Band Filling Control by Chemical Approach in Molecular Conductors, (TTM-TTP)$M_xM'_{1-x}Cl_4$ [M, M′ = Fe, Ga, Co, and Mn]

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TTM-TTP-based 1:1-composition organic conductors with counteranions containing alloyed metals, (TTM-TTP)$M_xM'_{1-x}Cl_4$ [TTM-TTP = 2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene; M, M′ = Fe, Ga, Co, and Mn], have been prepared. The degrees of oxidization of TTM-TTP molecules change with the ratio of monovalent ($FeCl_4^-$ and $GaCl_4^-$) and divalent anions ($CoCl_4^{2-}$ and $MnCl_4^{2-}$). Accordingly, the band filling of the donor HOMO is chemically changed. These salts have the same crystal structure, consisting of one-dimensional uniform donor stacks, and are highly conductive. The conductivity is essentially flat down to 100−200 K, but the room-temperature resistivity and the thermoelectric power systematically increase as the band filling decreases from half filling to empty.

Introduction

Over the past few decades, a considerable number of studies have been carried out for controlling physical properties of molecular-based conductors.[1] In these conductors, the ratio of organic donor molecules and counteranions, which decides the band filling, is one of the most important factors that determine the conducting properties and the nature of the insulating phases. Despite its importance, only very few attempts have been made to control band filling in the same crystal phase. For example, although a number of organic superconductors have been explored before now, most of them have a 2:1 composition and have quarter-filled bands. In these organic conductors, it is usually impossible to control the band filling; this is a remarkable characteristic of organic superconductors in contrast to high T_c superconductors. Recently, superconductivity in organic crystals on field effect transistors (FETs) has been found,[2] in which continuous control of carrier density is possible by applying an appropriate gate voltage. On the other hand, chemical control of carrier density in quasi two-dimensional organic conductors has been very recently achieved in BEDT-TTF salts with relatively large monovalent anions, $FeCl_4^-$ and $GaCl_4^-$, by mixing divalent anions, $CoCl_4^{2-}$ and $MnCl_4^{2-}$, with almost the same size (BEDT-TTF = bisethylenedithiotetrathiafulvalene; alternatively abbreviated as ET).[3−5]

Meanwhile, we have reported metallic organic conductors with 1:1 composition, (TTM-TTP)I_3,[6] (TTM-TTP)[$C(CN)_3$],[7] (TTM-TTP)$FeCl_{2.2}Br_{1.8}$,[8] and (TTM-TTP)$Fe_{0.9}Ga_{0.1}Cl_4$.[9] In contrast to the conventional 2:1 composition, these 1:1 salts have half-filled bands. Although for a long time 1:1 organic conductors had been believed to be inevitably insulators owing to the large correlation effects, these salts exhibited metallic conductivity at room temperature. (TTM-TTP)I_3 showed metallic behavior down to about 160 K, and (TTM-TTP)[$C(CN)_3$] showed a lower transition temperature, 70 K. These salts have uniform donor columns and are highly one-dimensional. These compounds, however, have a definite composition (1:1) similarly to the usual organic conductors. In the TTM-TTP salts of iron halides, $FeCl_4^-$ and $FeBr_4^-$, the donor molecules take either dimerized columns or uniform columns depending on their counteranions. Although the crystals with pure iron halides give the insulating dimerized phases, (TTM-

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Table 1. Crystallographic Data at Room Temperature of (TTM-TTP)$M_{1-x}M'_xCl_4$

	(TTM-TTP) $Fe_{0.95}Co_{0.05}Cl_4$	(TTM-TTP) $Ga_{0.7}Co_{0.3}Cl_4$	(TTM-TTP) $Fe_{0.6}Co_{0.4}Cl_4$	(TTM-TTP) $Mn_{0.1}Co_{0.9}Cl_4$
chemical form.	$C_{14}H_{12}S_{12}Fe_{0.95}Co_{0.05}Cl_4$	$C_{14}H_{12}S_{12}Ga_{0.7}Co_{0.3}Cl_4$	$C_{14}H_{12}S_{12}Fe_{0.6}Co_{0.4}Cl_4$	$C_{14}H_{12}S_{12}Mn_{0.1}Co_{0.9}Cl_4$
formula weight	762.66	773.26	763.86	765.31
shape	black plate	black plate	black plate	black plate
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a/Å	24.08(2)	24.163(4)	24.073(6)	24.32(1)
b/Å	5.838(9)	5.841(2)	5.847(7)	5.837(2)
c/Å	22.46(2)	22.577(4)	22.45(1)	22.576(6)
β/deg	118.94(4)	119	118.93(3)	119.94(3)
V/Å^3	2762(5)	2779.5(9)	2765(3)	2777(2)
Z	4	4	4	4
D_{calc}/g·cm^{-3}	1.834	1.848	1.835	1.830
λ/Å	0.710 69	0.710 69	0.710 69	0.710 69
reflections used	947 ($I > 4.00\sigma(I)$)	830 ($I > 4.00\sigma(I)$)	741 ($I > 4.00\sigma(I)$)	595 ($I > 4.00\sigma(I)$)
R/R_W[a]	0.136/0.171	0.074/0.086	0.064/0.075	0.049/0.052

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

TTP)FeX_4(PhCl)$_{0.5}$ [X = Cl and Br; PhCl = chlorobenzene], when we mix iron halides, $FeCl_4^-$ and $FeBr_4^-$, we have obtained the uniform phase with metallic behavior, (TTM-TTP)$FeCl_{2.2}Br_{1.8}$. Not only the halogen mixed salts but also metal mixed salts such as (TTM-TTP)$Fe_{0.9}Ga_{0.1}Cl_4$ afford the uniform metallic phases. These findings, together with the successful band-filling control in the BEDT-TTF transition metal halides, have made us attempt to mix the divalent metal halides Co(II)Cl_4^{2-} and Mn(II)Cl_4^{2-} with the monovalent anions Fe(III)Cl_4^- and Ga(III)Cl_4^- in TTM-TTP salts. By changing the ratio of metal halides with different charges, we have succeeded in obtaining the uniform metallic phases. In this report we present structures of TTM-TTP-based organic conductors with mixed anion salts, (TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$, (TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$, (TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$, and (TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$, with particular emphasis on the influence of band filling on the transport properties. Our results demonstrate that electrical resistivities and thermoelectric power exhibit systematical changes with the band filling, and that the half filling, which is a critical point in the one-dimensional Hubbard model, is not a singularity in the present system.

Experimental Section

Preparation. TTM-TTP was prepared as described in refs 10−13. Crystals were grown by electrochemical oxidation in chlorobenzene in the presence of the donor and the mixture of tetrabutylammonium salts of the corresponding metal halides[14] under a constant current of 0.5 μA at 26 °C for 1 or 2 weeks. As mentioned above, only the crystals which were grown in the presence of two anions gave the uniform phase. Obtained single crystals were in the shape of black blocks or plates with metallic luster. Although these salts contained nonstoichiometric anion mixtures, we could not control the composition continuously; various samples electrocrystallized by starting from different nominal anion ratios were investigated by EDS measurements, giving the same definite composition within the experimental error. These samples showed similar conducting behavior as well. Then we concluded that only the salts with these definite compositions are stable. In the combination of Fe and Co, when we started from an excess of $FeCl_4^-$ and a small amount of $CoCl_4^{2-}$ (typically Fe/Co = 100:1), (TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$ was obtained. (TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$ was obtained when comparable Fe and Co anions were used in electrocrystallization. In the case of intermediate anion ratios, no crystal was grown.

Structure Determination. The crystal structures of the four compounds were determined from single-crystal X-ray diffraction. Intensity data were measured by the ω scan technique on a Rigaku automated four-circle diffractometer AFC-7R with graphite monochromatized Mo Kα radiation ($2\theta < 60°$). The structures were solved by the direct method (SIR92).[15] 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.[16] The electronic band structures were calculated in the tight-binding approximation.

Transport Properties. Electrical resistivity was measured for single crystals by the four-probe method using a low-frequency AC current (10 μA). Electrical contacts to the crystals were made with 15 μm gold wires and gold paint. Thermoelectric power measurements were carried out by making two-probe electrical contacts attached to two heat sinks with gold foil and gold paint. These heat sinks were heated alternately to generate a temperature difference of about 0.5 K or less, and the resulting voltage was measured. The cycle of the heating was about 2 min from room temperature to 100 K and about 5 s to helium temperatures. All measurements of transport properties were performed along the donor columns.

Results and Discussion

Crystal Structures. Crystallographic data for the present four compounds are listed in Table 1, and the atomic numbering scheme is shown in Figure 1. The donors are located on inversion centers and the $M_xM'_{1-x}Cl_4$ ions (alloyed ions) are located on 2-fold axes. The donors form a uniform stack along the *b* axis, and the donor columns are tilted in two different directions (Figure 2). The donors at $z = 0$ are so inclined that the upper half of the molecule extends above the projection plane (Figure 2a), but the donors at $z = {}^1/_2$

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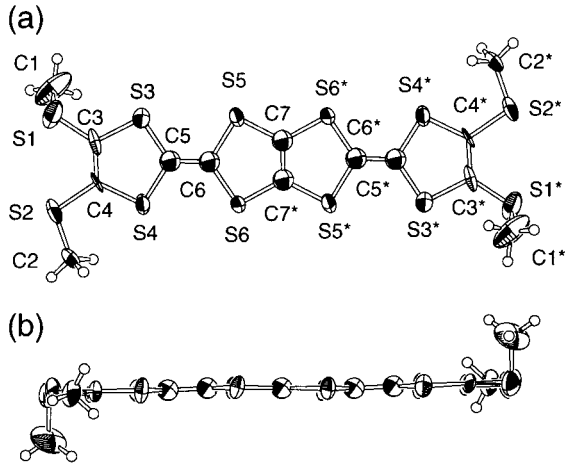

Figure 1. (a) ORTEP drawing and atomic numbering scheme of the TTM-TTP molecule in the crystal of (TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$. (b) Side view.

are inclined inversely. This is basically isostructural to (TTM-TTP)$[C(CN)_3]$[7] and to other TTM-TTP-based alloyed anion salts, such as (TTM-TTP)$FeBr_{1.8}Cl_{2.2}$[8] and (TTM-TTP)$Fe_{0.9}Ga_{0.1}Cl_4$.[9] The interplanar spacing of the donors and the displacement along the molecular long axis are listed in Table 2. These values are the same as those of other TTM-TTP-based organic metals with a 1:1 composition. Thus, the structures of the donor columns in these materials, including (TTM-TTP)I_3,[6] are practically the same. Because the metal ions are located on the 2-fold axes, two pairs of halogens in a MCl_4 unit are equivalent, respectively.

Estimation of the Degree of Band Filling. In the present metal alloyed salts, it was difficult to determine the composition from X-ray population analysis on account of the small difference of the electron numbers of the used metal atoms. So, the compositions of metal atoms were determined from EDS analysis to be (TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$, (TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$, (TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$, and (TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$. From this, we can estimate the band filling of the donor HOMO as 0.475, 0.35, 0.30, and 0.0, respectively, by considering the ratio of metal ions and their valences. This realizes several different occupancies between half-filled (0.50) and empty (0.0). Since the changes of bond lengths depending on the oxidation state of the TTP molecules are small owing to the large molecular size, we could not evaluate the band filling from the change of the bond lengths.

Table 2. Interplanar Spacing and Displacement of the Donors

	slip distance/Å	interplanar spacing/Å	ref
(TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$	4.75	3.40	
(TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$	4.74	3.41	
(TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$	4.75	3.41	
(TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$	4.73	3.42	
(TTM-TTP)$FeCl_{2.2}Br_{1.8}$	4.79	3.39	7
(TTM-TTP)$Fe_{0.9}Ga_{0.1}Cl_4$	4.76	3.40	8

Energy Band Calculation. Calculated intermolecular overlap integrals for the HOMO's of the donor molecules are listed in Table 3. In the present compounds, the donor molecules belonging to different columns cannot approach close to each other because of the steric hindrance of the terminal methyl groups and the tilted donor columns. Thus, the interchain interaction is very small; the ratio of the calculated intrastack (b) and interstack (p) overlap integrals is about 100:1, indicating a highly one-dimensional character along the crystallographic *b* axis.

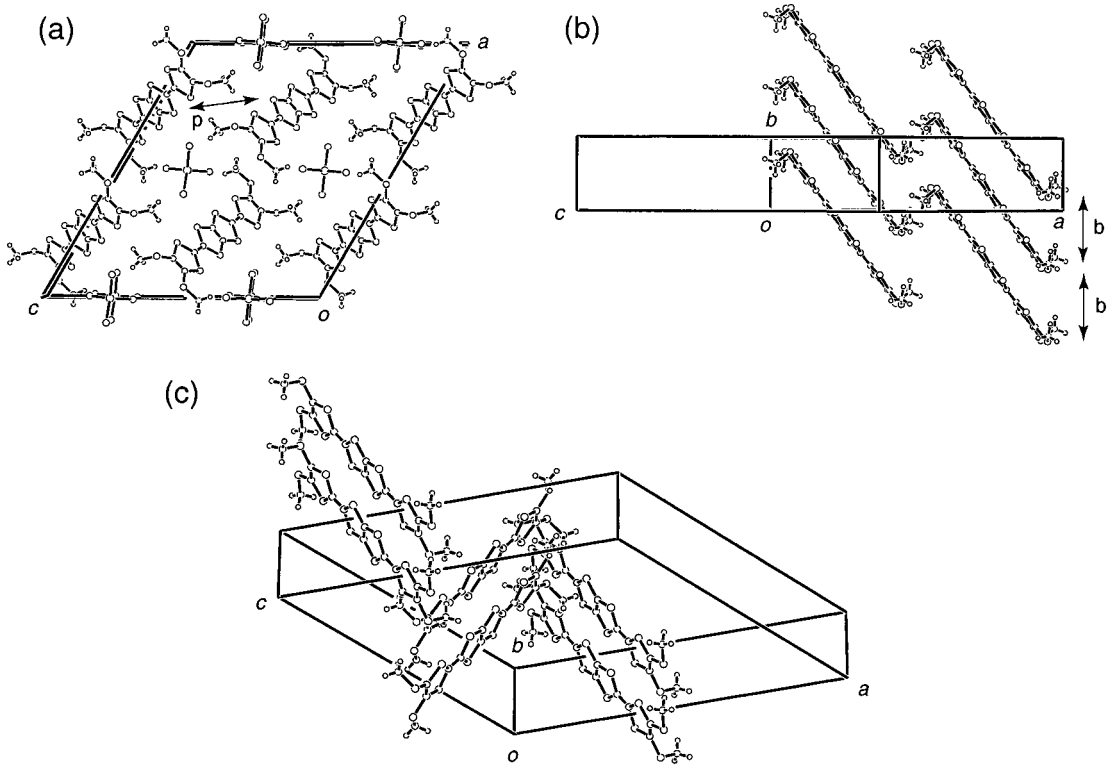

Figure 2. Crystal structure of (TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$: (a) projection along the *b* axis; (b) structure of the donor columns; (c) view of the alternatingly tilted donor columns.

Table 3. Overlap Integrals (*S*) of (TTM-TTP)$M_{1-x}M'_xCl_4$

	10^3S		
	b	p	ref
(TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$	−18.2	0.23	
(TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$	−20.4	0.18	
(TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$	−21.8	0.18	
(TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$	−20.0	0.16	
(TTM-TTP)$FeCl_{2.2}Br_{1.8}$	−21.2	0.13	7
(TTM-TTP)$Fe_{0.9}Ga_{0.1}Cl_4$	−20.9	0.18	8

Table 4. Electrical Conductivity of (TTM-TTP)$M_{1-x}M'_xCl_4$

	σ_{rt}/S cm^{-1}	E_a or T_{MI}	ref
(TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$	350	160 K	
(TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$	140	0.02 eV	
(TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$	85	0.025 eV	
(TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$	0.7	0.11 eV (T > 250 K) 0.02 eV (T < 100 K)	
(TTM-TTP)$FeCl_{2.2}Br_{1.8}$	700−1000	160 K	7
(TTM-TTP)$Fe_{0.9}Ga_{0.1}Cl_4$	190	200 K	8

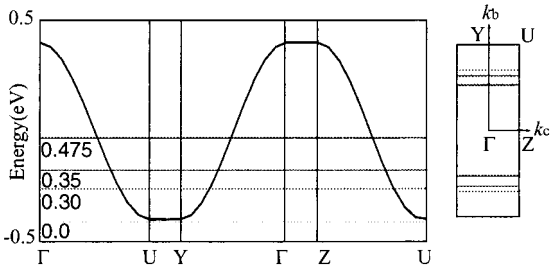

Figure 3. Tight-binding energy band structures and Fermi surfaces of (TTM-TTP)$M_{1-x}M'_xCl_4$.

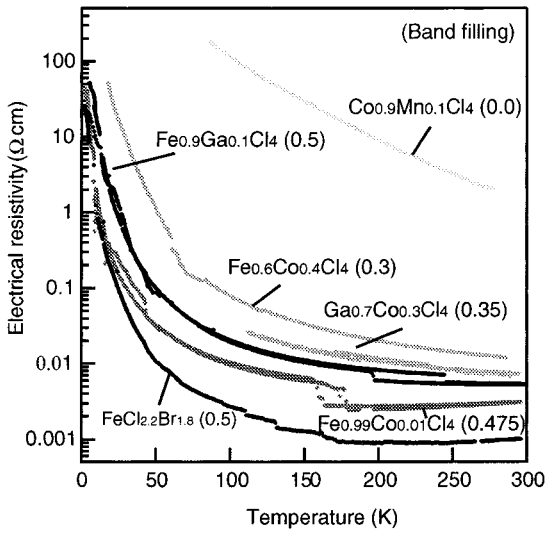

Figure 4. Electrical resistivity of (TTM-TTP)$M_{1-x}M'_xCl_4$ and (TTM-TTP)$FeCl_{2.2}Br_{1.8}$.

Figure 3 shows the calculated energy band structure and Fermi surface of the present materials. Despite the 1:1 composition, a one-dimensional Fermi surface exists on account of the uniform stacking structure. The values of the overlap integrals along the stacking direction and the resulting bandwidths are comparable to those of other TTM-TTP-based 1:1 composition metals. Thus, the band structures of the present salts, except the occupancies, are practically not altered from those of the half-filled salts.

Transport Properties. Figure 4 shows electrical resistivities of the present compounds, together with those of (TTM-TTP)$FeBr_{1.8}Cl_{2.2}$[8] and (TTM-TTP)$Fe_{0.9}Ga_{0.1}Cl_4$,[9] both of which have the same crystal and band structures and are exactly half-filled. This figure shows how the band filling changes the conducting behavior. (TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$, the band filling of which (0.475) is slightly less than 0.50, shows high room-temperature conductivity and retains metallic behavior down to about 160 K, at which a clear phase transition is observed. Judging from the pronounced positive resistivity versus temperature slope in the high-temperature region, the metallic conduction of this salt seems to be more stabilized than those of other half-filled salts. (TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$ and (TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$, the donor molecules of which are more oxidized, show moderately high room-temperature conductivities of 140 and 85 S cm^{-1}, respectively. These materials are, however, weakly semiconductive even at room temperature. The electrical resistivity of (TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$, whose HOMO is entirely empty, is semiconductive, and the room-temperature conductivity (0.07 S cm^{-1}) is much lower than those of the other compounds with uniform stacks.

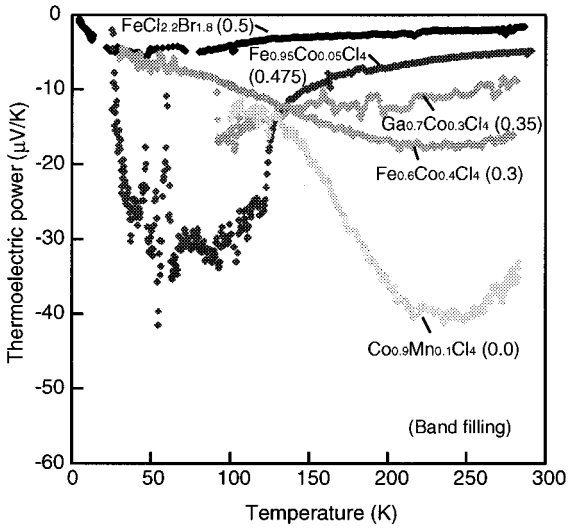

Figure 5. Thermoelectric power of (TTM-TTP)$M_{1-x}M'_xCl_4$ and (TTM-TTP)$FeCl_{2.2}Br_{1.8}$.

When the filling is slightly different from 0.5, there is only a small change in the metallic conduction. However, as the band filling deviates from the half filling, the conductivity gradually becomes semiconductive.

Figure 5 shows the temperature dependence of the thermoelectric power of the present four compounds as well as the half-filled (TTM-TTP)$FeCl_{2.2}Br_{1.8}$ salt.[8] The low-temperature behaviors of the thermopower of the present materials are complex and largely different from each other. However, when we focus on the room-temperature values, it is clearly found that as the band filling deviates from the half filling, the room-temperature thermopower shifts to negative directions. The half-filled salt (TTM-TTP)$FeCl_{2.2}Br_{1.8}$ shows nearly zero thermoelectric power, as predicted from the half-filled tight-binding band. The negative values of the other salts are consistent with the electron-like nature of the carriers (Figure 3). In the case of (TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$, the thermopower takes a small negative value (−4.8 μV/K) at room temperature. The thermoelectric power values of (TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$ and (TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$, however, are rather large

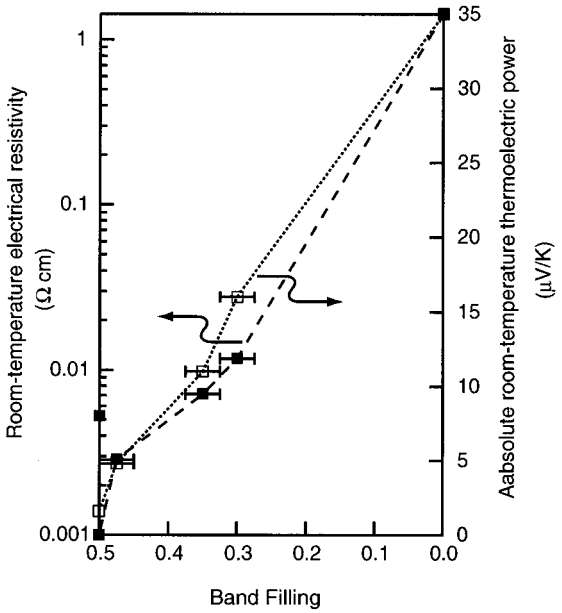

Figure 6. Room-temperature values of the absolute thermoelectric power and the logarithmic electrical resistivity.

negative room-temperature values (−11 and −16 μV/K, respectively), indicating the difference of the band filling. (TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$ takes the largest negative room-temperature value (−35 μV/K) among the present compounds.

Assuming a one-dimensional tight-binding band, the bandwidths of (TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$ and (TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$ are 0.82 and 0.87 eV, respectively. These values are almost the same and are consistent with the results of the band calculations (0.74 and 0.80 eV, respectively). This proves that the incorporation of the divalent anion does not change the bandwidths.

Discussion

Figure 6 shows the relation of the band filling to the logarithmic electrical resistivity and the absolute values of the room-temperature thermoelectric power. The logarithmic electrical resistivity and the thermoelectric power increase as the band filling decreases from half-filled to zero. Both the resistivity and the thermoelectric power seem to change continuously even in the half filling ($\rho = 0.5$), and the half filling is no longer a singularity. This sharply contrasts with the exact solution of the one-dimensional Hubbard model,[17] in which the system is a Mott insulator for all nonzero Coulomb repulsions U in the half filling but is always a paramagnetic metal in other fillings. The observed properties seem to be determined by a simple band model without considering U. This is partly because in Figure 6 we compare high-temperature properties. As shown in Figure 4, however, the transition temperatures to the insulating region do not exhibit any singularity at half filling. This may be attributed to the small-U character of the present compounds; the extended skeleton of the TTM-TTP molecule results in a considerable reduction of U in comparison with those of the conventional TTF donors. The observed continuous properties of the present system make us consider that, at least when applied to organic systems, the singular behavior of the half filling predicted from the Hubbard model is a fictitious one originating in the artificial truncation of the originally long-range Coulomb repulsion by maintaining only the on-site U.

Conclusion

We have prepared four new 1:1 composition TTM-TTP-based organic conductors with mixed metal halides of different charges (Fe(III)Cl_4^-, Ga(III)Cl_4^-, Co(II)Cl_4^{2-}, and Mn(II)Cl_4^{2-}), (TTM-TTP)$Fe_{0.95}Co_{0.05}Cl_4$, (TTM-TTP)$Ga_{0.7}Co_{0.3}Cl_4$, (TTM-TTP)$Fe_{0.6}Co_{0.4}Cl_4$, and (TTM-TTP)$Mn_{0.1}Co_{0.9}Cl_4$. All these compounds have uniform donor columns and are isostructural to each other. The degree of oxidation of donor molecules in the materials changes according to the ratio of the mixed anions, so that the band filling is controlled from 0.5 to 0.0. As the filling decreases to zero, the conducting behavior shifts from metallic to semiconductive. Band-filling control by alloying magnetic anions with different charges may be promising in controlling physical properties in many types of organic conductors.

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Supporting Information Available: X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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