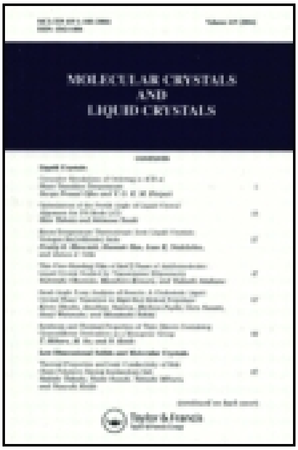

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Tetrathiapentalene-based organic conductors with magnetic counter anions

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TETRATHIAPENTALENE-BASED ORGANIC CONDUCTORS WITH MAGNETIC COUNTER ANIONS

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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 composition salts with metal halides. The salts of pure anions, (TTM-TTP)$MX_4(PhCl)_{0.5}$ (M = Fe, Ga; X = Cl, Br) are dimerized insulators, whereas when the halogenes (Cl/Br) or the metals (Fe/Ga) are alloyed, metallic salts with uniform columns are obtained.

Keywords: organic conductors; transport properties; magnetic measurements

INTRODUCTION

A large number of radical-cation salts of bis-fused tetrathiafulvalene (TTF) donors, which are called tetrathiapentalene (TTP) donors, show metallic conductivity [1]. As an exception, TTM-TTP makes many radical-cation salts with 1:1 composition, which are usually insulators even at room temperature. The radical cation salts of TTM-TTP with I_3^- and $C(CN)_3^-$ are, however, good electrical conductors at room temperature, and shows metallic behavior down to 160 K and 70 K, respectively, in spite of the half-filled band structure. These salts have one-dimensional donor columns [2,3].

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On the other hand, organic conductors including magnetic anions have attracted a great deal of attention because of their intriguing physical properties induced by π-d interactions [4].

In the course of preparative study of TTM-TTP salts including magnetic counter anions, we have obtained TTM-TTP-based organic conductors including magnetic anions with 1:1 composition; (TTM-TTP)$FeCl_4(PhCl)_{0.5}$, (TTM-TTP)$FeBr_4(PhCl)_{0.5}$ [5], (TTM-TTP)$GaCl_4(PhCl)_{0.5}$, (TTM-TTP) $GaBr_4(PhCl)_{0.5}$, (TTM-TTP)$GaBr_{2.0}Cl_{2.0}(PhCl)_{0.5}$ [6], (TTM-TTP)$FeBr_{1.8}$ $Cl_{2.2}$ [5], and (TTM-TTP)$Fe_{0.75}Ga_{0.25}Cl_4$. (TTM-TTP)$FeBr_{1.8}Cl_{2.2}$ is the first 1:1 composition organic metal with a magnetic counter anion.[5] In addition, we have found that the alloying of the metal atoms gives the uniform phase, (TTM-TTP)$Fe_{0.75}Ga_{0.25}Cl_4$ as well. Interestingly, only mixed anion salts form metallic compounds. The present paper describes crystal structures and physical properties of these salts.

EXPERIMENTAL

The present materials were made by electrochemical crystallization of TTM-TTP in the presence of $TBAMX_4$ (TBA = tetrabutyl ammonium; M = Fe, Ga; X = Cl, Br) in PhCl (PhCl = chlorobenzene), which afforded black needles or plates. Single crystal X-ray structure analyses were carried out for all compounds [7]. The compositions were determined from EDS and X-ray population analysis. Starting from different nominal compositions, we obtained the alloyed salts with a definite composition.

RESULTS

Crystal Structures and Transport Properties

The crystals that were grown in the presence of the pure MX_4 anions, as well as the mixed gallium halides, are essentially isostructual. They have β'-type dimerized donor columns [8], and a unit cell contains two donor molecules, two anions and a PhCl molecule that is incorporated from the solvent used for the crystal growth.

The electric conductivities of these materials are semiconductive even at room temperature and the room-temperature conductivities are $0.01-0.1\,\mathrm{Scm^{-1}}$ (Figure 1). These values are lower than those of (TTM-TTP)AuI_2 and (TTM-TTP)$AuBr_2$ ($10–40\,\mathrm{Scm^{-1}}$), which have weaker dimerization in the donor columns (β''-type) [9].

The crystals of (TTM-TTP)$FeBr_{1.8}Cl_{2.2}$ and (TTM-TTP)$Fe_{0.75}Ga_{0.25}$ Cl_4 have uniform donor columns, and these salts do not include any solvent molecule (Figure 2). These salts are isostructual to (TTM-TTP)

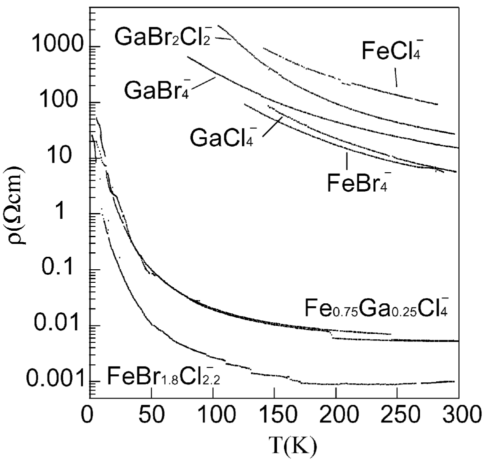

FIGURE 1 Electric resistivities of TTM-TTP-based salts with magnetic anions.

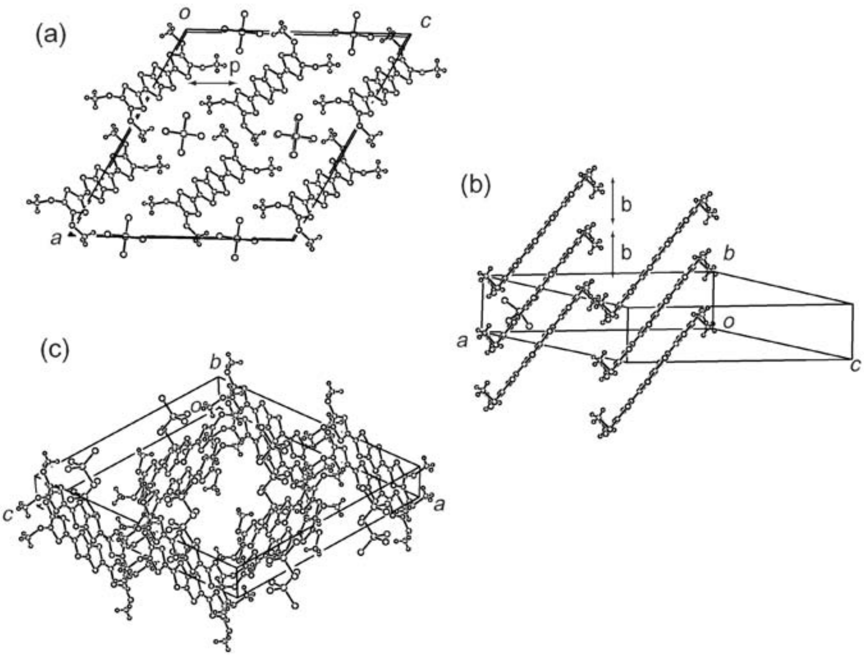

FIGURE 2 The crystal structure of (TTM-TTP)$Fe_{0.75}Ga_{0.25}Cl_4$, (a) view along the *b* axis, (b) structure of the columns, inclination of the donor columns.

[C(CN)$_3$] [3]. The donors are located on the inversion centers, and the anions are located on the two-fold axes. From this the composition is 1:1. The donors make uniform stacks along the *b* axis. These salts show high electric conductivity of about 1000−100 Scm^{-1} at room temperature and metallic behavior down to 190−160 K, at which these salts undergo metal-insulator transitions [5]. We have recently found that other mixed anion salts, (TTM-TTP)Co$_x$Fe$_{1-x}$Cl$_4$ and (TTM-TTP)Co$_x$Ga$_{1-x}$Cl$_4$, where the values of x are less than 0.05, have the same structure as well [10]. This indicates that not only mixed-halide (Cl/Br) salts but also mixed-metal (Fe/Ga/Co) salts form the uniform structure. However, we have obtained the dimerized phase (TTM-TTP)GaBr$_{2.0}$Cl$_{2.0}$(PhCl)$_{0.5}$, when GaCl$_4^-$ and GaBr$_4^-$ are mixed.

Magnetic Measurements

Static magnetic susceptibilities of (TTM-TTP)FeX$_4$(PhCl)$_{0.5}$ and (TTM-TTP)FeBr$_{1.8}$Cl$_{2.2}$ were measured [5]. They follow the Curie-Weiss law in the whole temperature range with the Weiss temperatures of −1.0, −2.4 and −2.4 K for the FeCl$_4$, FeBr$_4$ and FeBr$_{1.8}$Cl$_{2.2}$ salts, respectively. Because of the long distance between the anions and of the insulating nature of the donor networks, magnetic interactions of these materials are relatively weak.

In order to make clear the spin state of the donor molecules, we have measured static magnetic susceptibility and ESR of (TTM-TTP) GaCl$_4$(PhCl)$_{0.5}$, which has the same structure as (TTM-TTP)FeX$_4$ (PhCl)$_{0.5}$, but includes no magnetic anions (Figure 3). Despite the insulating ground state corresponding to the strongly dimerized structure,

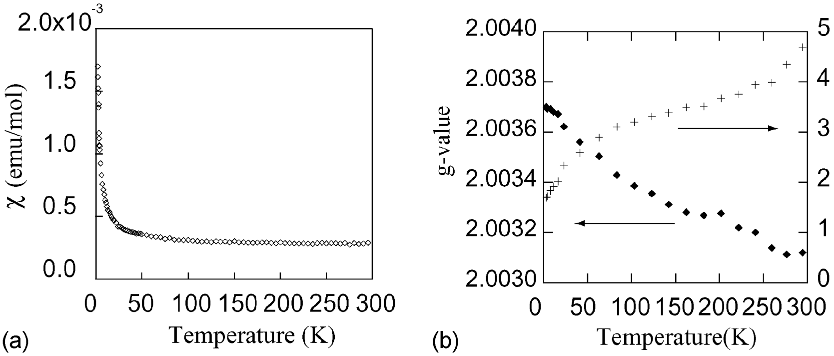

FIGURE 3 Temperature dependence of (a) the static magnetic susceptibility, (b) the g-value, and the line width of (TTM-TTP)GaCl$_4$(PhCl)$_{0.5}$.

the spin susceptibility did not change from room temperature to low temperatures. The g-value and the line width also did not show any striking changes in all temperature range.

CONCLUSION

We have prepared TTM-TTP-based 1:1 organic conductors containing magnetic anions. The structures and properties of these materials are dramatically changed by the counter anions. Though they have half-filled band structures, some of them with mixed anion salts have uniform donor columns and show metallic behavior. The magnetic interactions of these salts are, however, very weak because of the long distances between the anions and the insulating ground states induced by the dimerized structures.

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