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Electronic Structure of (BEDT-TTF)CuCl$_2$ Complex

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The X-ray photoelectron spectra and the ESR spectra of the (BEDT-TTF)CuCl$_2$ complex were taken. The analysis of the X-ray photoelectron spectra shows that the Cu atoms in (BEDT-TTF)CuCl$_2$ are in a mixed-valence state consisting of mono and bivalent cations and the concentration ratio of Cu(I) and Cu(II) is determined to be 2:1. The ESR signals show the presence of the BEDT-TTF cation radical and Cu(II)Cl$_2$. The temperature dependence of the magnetic susceptibility of these components were obtained from the ESR data.

A new family of organic conductors, based on 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene (BEDT-TTF), has been synthesized[1] and some of them are the first sulfur-based organic superconductors, (BEDT-TTF)$_2$ReO$_4$(T_c=2 K) at 0.4 GPa pressure[2] and (BEDT-TTF)$_2$I$_3$(T_c=1.5 K) at ambient pressure.[3] Following these complexes, a large number of BEDT-TTF salts have been synthesized in an attempt to obtain an organic superconductor with a high critical temperature. Many BEDT-TTF salts ever known have compositions (BEDT-TTF)$_2$X or (BEDT-TTF)$_3$X$_2$ where X is a monovalent anion such as PF$_6^-$,[4] AsF$_6^-$,[5] InBr$_4^-$,[6] ClO$_4^-$,[7] I$_3^-$,[8–10] or other polyhalide series. (BEDT-TTF)X(THF)$_{0.5}$ (X=ReO$_4^-$ and IO$_4^-$) salts form 1:1 salts which consist of four independent complex units in the unit cell.[11] The new type of the 1:1 salt of (BEDT-TTF)CuCl$_2$ was recently found by us.[12] In this paper, we report the results of the measurement of the X-ray photoelectron and ESR spectra of the (BEDT-TTF)CuCl$_2$ complex.

Experimental

Black prism crystals were prepared by the diffusion method of BEDT-TTF and CuCl$_2$·2H$_2$O in 1,1,2-trichloroethane. The X-ray photoelectron spectra were recorded on a JEOL model JESCA-3A spectrometer. Aluminium $K_{\alpha 1,2}$ radiation (1486.6 eV) was used as the X-ray excitation source and the measurements were carried out at 5×10^{-8} Torr or below. The ESR spectra were taken by a Varian E112 at X-band with a continuous helium flow cryostat and a rectangular microwave cavity.

Results and Discussion

Figure 1 shows the X-ray photoelectron spectra (ESCA) of the (BEDT-TTF)CuCl$_2$ complex together with CuCl$_2$·2H$_2$O and CuCN. The cupric compound has intense satellites on the higher binding energy sides of the 2p$_{1/2}$ and 2p$_{3/2}$ peaks, however, the cuprous compound has no satellite associated with these bands.[13] Such a satellite pattern may be explained by the difference in the electronic structures of 3d^9 for Cu(II) and 3d^{10} for Cu(I), respectively. The half-width (γ_ω) and intensity (γ_i) ratios of the satellite to the main 2p$_{3/2}$ peak are estimated to be γ_ω=1.66 and γ_i=0.4 for CuCl$_2$·2H$_2$O. However, these values are γ_ω=1.4 and γ_i=0.15 for the (BEDT-TTF)CuCl$_2$ complex. Accordingly, the ESCA spectrum of (BEDT-TTF)CuCl$_2$ is considered as the overlap of the signals of Cu(I) and Cu(II) in the 2p energy region. The dashed line of the 2p$_{3/2}$ peak shows the contribution of Cu(II) to the ESCA line shape of the (BEDT-TTF)CuCl$_2$ complex and the ratio of area of the dashed line part and the remaining part of the 2p$_{3/2}$ peak is estimated to be 1:2. That is, the Cu atoms in (BEDT-TTF)CuCl$_2$ are in a mixed-valence state consisting of mono and bivalent

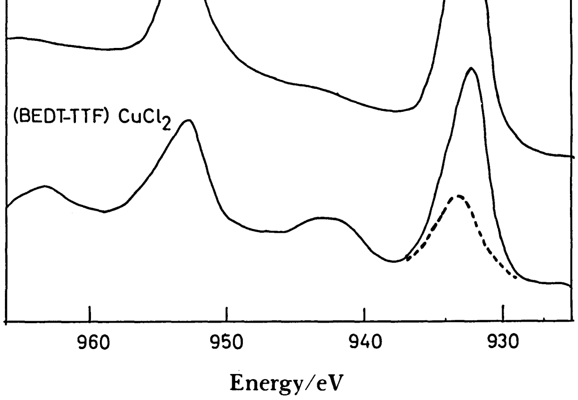

Fig. 1. X-Ray photoelectron spectra of CuCl$_2$·2H$_2$O, CuCN, and (BEDT-TTF)CuCl$_2$.

cations and the concentration ratio of $[Cu(I)Cl_2]^-$: $[Cu(II)Cl_2]$ or $[BEDT\text{-}TTF\cdot]^+$:[BEDT-TTF] is determined to be 2:1.

The ESR spectra of (BEDT-TTF)$CuCl_2$ were measured over a temperature range of 4—300 K as is shown in Fig. 2. The numbers in parenthesis mean the relative intensity ((peak value/gain value)$\times 10^6$) of the maximum ESR peak. Bands I and II are the ESR signals of the impurity of $CuCl_2\cdot 2H_2O$.[14] The sharp band III with $g=2.009$ can be assigned to the unpaired π-electron of the BEDT-TTF cation radical[15] and the broad band IV with $g=2.003$ to the d electron of $Cu(II)Cl_2$.

The ESR spectra can be expressed by the following equation:

$$I = \sum_i \frac{2B_iA_i^3(H_i-H)}{[1+A_i^2(H_i-H)^2]^2}. \qquad (1)$$

The parameters A_i, B_i, and H_i are determined by the best fit of Eq. 1 to the observed ESR spectra and the magnetic susceptibility $X_i(T)$ of the i-th component at temperature T is given by the absolute intensity of $(\pi B_i/A_i)_T$ of the ESR signal,

$$X_i(T) = C\left(\frac{\pi B_i}{A_i}\right)_T. \qquad (2)$$

The coefficient C is estimated with the observed static magnetic susceptibility at room temperature of $X(290\text{ K})=9\times 10^{-4}$ emu mol^{-1} by the following equation:

$$X(290\text{K}) = C\sum_i \left(\frac{\pi B_i}{A_i}\right)_{T=290\text{K}}. \qquad (3)$$

The value of $X(290\text{ K})$ was corrected by considering the diamagnetic effect of the constituting atoms. The temperature dependences of the susceptibilities X_{III} and X_{IV} are shown in Figs. 3 and 4.

Band III is the ESR signal of the BEDT-TTF radicals with $g=2.009$ at room temperature and with the temperature-independent line-width of $\Delta H \approx 20$G. The susceptibility X_{III} seems to be independent of temperature above 240 K and decreases gradually from

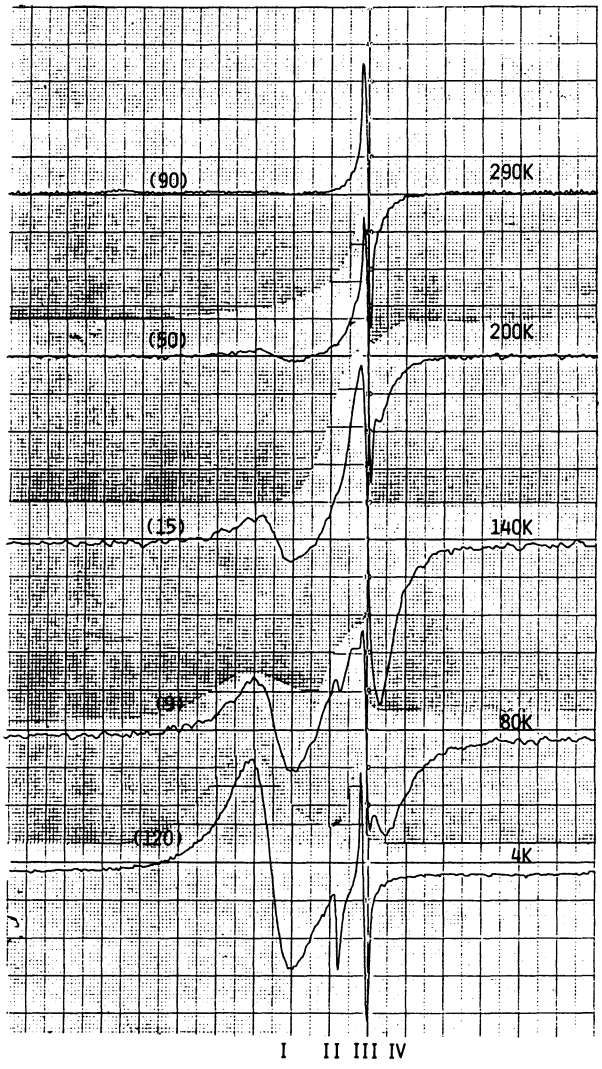

Fig. 2. ESR spectra of (BEDT-TTF)$CuCl_2$. The numbers in parenthesis mean the relative intensity.

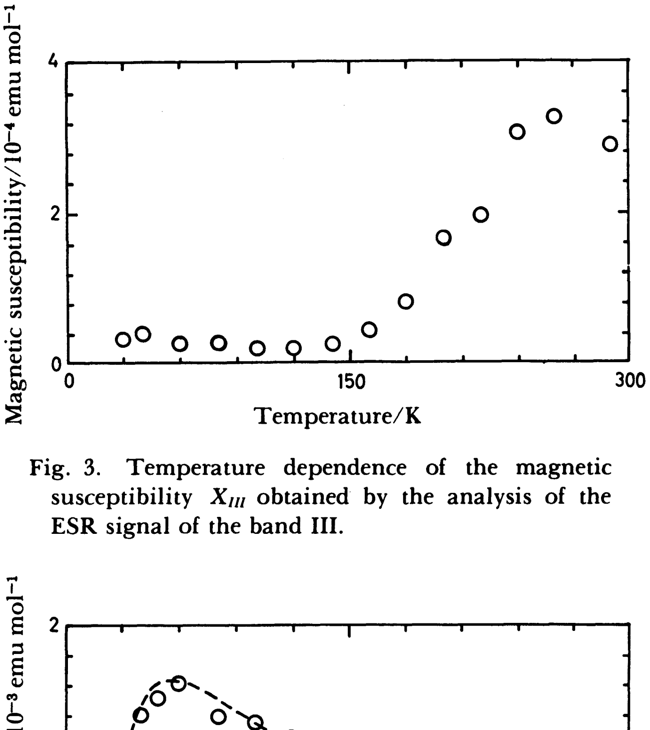

Fig. 3. Temperature dependence of the magnetic susceptibility X_{III} obtained by the analysis of the ESR signal of the band III.

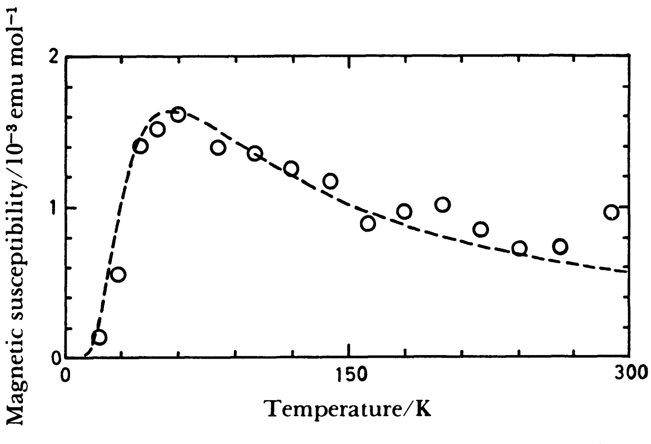

Fig. 4. Temperature dependence of the magnetic susceptibility X_{IV} obtained by the analysis of the ESR signal of the band IV. (∘∘∘∘: Obsd., ------: Calcd.)

240 to 140 K. After that, X_{III} remains constant down to 10 K. Then, the susceptibility below 240 K is described by the singlet-triplet model as follows:16)

$$X(T) = \frac{0.750\,g^2}{T} n_{\mathrm{III}} \exp(-J/kT), \tag{4}$$

where $g=2$ and $J=850$ K. $n_{\mathrm{III}}=0.78$ is the mole number of the BEDT-TTF cation radical per one mole of (BEDT-TTF)CuCl$_2$. This value ($\approx 3/4$) is in agreement with the value (2/3) determined by the ESCA experiment. However, the calculated susceptibility above 240 K increases with the temperature and has no maximum peak below 300 K although the observed susceptibility does not change with temperature. Such temperature-independent susceptibility from 240 to 300 K may be described by the Pauli paramagnetism of the one-dimensional model. As BEDT-TTF molecules form the one-dimensional stacking column along the c axis (Fig. 5) and the overlap between the π- molecular orbitals along the stacking column forms the one-electron tight-binding band with a bandwidth 4t, the calculated $X(T)$ is given by the simple Pauli susceptibility17),

$$X = \frac{N_0\,\mu_B^2}{\pi t \sin(\rho\pi/2)}, \tag{5}$$

where N_0 is Avogadro's number, μ_B is the Bohr magneton and $\rho=4/3$ is the number of carrier electrons per BEDT-TTF molecule. Accordingly, the observed susceptibility of ca. 3×10^{-4} emu mol^{-1} at room temperature gives $t\approx 0.19$ eV. Such large value of the transfer integral may be explained by the short interplanar distance of 3.39 A and the two-dimensional interaction of BEDT-TTF molecules.12) The above-mentioned change of the magnetic susceptibility in the vicinity of 240 K may be explained by the metal-insulator transition due to the Peierls instability.

The temperature dependence of the susceptibility X_{IV} of band IV can be depicted by the following Bleaney-Bowers equation16) for the dimerization of Cu(II)Cl$_2$,

$$X(T) = \frac{0.125\,g^2}{T}\,\frac{2\,n_{\mathrm{IV}}}{1+\frac{1}{3}\exp(J/kT)}, \tag{6}$$

where $g=2$ and $J=90$ K. The magnitude of the g value obtained ($g\approx 2.00$) is almost similar to that of Cu(II).18) $n_{\mathrm{IV}}=0.245$ is the mole number of Cu(II)Cl$_2$ per one mole of (BEDT-TTF)CuCl$_2$. This value ($\approx 1/4$) is comparable with the value (1/3) determined by the ESCA experiment. The difference between these two values obtained by the ESCA and the magnetic susceptibility measurements may be due to the presence of the impurity of CuCl$_2\cdot$2H$_2$O. These facts mean that the crystal of the (BEDT-TTF)CuCl$_2$ complex consists of the columns of the stack of BEDT-TTF and the dimers of [Cu(II)Cl$_2$]$_2$ and [Cu(I)Cl$_2$]$^{2-}_2$. However, the crystal belongs to the space group of $P\bar{1}$ ($Z=1$) and the projection of the structure along the c axis is shown in Fig. 5.12) Accordingly, all of BEDT-TTF molecules and CuCl$_2$ molecules are crystallographically equivalent and the charge carrier delocalizes along each column of BEDT-TTF and CuCl$_2$.

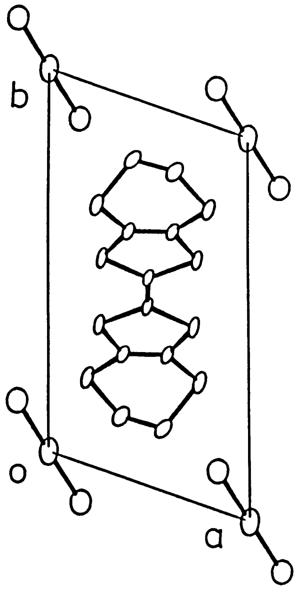

Fig. 5. Projection of the structure of (BEDT-TTF)-CuCl$_2$ along the c axis.12)

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