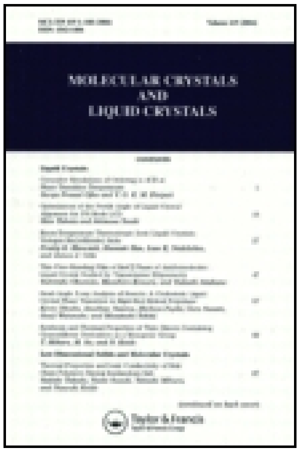

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MAGNETIC AND TRANSPORT PROPERTIES OF ORGANIC RADICAL ION SALTS CONTAINING METAL IONS

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Abstract Two isomorphous TMTSF cation radical salts with tetrachlorometalate anion, TMTSF•FeCl4 ($\rho_{\rm rt}$ = 40 Ωcm), and TMTSF•GaCl4 ($\rho_{\rm rt}$ = 20 Ωcm) were prepared. The crystal containing tetrachloroferrate anion undergoes an antiferromagnetic ordering below T_N = 4K with the easy axis perpendicular to the TMTSF stacking direction. X-ray crystallographic analysis of the crystal reveals that Cl atoms of the anions closely contact with Se atoms of the donor molecules and suggests that the spin ordering is mediated by magnetic interaction between donors and anions.

INTRODUCTION

Synthesis of the molecular compounds in which conduction electrons are interacting with localized spins is one of the strategies for obtaining organic ferromagnetic conductors with high transition temperature.[1] In case the conduction electrons on a π-system such as partially oxidized donor molecules magnetically couple with localized spins on counter anions, the spin system with the ferromagnetic coupling (so-called double exchange interaction[2]) can be established. From this point of view, a radical ion salt of TMTSF, which contains a magnetic anion tetrachloroferrate, was prepared in the present study.

Some of ion radical salts of typical organic donors that have paramagnetic counter anion were reported.[3,4] However, in most of these salts a magnetic interaction between the carrier electrons on the donors and the spins on the counter anions is very small. There are only a few radical ion salts in which a magnetic interaction between itinerant electrons and localized spins show up as relevant to the metal-insulator phenomena.[4] We have chosen tetrachloroferrate as a counter ion because the anion has the highest spin multiplicity among the tetrahalogeno-3*d*-transition-metalates which are represented as

MX_4^{q-} (M = transition metal; X = Cl, Br; *q* = 1,2). In addition, the ferrate anion with Fe^{3+} has only one negative charge (*q* = 1), like many anions that are contained ordinarily in organic conductors and may be easier to form simple salts, whereas the other 3*d*-transition metalates are dianion.

In order to examine a behavior of the spins on donor molecules, a radical ion salt with tetrachlorogallate ($GaCl_4^-$), which is non-magnetic but has almost the same size as tetrachloroferrate, was also prepared.

PREPARATION OF TMTSF•MCl_4 (M=Fe, Ga)

Single crystals of tetrachloroferrate salt of TMTSF were prepared by two methods. Through the ordinary electro-crystallization in 1,1,2-trichloroethane with Pt electrodes under the existence of supporting electrolyte *n*-Bu_4N•$FeCl_4$, black needles were obtained. Similar shaped crystals were obtained as well by slow evaporation from acetonitrile-THF solution of TMTSF and $FeCl_3$. In the latter case, TMTSF is oxidized by $FeCl_3$ and oxidant $FeCl_3$ is turned into $FeCl_4^-$ and $FeCl_2$. These crystals obtained by the two different methods showed identical magnetic and transport properties and were confirmed to be structurally identical, by X-ray crystallographic analysis.[5] X-ray crystallographic analysis revealed that a ratio of donor to anion is 1:1 and is consistent with a Se:Fe ratio which was measured by ICP analysis. Single crystals of tetrachlorogallate salt were obtained by the electro-crystallization with supported electrolyte *n*-Bu_4N•$GaCl_4$ under the same condition as in the case of tetrachloroferrate. The X-ray crystal structure analysis of the salt shows that the gallate salt and ferrate salt are isomorphous.[6]

CRYSTAL STRUCTURE OF TMTSF•MCl_4 (M=Fe, Ga)

FIGURE 1(a) shows the crystal structure of the cation radical salt TMTSF•$FeCl_4$. One can find two types of donor column (FIGURE 1(b)), column *A* and column *B*, in the crystal. In column *A*, the long axis of each $TMTSF^{+\bullet}$ is aligned in one direction and the donors are dimerized as shown in FIGURE 1b. On the other hand, in column *B* $TMTSF^{+\bullet}$ is arranged orthogonal with each other. The crystal structure is clearly different from that of Bechgaard salts $(TMTSF)_2X$ (X=BF_4, ClO_4, PF_6, etc.)[7], which may be caused by the different charge of donor and/or by the relatively large anion size.

The arrangement of donors in column *B* is interesting from the view point of higher dimensionality of intermolecular interaction in a conductive organic ion radical salt.[8]

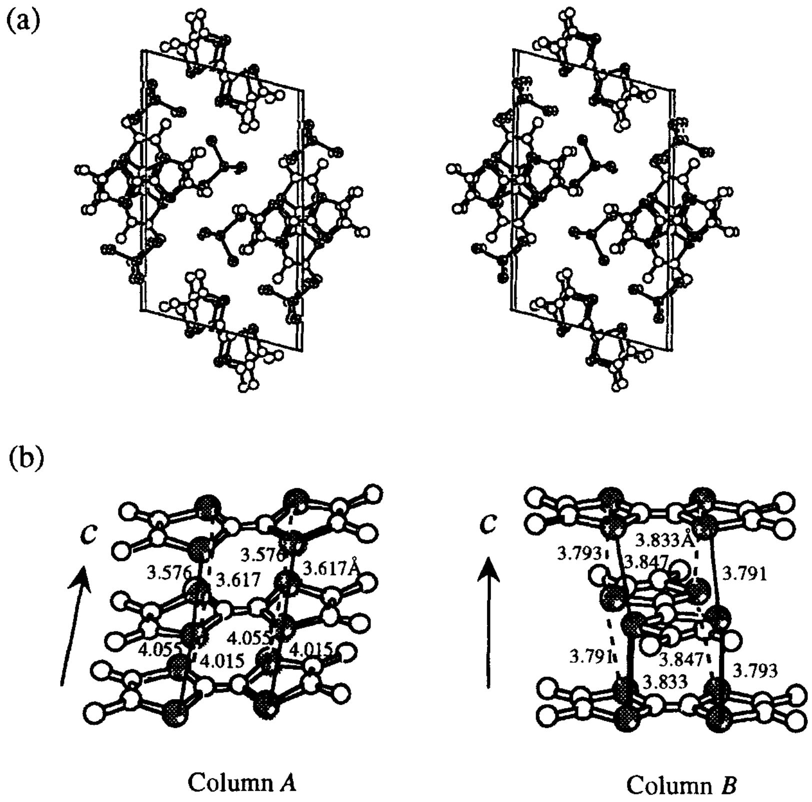

FIGURE 1 (a) Crystal structure of TMTSF•FeCl$_4$. (stereo view) (b) Columnar structure of TMTSF in the crystal of TMTSF•FeCl$_4$. Intermolecular Se•••Se contacts and distances are also indicated. Hydrogen atoms are omitted for clarity.

The crystal of TMTSF•GaCl$_4$ has isomorphous structure of TMTSF•FeCl$_4$. The donor stacking was observed to be nearly identical for these two metalate salts. The size and ionicity of tetrachloroferrate and tetrachlorogallate may be the suitable for this unique crystal structure.

TRANSPORT AND MAGNETIC PROPERTIES OF TMTSF•MCl$_4$ (M=Fe, Ga)

Reflecting a radical salt (1:1 salt) feature, the crystal of TMTSF•GaCl$_4$ does not show very large conductivity. The crystal is semiconducting with ρ_{rt} = 20 Ωcm and a thermal activation energy E_a = 0.06 eV (between 120 K and 300 K). In the case of TMTSF•FeCl$_4$, a transport property is similar to that of TMTSF•GaCl$_4$. At temperatures between 200 K and 300 K, it shows semiconducting behavior with E_a = 0.06 eV and ρ_{rt} = 40 Ωcm. From a view point of the crystal structure, it is natural that these two salts show same transport behavior reflecting same donor packing in the crystals. This result shows that there is no effect of spin moment on the magnetic anion FeCl$_4^-$ to electrical conductivity in this temperature range.

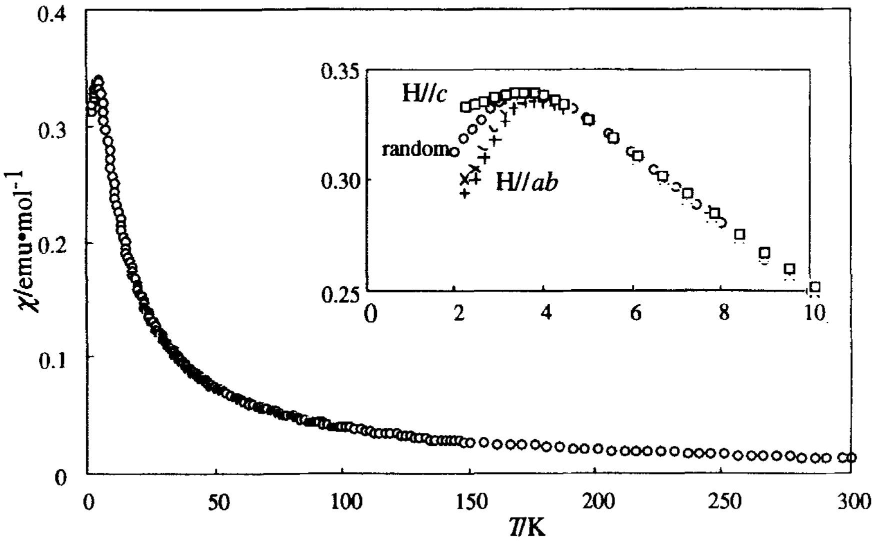

FIGURE 2 Temperature dependence of magnetic susceptibility of TMTSF•FeCl$_4$. The inset magnifies the low temperature susceptibility as a function of temperature for two field directions, *c* being the donor stacking axis.

Magnetic susceptibility(χ) of TMTSF•FeCl$_4$ was measured by a SQUID magnetometer (H_{ext} = 5 kOe) at temperatures between 2 K and 300 K and the χ vs. T plot is shown in FIGURE 2. The value of χT at 300 K (= 4.2) is close to 4.375 which agrees with an expected value for the $S=5/2$ and g = 2 spin. This χT value suggests that the measured susceptibility is mainly due to the spins of Fe^{3+}($S=5/2$). The contribution of $TMTSF^{+\bullet}$ to the total susceptibility is too small to be explicitly observed, probably because of the strong antiferromagnetic interaction in the donor stack or the dimerized nature of the donor stack. This is consistent with the fact that $TMTSF{\bullet}GaCl_4$ shows almost only diamagnetic susceptibility at temperatures up to 370 K. It suggests the strong antiferromagnetic interaction in the column or intradimer singlet formation. In radical ion salt or charge transfer complex, strong intermolecular antiferromagnetic interaction is usual, as observed for TCNQ anion radical salt.[9]

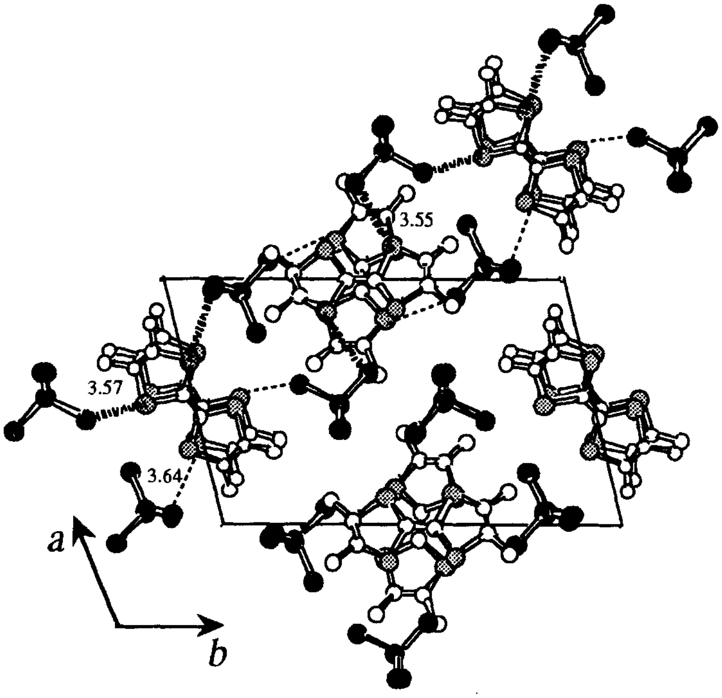

FIGURE 3 Intermolecular Se•••Cl contacts in the crystal of $TMTSF{\bullet}FeCl_4$ viewed normal to the *ab* plane. The thick line shows the contact in an upper layer and the broken line shows the contact in a lower layer.

Temperature dependence of the susceptibility of $TMTSF{\bullet}FeCl_4$ indicates intermolecular antiferromagnetic interaction.[10] As shown in FIGURE 2, the χ-value decreases below 4 K, suggesting that antiferromagnetic spin ordering occurs at $T_N = 4$ K. The anisotropy of χ as shown in the inset of FIGURE 2 is also typical of antiferromagnet; magnetic moments are found to lie within the *ab* plane, *i.e.* normal to the donor stacking column.

On the other hand, the gallate salt does not exhibit a magnetic ordering in the temperature range between 2 K and 370 K. The magnetic susceptibility measurement of the TMTSF•$GaCl_4$ suggests that the ground state spin multiplicity is singlet.

In order to examine an origin of antiferromagnetic interaction in the crystal of TMTSF•$FeCl_4$, we pay attention to the crystal structure of the salt more closely. From the structural analysis one can find that the magnetic anions are fairly isolated from each other in the crystal.[11] By contrast, many Se•••Cl contacts with short distances (< 3.65 Å) are present between donors and anions (see FIGURE 3). Therefore, the antiferromagnetic interaction between $FeCl_4^-$ is likely to be mediated by the donor molecules. That is to say, the magnetic interaction between donors and anions is large enough to cause the magnetic ordering below 4 K. Considering the non-magnetic on the $TMTSF^{+\bullet}$, as evidenced by the magnetic measurement of the gallate salt, the antiferromagnetic ordering in the ferrate salt may be mediated via the dimer singlet. In this view, the mechanism of the spin ordering in the present d-π system may be quite unique and deserve further investigation.

CONCLUSION

In summary, the crystal of the cation radical salt TMTSF•$FeCl_4$ was prepared and found to be composed of two kinds of donor columns, both of which appear to magnetically couple the anions via the close Se•••Cl contacts. The localized spins on the anions order antiferromagnetically below T_N = 4K perhaps via exchange interaction through the cation radical of donor molecules.

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5 Crystallographic data for TMTSF•FeCl$_4$: formula $C_{10}H_{12}Se_4FeCl_4$; Fw = 645.70; triclinic; Space group $P\bar{1}$; a = 12.705(7)Å, b = 20.178(5), c = 7.568(2); α = 93.54(2)°, β = 94.28(3), γ = 75.60(3); V = 1871(1)Å^3; Z = 4; D_{calc} = 2.29; radiation MoKα (λ = 0.71073 Å) ; R = 0.067, R_w = 0.051 for 1714 unique reflections.

5 Crystallographic data for TMTSF•GaCl$_4$: formula $C_{10}H_{12}Se_4GaCl_4$; Fw = 659.58; triclinic; Space group $P\bar{1}$; a = 12.724(3)Å, b = 20.196(6), c = 7.576(2); α = 93.20(3)°, β = 94.05(2), γ = 75.87(2); V = 1881.6(9)Å^3; Z = 4; D_{calc} = 2.33; radiation MoKα (λ = 0.71073 Å) ; R = 0.074, R_w = 0.087 for 3507 unique reflections.

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11 The shortest intermolecular Cl•••Cl distance is 3.78(3)Å, but all other intermolecular Cl•••Cl distances are longer than 4.0 Å. These distances are enough longer than the twice Van der Waars radius of Cl (3.50 Å) and hence the direct magnetic interaction may be negligible between anions.