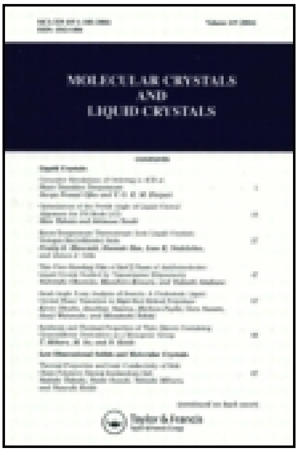

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Crystal Structure and Physical Properties of BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) Salt Coupled with a Photo-Sensitive Transition Metal Complex

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Crystal Structure and Physical Properties of BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) Salt Coupled with a Photo-Sensitive Transition Metal Complex

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A new salt of BEDT-TTF with photo-sensitive transition metal complex $[RuCl_5(NO)]^{2-}$ has been synthesized. The crystal structure was determined and attributed to the κ-type salt. Although calculated band structure shows two dimensional Fermi surfaces and predicts a metallic behavior, the resistivity shows semiconducting temperature dependence up to 6 kbar. Both the ESR signals of $BEDT\text{-}TTF^{+}$ and $NO^{\cdot}$ exhibited a photo-induced effect.

Keyword Organic conductors; BEDT-TTF; photo-induced effect

INTRODUCTION

Organic charge-transfer salts have been rigorously investigated since the discovery of the superconductivity for $(TMTSF)_2PF_6$ in 1980. Recent searches in this field are mainly on the materials having multifunctionality coupled with transport and magnetic properties. For example, the first organic superconductor containing paramagnetic anion complex : β"-$(BEDT\text{-}TTF)_4(H_3O)Fe(C_2O_4)_3C_6H_5CN$ and the organic superconductor coexisting with antiferromagnetic phase : κ-$(BETS)_2FeBr_4$ has been reported in 1995[1] and 1999[2]. The study on BETS salts[3] showed strong influence of the anion layer on the conduction electrons. In order to control the conducting and magnetic properties by photo-irradiation, we have used the photo-sensitive anion complex $[RuCl_5(NO)]^{2-}$ as a counter anion. Nitrosyl metal complexes : $ML_n(NO)$(M = Fe, Ru, Os, L = ligand) are well known to have persistent photo-induced metastable states at low temperature[4]. Some organic charge-transfer salts with $[Fe(CN)_5(NO)]^{2-}$ are already known[5], however, no irradiation effect has been reported. In this paper, we report on the first example of the photo-induced effect on an organic charge-transfer salt.

EXPERIMENTAL

The title compound was prepared by the electrical oxidization of BEDT-TTF in benzonitrile with $K_2[RuCl_5(NO)]$ and 18-crown-6 as supporting electrolytes. X-ray diffraction data were collected with a RIGAKU AFC-5S diffractometer. Band calculation was performed based on tight binding extended Hückel approximation. The resistivity under high pressure was measured by four probe method. The pressure was monitored by the resistivity of manganin wire. EPR spectra were measured by an X-band JES-TES 300 spectrometer. The sample was irradiated with 400-500 nm light by using filtered Hg lamp.

CRYSTAL STRUCTURE

Crystal data of κ -(BEDT-TTF)$_4$[RuCl$_5$(NO)]C$_6$H$_5$CN are as follows: triclinic, $P\bar{1}$, $Z = 1$, $a = 11.898(3)$Å, $b = 17.164(3)$Å, $c = 8.749(2)$Å, $\alpha = 92.62(1)°$, $\beta = 95.11(2)°$, $\gamma = 95.41(2)°$, $V = 1768.9(6)$Å^3, $R = 0.079$. The structure comprises the layers of anions(Fig.1(a)) and cations(Fig.1(b)). All layers are parallel to the *ac* plane.

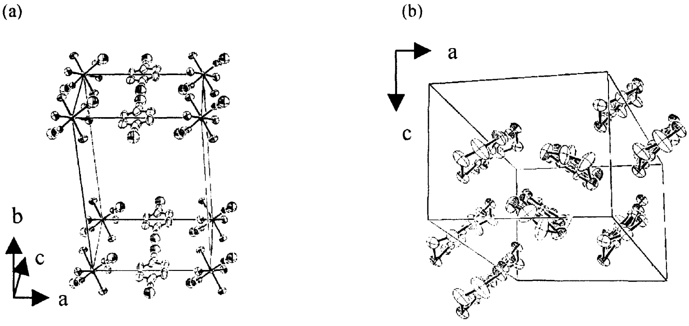

Fig.1 Crystal structure of κ -(BEDT-TTF)$_4$[RuCl$_5$(NO)]C$_6$H$_5$CN, (a) anion layer, (b) BEDT-TTF layer, Hydrogen atoms were omitted for clarity.

As shown in Fig.1(b), this salt has κ -type arrangement of BEDT-TTF. Two crystallographically independent BEDT-TTF molecules exist in the unit cell. Central C=C and C-S bond lengths[6] suggest that both molecules have the same oxidation state of +1/2, which is in agreement with the chemical formula assuming the valence of the ruthenium anion to be divalent. As for the anion layer, [RuCl$_5$(NO)]$^{2-}$ and C$_6$H$_5$CN have inversion disorder. CN and NO groups occupy two positions.

ELECTRICAL TRANSPORT

The conductivities at room temperature and 100 K for the title compound are about 10^{-3} Scm^{-1} and about 10^{-7} Scm^{-1}, respectively.

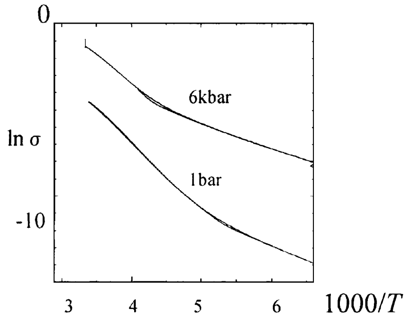

Fig.3 The Arrhenius plot of κ-(BEDTTTF)$_4$[RuCl$_5$(NO)]C$_6$H$_5$CN

As shown in Fig.3, the Arrhenius plot indicates a transition with a small hysteresis around 200 K. The existence of the hysteresis is typical of first order phase transition. The activation energies below and above 200 K are 0.15eV and 0.45 eV, respectively.

Semiconducting behavior is retained up to 6 kbar. With increasing pressure, the transition temperature shifts to 240 K, and the activation energies in the low and high temperature phases become 0.04 eV and 0.15 eV, respectively.

BAND CALCULATION

The band structure, the electronic density of states, and the Fermi surface of the title compound are shown in Fig.4. Transfer integrals are listed in Table 1. As shown in Fig.4, a hole-like Fermi surface and an electron-like one appear around X- and M-point, respectively. Thus, the band structure indicates that this salt is not a band insulator. Despite of the dimerization, the HOMO bands do not split. Generally, the weak dimerization and large band width do not favor the Mott insulating state The intermolecular Coulomb repulsion, which we ignored in the calculation, may be culpable for the charge localization.

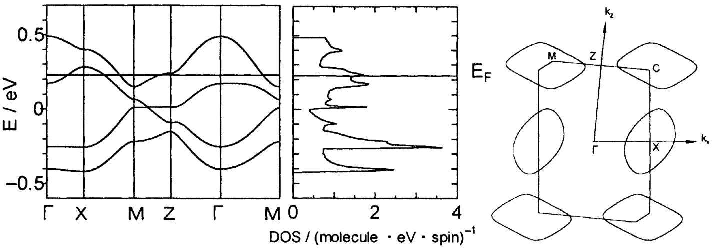

Fig.4 The band structure, the density of states, and the Fermi surface of
κ -(BEDTTTF)$_4$[RuCl$_5$(NO)]C$_6$H$_5$CN

Table 1 Transfer integrals (meV), the labeling of the molecules relates to Fig.1(b)

II_{I}-c	II+c	275	I	II_{I}-c+a	71
I	I_{I}-c+a	132	II	I_{I}-c+a	71
I	I_{I}+a	126	I	II+c	62
II	II_{I}-c	125	II_{I}-c	I_{I}	- 62

EPR MEASUREMENT

EPR spectra of single crystal κ -(BEDT-TTF)$_4$[RuCl$_5$(NO)]C$_6$H$_5$CN at 10 K are shown in Fig.5. The direction of the external magnetic field is parallel to the *a* axis(in-plane). The least square fitting gives two broad signals with Lorenzian shape due to BEDT-TTF$^+$ (g=2.0031) and a narrow signal with Gaussian shape which exhibit hyperfine structure due to the coupling with a ^{14}N nucleus(I=1)(g=2.0050,A=0.51mT). After photo-irradiation for 15 minutes, the EPR signal of NO$^{\cdot}$ decreases, while that of BEDT-TTF$^+$ slightly increases. A straitforward interpretation is that the electron on the NO$^{\cdot}$ is partly injected into the conducting layer of BEDT-TTF. The investigation of the irradiation effect on the conductivity is in progress.

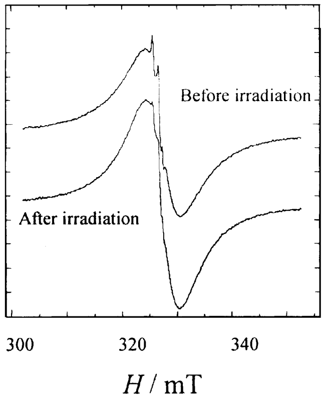

Fig.5 EPR spectra of κ-(BEDTTTF)$_4$[RuCl$_5$(NO)]C$_6$H$_5$CN at 10K

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