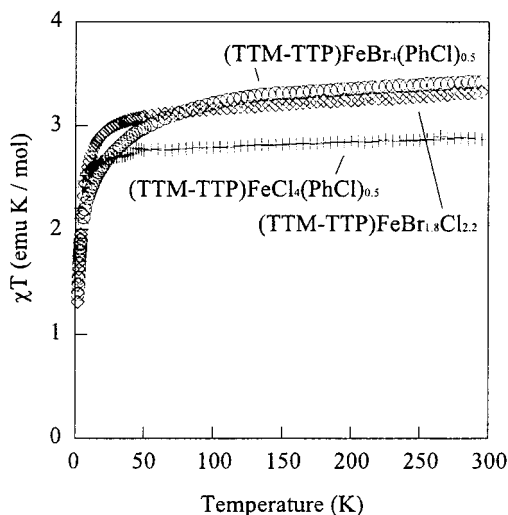
**Figure 8.** Thermoelectric power of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> and (TTM-TTP)FeCl<sub>4</sub>(PhCl)<sub>0.5</sub>.

of (TTM-TTP)I<sub>3</sub> and (TTM-TTP)[C(CN)<sub>3</sub>], indicating that this salt is considered a one-dimensional metal along the crystallographic *b*-axis.

**Transport Properties.** (TTM-TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub> shows a low conductivity of 0.01 and 0.17 S cm<sup>-1</sup> for X = Cl, Br, respectively. These low values are related to the β'-type structure with strong dimerization. These salts are insulators even at room temperature. The activation energies of the Cl and Br salts are estimated as 0.07 and 0.05 eV from the temperature dependence of the electric conductivity. These values are lower than the energy gap calculated from the band calculation (0.37 and 0.27 eV) and almost the same as the activation energies of (TTM-TTP)AuI<sub>2</sub> and (TTM-TTP)AuBr<sub>2</sub> (0.03 and 0.07 eV)<sup>4</sup> (Figure 7).

The thermoelectric power of (TTM-TTP)FeCl<sub>4</sub>(PhCl)<sub>0.5</sub> shows a small negative value at room temperature (-7.9 μV/K at room temperature). As the temperature is lowered, the thermopower diverges in the positive direction, crossing zero at about 140 K (Figure 8).

(TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> shows a very high conductivity, about 1000 S cm<sup>-1</sup> at room temperature. The resistivity is basically metallic down to about 160 K, below which the salt becomes an insulator (Figure 7).



**Figure 9.**  $\chi T$  plot of static magnetic susceptibility of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> and (TTM-TTP)FeX<sub>4</sub>(PhCl)<sub>0.5</sub>.

This behavior closely resembles that of (TTM-TTP)I<sub>3</sub> and (DMTSA)BF<sub>4</sub>.<sup>1,2</sup> Among these materials, (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> shows the highest electric conductivity at room temperature. The metal-insulator transition temperature is higher than that of (TTM-TTP)[C(CN)<sub>3</sub>] (70 K) and almost the same as that for (TTM-TTP)I<sub>3</sub> (Figure 7).<sup>1,3</sup>

The thermoelectric power of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> takes a negative finite value (-1.7 μV/K at room temperature) and is approximately constant from room temperature to about 50 K. This suggests that (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> has a half-filled band. Although the thermoelectric power of (TTM-TTP)I<sub>3</sub> and (DMTSA)BF<sub>4</sub> diverges to infinity at low temperatures,<sup>1,2</sup> that of (TTM-TTP)FeBr<sub>1.8</sub>Cl<sub>2.2</sub> takes a minimum value at around 50 K (about -6 μV/K) and turns to zero at lower temperatures (Figure 8).

**Magnetic Properties.** The magnetic susceptibilities of the present compounds are shown in Figure 9. The temperature dependence of the magnetic susceptibility of the FeCl<sub>4</sub><sup>-</sup>, FeBr<sub>4</sub><sup>-</sup>, and alloyed anion salts shows Curie-Weiss behavior over the entire temperature range from 2 to 300 K, and the Weiss temperatures are -1.0, -2.6, and -2.6 K for the FeCl<sub>4</sub><sup>-</sup>, FeBr<sub>4</sub><sup>-</sup>, and FeBr<sub>1.8</sub>Cl<sub>2.2</sub><sup>-</sup> salts, respectively. The Curie constants 2.89, 3.47, and 3.32 emu K/mol are essentially in agreement with the Fe<sup>3+</sup> *S* = 5/2 value, demonstrating that the magnetism originates in the high-spin Fe<sup>3+</sup> (*S* = 5/2).

Contrary to our expectation, the small Weiss temperatures indicate that magnetic interactions in these materials are weak. It is considered that these weak interactions are due to the insulating electronic state of the donors and the long distances between the FeX<sub>4</sub><sup>-</sup> ions. The former suppresses the d- $\pi$  interaction between the donor and the FeX<sub>4</sub><sup>-</sup> ion and the latter suppresses the d-d interaction between the FeX<sub>4</sub><sup>-</sup> ions. Hence, for all salts, the indirect d- $\pi$  interactions make comparatively small contributions to the Weiss temperatures.<sup>12</sup>

**Chemical Comparisons.** The alloyed anion phase, having uniform donor columns, was obtained only when

(12) Katsuhara, M.; Kurai, H.; Mori, T.; Kobayashi, H.; Kobayashi, A., in preparation.

electrochemical crystal growth was carried out in the presence of two anions,  $FeCl_4^-$  and  $FeBr_4^-$ . This seems to be surprising, but it has been well-known that there are some phases that are obtained only when electrolytes are mixed: for example,  $\theta$ - $(ET)_2I_3$  and  $\kappa$ - $(ET)_2I_3$ .<sup>13,14</sup>

It is interesting that although the  $I_3^-$ ,  $C(CN)_3^-$ , and  $FeBr_{1.8}Cl_{2.2}^-$  salts have almost the same electrical band structure, only  $(TTM-TTP)[C(CN)_3]$  has a lower M-I transition temperature. The interplanar distance (3.4 Å) and the displacement (4.8 Å) in the donor columns are the same within the experimental error. The lattice constants along the stack are 5.778(1) Å (for the  $I_3^-$  salt), 5.874(1) Å ( $FeBr_{1.8}Cl_{2.2}^-$ ), and 5.881(8) Å ( $C(CN)_3^-$ ); there is no systematic change. Thus, the structures in the chain are considered to be practically unchanged. The lattice constant along the  $c$  axis shrinks from  $11.225(3) \times 2 = 22.45$  Å ( $I_3^-$ ) and 22.772(4) Å ( $FeBr_{1.8}Cl_{2.2}^-$ ) to 21.00(7) Å in the  $C(CN)_3^-$  salt. Accordingly, the lattice volume contracts from  $670.2(3) \times 4 = 2681$  Å<sup>3</sup> ( $I_3^-$ ) and 2825(1) Å<sup>3</sup> ( $FeBr_{1.8}Cl_{2.2}^-$ ) to 2592 Å<sup>3</sup> ( $C(CN)_3^-$ ). As a consequence, the interchain interaction, particularly that along the  $c$  axis, is expected to be enhanced in the  $C(CN)_3^-$  salt. This is a possible origin of the low transition temperature of the  $C(CN)_3^-$  salt.

(13) Kobayashi, H.; Kato, R.; Kobayashi, A.; Nishino, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1986**, 789, 833, 957.

(14) Kobayashi, A.; Kato, R.; Kobayashi, H.; Moriyama, S.; Nishino, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1986**, 459.

## Conclusion

The first 1:1 donor/anion composition organic metal with magnetic anions,  $(TTM-TTP)FeBr_{1.8}Cl_{2.2}$  has been prepared. This compound has uniform donor columns and shows high electric conductivity at room temperature and metallic behavior down to 160 K despite the 1:1 composition. On the other hand, the salts with pure anions,  $(TTM-TTP)FeX_4(PhCl)_{0.5}$  ( $X = Cl, Br$ ), are insulators even at room temperature. This difference in conducting properties originates from the difference in the donor columns: one has uniform donor columns and the others have dimerized ones. Unfortunately, the SQUID measurements show that the magnetic interactions in the present compounds are weak. This weak magnetic interaction is related to the band-insulator-type electronic structure and the long distance between the  $FeX_4^-$  ions.

**Acknowledgment.** This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (B) of Molecular Conductors and Magnets (No. 11224203) from the Ministry of Education, Science, and Culture, Japan.

**Supporting Information Available:** An X-ray crystallographic file is available free of charge via the Internet at <http://pubs.acs.org>.

CM000404Q