A Molecular Antiferromagnet TMTSF·FeCl$_4$

Reiji Kumai,*[†] Atsushi Asamitsu,[†] and Yoshinori Tokura[†,††]
[†]*Joint Research Center for Atom Technology (JRCAT), Tsukuba 305*
[††]*Department of Applied Physics, The University of Tokyo, Hongo, Tokyo 113*

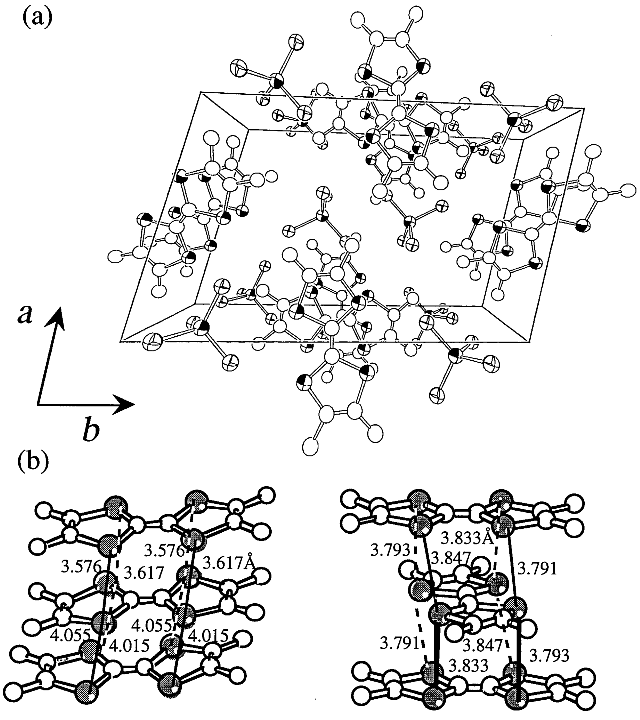
(Received May 24, 1996)

A semiconducting organic radical cation salt with a magnetic anion, TMTSF•FeCl$_4$ (ρ_{rt} = 40 Ωcm), was prepared. The crystal undergoes an antiferromagnetic ordering below T_N = 4K with the easy axis perpendicular to the TMTSF stacking direction. X-ray crystallographic analysis 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.

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 couples 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.

Single crystals of tetrachloroferrate salts of TMTSF were prepared by two methods. Through the ordinary electrocrystallization in 1,1,2-trichloroethane with Pt electrodes under the existence of supporting electrolyte n-Bu$_4$N · 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 isomorphous 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. Reflecting a radical salt (1:1 salt) feature, the crystal of TMTSF•FeCl$_4$ does not show very large conductivity. The crystal is semiconducting with ρ_{rt} = 40 Ωcm and a thermal activation energy E_a = 0.06 eV (between 200 K and 300 K).



Column *A* Column *B*

Figure 1. (a) Crystal structure of TMTSF•FeCl$_4$. (b) Two types of columnar structure of donors in the crystal of TMTSF•FeCl$_4$. Intermolecular Se•••Se distances are also indicated. Hydrogen atoms are omitted for clarity.

Figure 1a shows the crystal structure of the cation radical salt TMTSF · FeCl$_4$. One can find two types of donor column (Figure 1b), 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)$_2$X (X=BF$_4$, ClO$_4$, PF$_6$, etc.), 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. Recently some cross-type dimeric TTF donors have been prepared for this purpose.[6] Here, such a cross-type stacking can be obtained using the ordinary planar donor TMTSF.

Magnetic susceptibility (χ) of the salt 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

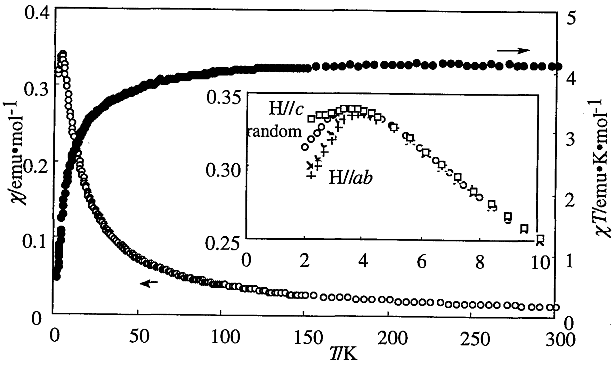


Figure 2. Temperature dependence of magnetic susceptibility of TMTSF•$FeCl_4$. The inset magnifies the low temperature susceptibility as a function of temperature for two field directions, *c* being the donor stacking axis.

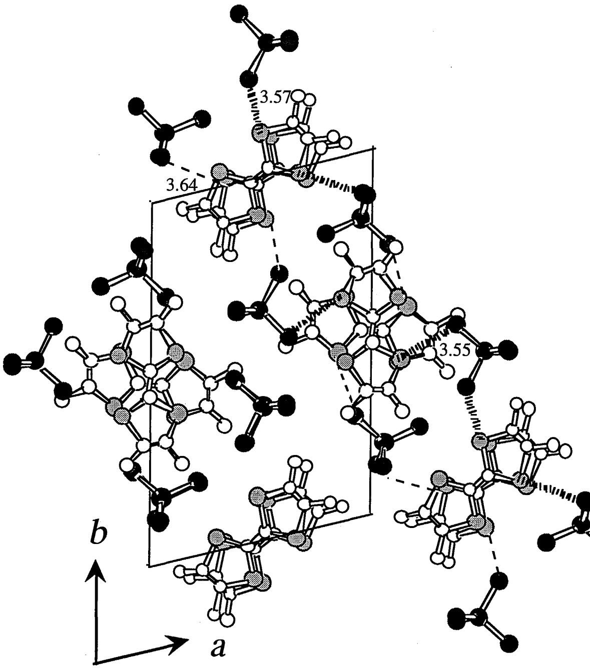


Figure 3. Se•••Cl contacts in the crystal of TMTSF•$FeCl_4$ viewd normal to the *ab* plane. The thick line (ıııııııı) shows the contact in a upper layer and bloken line (..........) the contact in a lower layer.

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. Temperature dependence of the susceptibility indicates intermolecular antiferromagnetic interaction.[7] As shown in Figure 2, the χ-value decreases below 4K, suggesting that antiferromagnetic spin ordering occurs at T_N = 4K. 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.

From the structural analysis one can find that the magnetic anions are fairly isolated from each other in the crystal.[8] 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 4K.

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.

This work partly supported by NEDO, was performed in JRCAT under the joint research agreement between NAIR and ATP.

References and Notes

1 a) A. Izuoka, R. Kumai, T. Tachikawa, and T. Sugwara, *Mol. Cryst. Liq. Cryst.*, **218**, 213 (1992). b) E. Dormann, M. J. Nowak, K. A. Williams, R. O. Angus Jr., and F. Wudl, *J. Am. Chem. Soc.*, **109**, 2594 (1987).
2 C. Zenner, *Phys. Rev.*, **82**, 403 (1951).
3 a) T. Sugano, H. Takenouchi, D. Shiomi, and M. Kinoshita, *Synth. Met.*, **41**, 2217 (1991). b) H. Endres, *Acta Cryst.*, **C43**, 439 (1987). c) T. Mallah, C. Hollis, S. Bott, M. Kurmoo, and P. Day, *J. Chem. Soc. Dalton Trans.*, **1990**, 859. d) A. W. Graham, M. Kurmoo, and P. Day, *J. Chem. Soc., Chem. Commun.*, **1995**, 2061. e) J. A. Ayllón, I. C. Santos, R. T. Henriques, M. Almeida, E. B. Lopes, J. Morgado, L. F. Veiros, and M. T. Duarte, *J. Chem. Soc., Dalton Trans.*, **1995**, 3543. f) Y.-K. Yan and D. M. P. Mingos, *Chem. Soc. Rev*, **1995**, 203. And references cited therein.
4 a) F. Goze, V. N. Laukhin, L. Brossard, A. Audouard, J. P. Ulmet, S. Askenazy, T. Naito, H. Kobayashi, A. Kobayashi, M. Tokumoto, and P. Cassoux, *Synth. Met.*, **71**, 1901 (1995). b) J. Yamaura, K. Suzuki, Y. Kaizu, T. Enoki, K. Murata, and G. Saito, *J. Phys. Soc. Jpn.*, in printing.
5 Crystallographic data for TMTSF•$FeCl_4$: formula $C_{10}H_{12}Se_4FeCl_4$; Fw = 1093.75; 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} = 3.88; radiation MoKα (λ = 0.71073 Å) ; R = 0.067, R_w = 0.051 for 1714 unique reflections.
6 a) J. Tanabe, T. Kudo, M. Okamoto, Y. Kawada, G. Ono, A. Izuoka, and T. Sugawara, *Chem. Lett.*, **1995**, 579. b) K. Takimiya, Y. Shibata, K. Imamura, A. Kashihara, Y. Aso, T. Otsubo, and F. Ogura, *Tetrahedron Lett.*, **36**, 504 (1995).
7 A Curie-Weiss plot shows Weiss temperature θ = -7.5 K.
8 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.