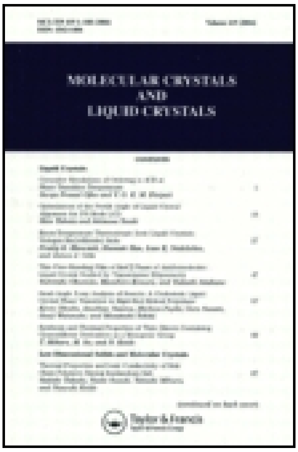

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Solid State Properties of Charge Transfer Complexes of TTF Derivatives with 3D-Transition Metal Halides

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SOLID STATE PROPERTIES OF CHARGE TRANSFER COMPLEXES OF TTF DERIVATIVES WITH 3D-TRANSITION METAL HALIDES

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Abstract We investigated structure, electronic and magnetic properties of organic conductors with 3d-transition metal halide anions. The crystal structure investigation in (TTM-TTF)$CuBr_4$ shows a novel type of nonplanar TTM-TTF^{2+} structure. Susceptibilities obey the Curie's law, suggesting the absence of magnetic interactions between Cu^{2+} magnetic moments. (BEDT-TTF)$_6Cu_2Br_6$ is a two-dimensional conductor with the mixed valence state of Cu^{2+}/Cu^{+}. A structural transition with a first order nature is found at T_c=59K, which is related to the deformation of $CuBr_4^{2-}$ ligand. The application of pressure modifies the transition to a metal-semiconductor one. An antiferromagnetic long range order accompanied by a short range order is observed at T_N=7.5K. This suggests the presence of strong antiferromagnetic interactions achieved by the coupling between Cu^{2+} localized moments and donor π-electrons.

INTRODUCTION

Organic donors belonging to the TTF family give conducting charge transfer complexes with many kinds of anions, leading to organic metals and superconductors, where the π-electronic systems play an essential role in transport properties.[1] Among these charge transfer complexes, complexes with 3d-transition metal anions provide interesting solid state properties with the coexistence of electron transport behaviors and magnetism. Namely, the π-electrons on the donors work as conducting carriers, while localized magnetic moments of 3d-transition metal ions contribute to magnetism. Interactions between π-electrons and 3d-transition metal localized spins (π-d interaction) will give novel organic magnetic conductors, which will be candidates for organic analogues of ordinary magnetic metals with the s-d interactions. In the case of semiconductive organic materials, the π-d interaction is not effective to provide magnetic interactions. However, even in semiconductive materials, superexchange interactions through the π-electronic system of donor molecules will contribute to enhance magnetic interactions between localized magnetic moments of d-electrons, if there are shorter atomic contacts between a donor and a magnetic anion than the corresponding van der Waals distances. Therefore, the participation of the π-electrons gives a new type of organic magnets on the basis of molecular crystals. From this view point, we have been developing charge transfer complexes of BEDT-TTF (bis-(ethylenedithio)-tetrathiafulvalene) and TTM-TTF (tetra-(methylthio)-tetrathiafulvalene) with 3d-transition metal halide anions and investigating their transport and magnetic properties. In this paper, we present the experimental results on structures, electronic and magnetic properties for two complexes; (TTM-TTF)$CuBr_4$ and $(BEDT\text{-}TTF)_6Cu_2Br_6$. The latter was revealed to be a typical organic magnetic conductor where the π-d interactions play an important role to give the novel cooperation of transport and magnetic systems.

EXPERIMENTAL RESULTS AND DISCUSSION

(TTM-TTF)$CuBr_4$

The X-ray analysis of (TTM-TTF)$CuBr_4$ gives a monoclinic structure $C_{2/n}$ with a=8.2816(8)Å, b=17.777(1)Å, c=16.0234(9)Å, β=107.151(5)°, V=2254.0(3)$Å^3$, z=4, as shown in Fig.1. The valence states are found to be Cu^{2+} and TTM-TTF^{2+}. A $CuBr_4^{2-}$ anion has a distorted tetrahedral form. The shortest atomic distances between a donor and a $CuBr_4^{2-}$ ion are estimated to be Br-C=3.48Å and Br-S=3.507Å, which are considerably smaller than the corresponding van der Waals distances. These short atomic contacts bring about a linear inter-molecular network parallel to the a-axis. This might suggest the presence of possible superexchange paths via TTM-TTF donors between Cu^{2+} ions. The structure of a TTM-TTF molecule deviates strongly from a planar one. The dihedral angle between two connected five-membered rings is 46°, and the C-C bond between the two five-membered rings has a single bond nature with the length of 1.541(3)Å. In general, the C-C bond distance is elongated towards the single bond distance as the

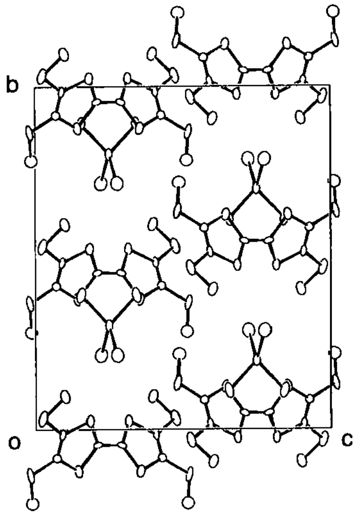


Fig.1. Crystal structure of (TTM-TTF)$CuBr_4$.

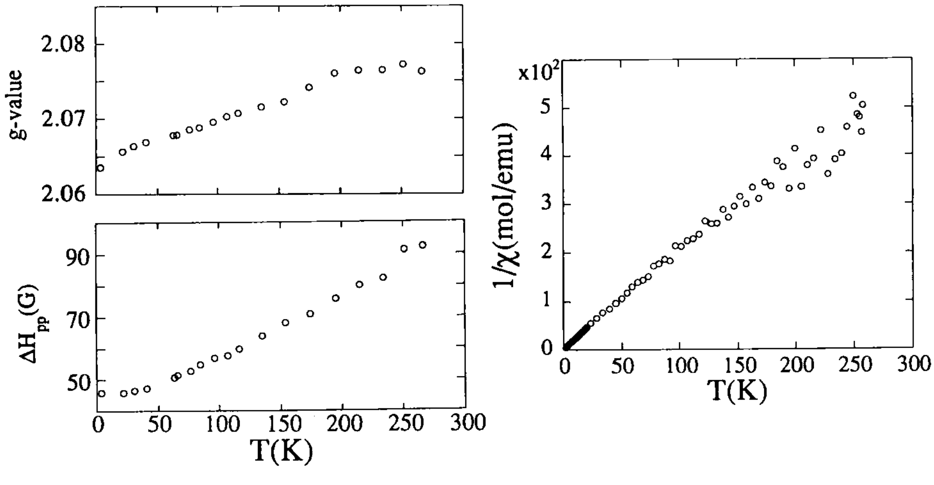


Fig.2. Temperature dependence of ESR linewidth ΔH_{pp}, g-values and magnetic susceptibilities χ in (TTM-TTF)$CuBr_4$, where the field is applied parallel to the b-axis.

valence of TTM-TTF increases.[2-5] There have been reports[2,3] on TTM-TTF complexes having the TTM-TTF^{2+} valence state, $(TTM\text{-}TTF)^{2+}(Br_3^-)_2$ and $(TTM\text{-}TTF)^{2+}(AuCl_4^-)_2$, where a deviation from a planar structure is small and the C-C bond distance ranges 1.43Å which is intermediate between the single and double bond distances. The present result suggests an anomalous molecular structure of TTM-TTF^{2+}, which strongly deviates from the TTM-TTF^{2+} structure in ordinary charge transfer complexes. Conductivity measurements show semiconductive properties with ρ_{rt}~$3x10^{11}\Omega$ cm. The low conductivities are considered to be related to the ionic structure with complete charge transfer between TTM-TTF^{2+} and $CuBr_4^{2-}$ in the compound. Figure 2 shows temperature dependence of ESR spectra in the applied field parallel to the b-axis and magnetic susceptibilities. The ESR spectra have a single Lorentzian lineshape with the linewidth of ΔH=90G and the g-value of g_b=2.075 at room temperature, and are assigned to Cu^{2+} ions. The g-value, g_b, decreases linearly as temperature is lowered, while the linewidth decreases by about 50% when temperature is lowered from room temperature to 4.2K. The decrease in the g-value demonstrates that the distortion of the Br ligand from a tetrahedral symmetry is enhanced at low temperatures. The magnetic susceptibilities obey the Curie-Weiss law with a small negative Weiss constant Θ=-0.5K. Therefore, the magnitude of exchange interactions between Cu^{2+} magnetic moments is negligibly small although the crystal structure suggests the presence of inter-molecular interactions.

$(BEDT\text{-}TTF)_6Cu_2Br_6$

$(BEDT\text{-}TTF)_6Cu_2Br_6$ has a two-dimensional arrangement of BEDT-TTF donors in the bc-plane, which forms a conducting sheet with π-electron carriers.[6] In the conducting BEDT-TTF layer which is isolated by adjacent copper bromide anion layers, there coexist neutral BEDT-TTF and partially charged BEDT-$TTF^{+3/4}$ with the ratio of 1:2. The extended Hückel band calculation suggests a metallic electronic structure with a 1/4 filled conduction band for this compounds. In the anion layers, both $CuBr_4^{2-}$ and $CuBr_2^-$ ions are randomly distributed with the ratio of 1:1. Here, $CuBr_4^{2-}$ has a planar structure with magnetic Cu^{2+} (S=1/2), while $CuBr_2^-$ with the monovalent state Cu^+ has a linear configuration. The mixed valence state of Cu^{2+}/Cu^+ is favorable for interactions between magnetic Cu^{2+} moments and π-conduction carriers.

Resistivities show semiconductive behavior with ρ_{rt}~4.1Ω cm and

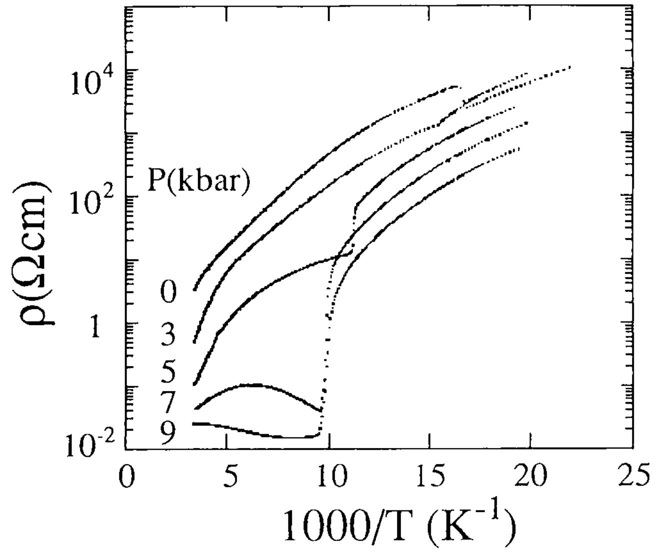


Fig.3. Temperature dependence of resistivities ρ at several pressures for $(BEDT\text{-}TTF)_6Cu_2Br_6$.

the activation energy E_a=0.07eV. Although the semiconductive properties contradict the metallic state predicted by the band calculation, the highly conductive properties is suggestive of the electronic state which is situated in the vicinity of the metallic structure. This is demonstrated by the conductivity behaviors in high pressures. The application of pressure strongly enhances conductivities and the resistivity values are reduced by about 140 times at 12kbar. Temperature dependence of resistivities is shown in Fig.3 at several pressures. In ambient pressure, a phase transition takes place at T_c=59K, as indicated as an abrupt change in the resistivities in Fig.3. Applied pressure makes the transition temperature elevated, and T_c reaches 104K around 7kbar, where the high temperature phase above T_c becomes metallic.

Figure 4 shows temperature dependence of specific heats. An anomaly having a first order nature is observed at T_c, where the magnitude of the anomalous part is about 10% of the total specific heat. In ambient pressure, ESR spectra assigned to Cu^{2+} are observed with the linewidth of ΔH~100G at room temperature.[7,8] The

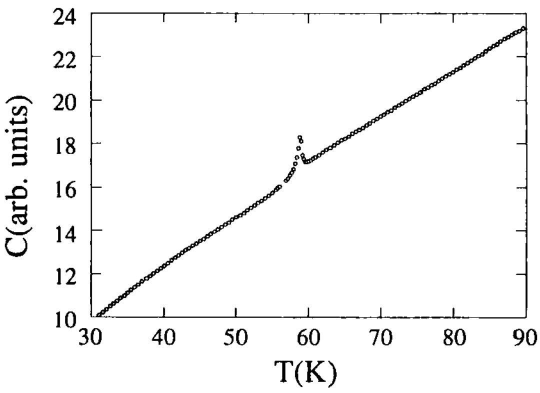


Fig.4. Temperature dependence of specific heats C for (BEDT-TTF)$_6$Cu$_2$Br$_6$.

g-value has an abrupt change at T_c=59K, above and below which the g-values have a weak temperature dependence. ΔH is almost independent of temperature above T_c, and, after it drops to 45G at T_c, it gradually decreases as the lowering of temperature. From the angular dependence of the g-values, the phase transition is related to the distortion of $CuBr_4^{2-}$ from a planar to a tetrahedral ligand structure. In Fig.5 is shown temperature dependence of spin susceptibilities obtained after the correction of the Pascal diamagnetic contribution. Above T_c, the magnetic susceptibilities obey the Curie-Weiss law with the Weiss temperature Θ=-140K, suggesting the presence of considerably large antiferromagnetic interactions acting between localized Cu^{2+} magnetic moments. The magnitudes of the magnetic susceptibilities are reduced by about a half at T_c, and below T_c, a broad peak appears around 25K which is considered to be associated with a magnetic short range order. A possible explanation for the large decrease in the magnitudes of the magnetic susceptibilities at T_c is that the distortion of $CuBr_4^{2-}$ ligand enhances antiferromagnetic interactions. Finally, we observe a small anomaly at T_N=7.5K. Taking into consideration the experimental results of the ESR study exhibiting the abrupt increases of the linewidth at T_N,[7,8] the anomaly at T_N is proved to indicate the occurrence of a three dimensional magnetic long range ordering. As the anion layer forms a planar network of Cu ions with the number of nearest neighbors z=4, we employ the theoretical model

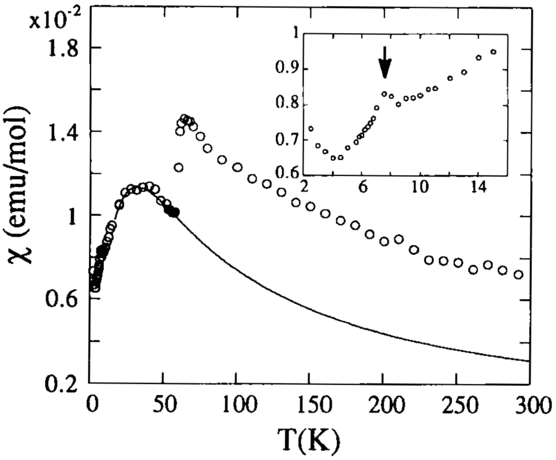


Fig.5 Temperature dependence of spin susceptibilities χ for $(BEDT\text{-}TTF)_6Cu_2Br_6$. The solid line denotes J=-17K.

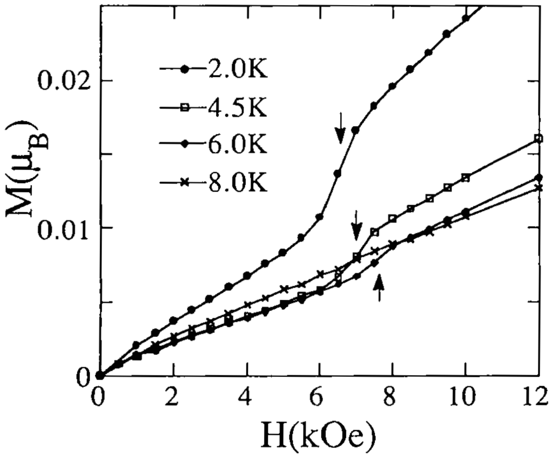
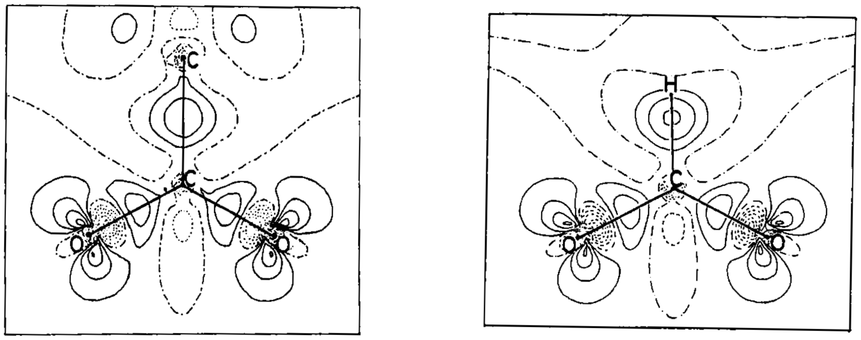


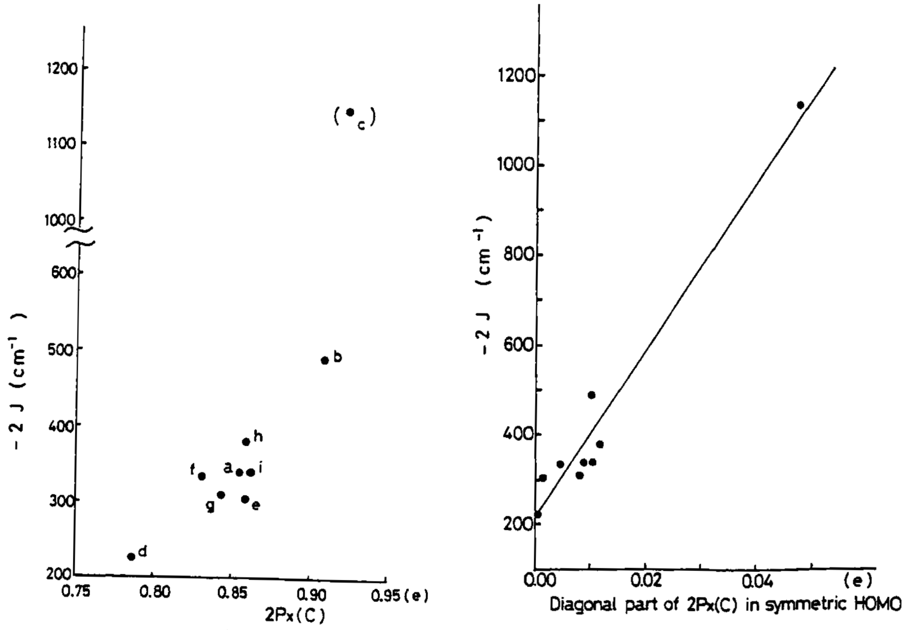
Fig.6 Magnetization curves of $(BEDF\text{-}TTF)_6Cu_2Br_6$ at several temperatures.

of a square planar two-dimensional Heisenberg antiferromagnet in order to analyze the behavior of the magnetic susceptibilities around the short range order hump.[9] A best fitting to the observed susceptibilities gives the magnitude of the exchange interaction J=-17K. Figure 6 shows magnetization curves at several temperatures. A weak anomaly, which is about 1% of the total magnetic moment is observed at



(a) (b)

FIGURE 1 Theoretical deformation densities for (a) CH_3COO^- and (b) $HCOO^-$ ions. The contour interval is 0.2 e $Å^{-3}$. The negative contours are dotted, the zero contours chain-dotted.



(a) (b)

FIGURE 2 The average $-2J$ value of $[Cu(RCOO)_2\ L]_2$ *versus* (a) the $2p_x$ electron population of the central C atom and (b) the diagonal part of $2p_x$(C) in the symmetric HOMO. (a)-(i) stand for R=CH_3, H, $SiMe_3$, CCl_3, $CHCl_2$, CH_2Cl, CF_3, CH_2CH_3, CMe_3, respectively.

$(BEDT\text{-}TTF)_6Cu_2Br_6$ is a two-dimensional conductor with π-conducting carriers. The anion layers consisting of $CuBr_4^{2-}$ and $CuBr_2^-$ have the mixed valence state Cu^{2+}/Cu^+. A structural phase transition is observed at T_C=59K, which is associated with the distortion of the $CuBr_4^{2-}$ ligand from a planar to a tetrahedral structure. The application of pressure modifies the transition to be a metal-semiconductor transition, accompanying the elevation of T_C. Magnetic susceptibilities obey the Curie-Weiss law with extremely large antiferromagnetic interactions (Θ =-140K). The structural transition induces a reduction in the magnitude of the magnetic susceptibilities, suggesting the enhancement in the interactions. Below T_C, an anomaly related to a magnetic short range order is observed around 25K, which is explained with the two-dimensional Heisenberg antiferromagnet. A three dimensional antiferromagnetic long range order is found at T_N=7.5K. The strong antiferromagnetic interactions and the presence of the three dimensional magnetic ordering are considered to be achieved by the coupling between Cu^{2+} localized spins and π-conduction carriers of organic donors. This is the first example which shows that the π-d interactions bring about the cooperation of the transport system and the magnetic system in an organic conductor.

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