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CRYSTAL STRUCTURE AND REFLECTION SPECTRA OF $(DBTTF)_2$-(Cu_2Br_6) COMPLEX

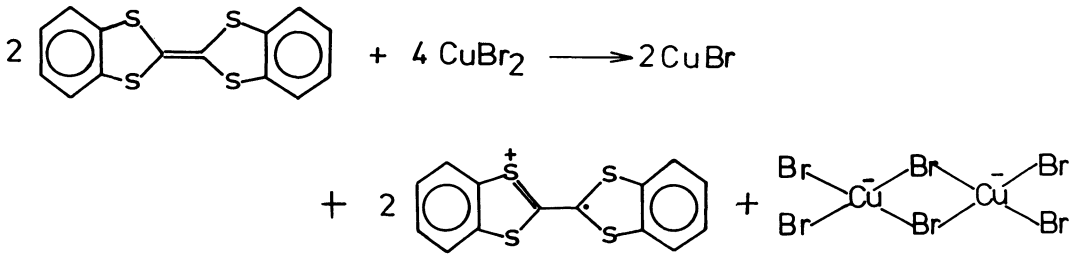
Masashi TANAKA,* Masako HONDA,† Chuji KATAYAMA,†
Hitoshi FUJIMOTO,† and Jiro TANAKA†

Department of Chemistry, College of General Education,
Nagoya University, Nagoya 464
Department of Chemistry, Faculty of Science,
Nagoya University, Nagoya 464

X-Ray and optical reflection measurements of $(DBTTF)_2$-(Cu_2Br_6) single crystals were carried out. The single crystal of the complex consists of stacking columns of the cation molecules $DBTTF^+$. The analysis of the reflection spectra of $(DBTTF)_2$-(Cu_2Br_6) single crystals shows that the electronic structure of $DBTTF^+$ cation system is typical of the dimer type configuration.

There has been considerable interest recently in organic conductors which have highly anisotropic electrical, optical and magnetic properties. Tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is one of them which received the most detailed attention.[1] After the discovery of the complex of TTF-TCNQ, many compounds with fulvalene rings were synthesized to obtain the radical salts with high electrical conductivity. Dibenzotetrathiafulvalene(DBTTF) is one of these compounds[2] and the direct oxidation of DBTTF by metal halides were reported to yield radical salts such as $(DBTTF)_8(SnCl_6)_3$,[3,4] $(DBTTF)_3(SnBr_6)$,[3,4] and $(DBTTF)_2(Cu_2Cl_6)$.[5] These complexes were formed by transfering the electron from the organic donor of DBTTF to the inorganic acceptor. In the present paper, we report the crystal structure and the reflection spectra of the single crystal of $(DBTTF)_2$-(Cu_2Br_6) complex.

The crystal of $(DBTTF)_2$-(Cu_2Br_6) complex was prepared by using the close system-evaporation crystallizer transfering DBTTF and $CuBr_2$ from solid sources to an acetonitrile solution and DBTTF seems to be oxidized according to the next reaction.



The complex crystallizes in the form of the dark reddish plates and the space group is triclini, $P\bar{1}$. The unit cell dimensions are a=9.982, b=12.122, c=7.893Å, α=83.70, β=112.80, and γ=104.97°. The structure was solved by the Monte-Carlo direct method with the aids of MULTAN78 program system using 2678 non-zero unique reflections and refined on F^2 by the full-matrix least squares program. The final R factor is 0.039. The projection of the complex along the c axis are shown in Fig. 1 and the stacking of DBTTF molecules is illustrated in Fig. 2. The stacking column of the cation molecules of DBTTF elongates along the c axis with an interplanar distance of about 3.5Å and two DBTTF molecules form the dimer system in the unit cell. The length(1.397Å) of the central C=C bond in the DBTTF cation is longer than that(1.336Å) of the neutral DBTTF molecule.[6] This fact means that the DBTTF cation radical has the structural formula shown in the reaction equation. All calculations for the x-ray analysis were made on a FACOM M-382 computer of Nagoya University.

The reflection spectra were observed for the polarizations parallel and perpendicular to the b axis on the developed plane of (101) and parallel to the L

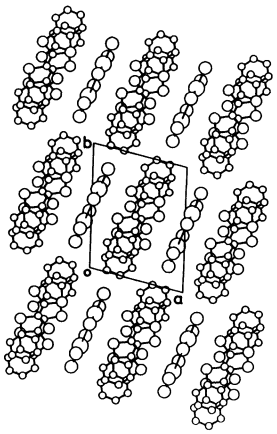


Fig. 1. Projection of $(DBTTF)_2(Cu_2Br_6)$ crystal along the c axis.

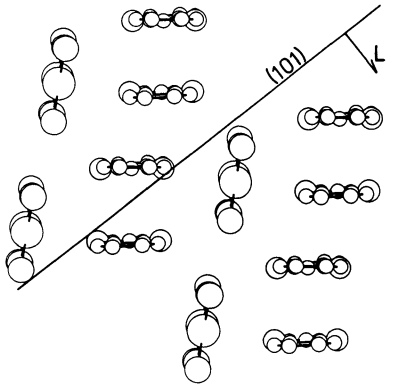


Fig. 2. Stacking of DBTTF molecules in $(DBTTF)_2(Cu_2Br_6)$ crystal.

direction on the (010) plane as are shown in Figs.1 and 2. The reflectivity R can be expreesed by the following equation,

$$R = \frac{1 + |\varepsilon| - \sqrt{2(|\varepsilon| + \varepsilon_1)}}{1 + |\varepsilon| + \sqrt{2(|\varepsilon| + \varepsilon_1)}}$$

using the semiclassical Lorentz dielectric function,

$$\varepsilon(\omega) = \varepsilon_{core} + \sum_j \frac{\Omega_j^2}{\omega_j^2 - \omega^2 - i\omega\gamma_j} = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function and $|\varepsilon| = \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}$. By using them, the best fit of the above-mentioned equation to the observed reflectivity is obtained and the calculated reflection spectra are depicted in Fig. 3 in order to compare with the observed ones. The obtained parameters (Ω_j, ω_j, and γ_j) are shown in Table 1. The oscillator strength f is estimated by using the equation

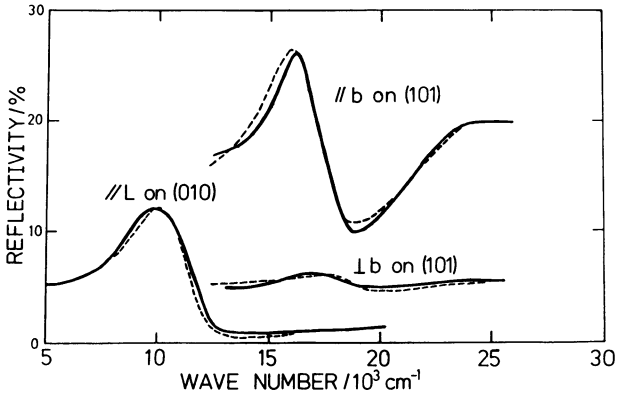


Fig. 3. Reflection spectra of $(DBTTF)_2$-(Cu_2Br_6) (——: obsd., ---: calcd.)

$$f = \frac{m_e}{4\,\pi\,N\,e^2}\,\Omega_j^2 \quad .$$

Here, m_e is the electron mass and N is the number density of DBTTF cation molecule ($N=2.35\times10^{21}$ cm^{-3}).

The 9900 cm^{-1} band in the L axis spectrum can be assigned to the CT_1 band of a dimer type system classified by Tanaka, *et al.*[7] and the 16000 and 18500 cm^{-1} bands in the spectra on the (101) plane to the LE bands of $DBTTF^{+}$ cation radical.[8] For the dimer system, the allowed transition from the ground state to the charge transfer CT_1 state has the transition energy given by,[5]

$$\Delta E_{CT_1} = \frac{U + \sqrt{U^2 + 16\,t^2}}{2} \quad ,$$

where t is the transfer integral and U is the Coulomb interaction term. Furthermore, the oscillator strength of the CT_1 band can be expressed as

$$f = 3\times1.085\times10^{11}\frac{4\,t^2}{\sqrt{U^2 + 16\,t^2}}\,|R_{12}|^2 \quad ,$$

Table 1. Dielectric Parameters of the Lorentz Fits of Reflectivity Data for $(DBTTF)_2(Cu_2Br_6)$

	//L on (010)	//b on (101)		⊥b on (101)	
ε_{core}	1.702	2.203		2.200	
Ω_j / cm^{-1}	7600	14600	23300	4600	14000
ω_j / cm^{-1}	9900	16000	23700	18500	30000
γ_j / cm^{-1}	2550	2500	6600	2800	9000
f	0.27	1.0		0.1	

where R_{12}=3.5 Å is the distance between the cation molecules of DBTTF. Then, the observed oscillator strength f_{obsd} on (010) equals to the next equation,

$$f_{obsd} = f \cos^2(\Theta) \quad .$$

Here Θ=52° is the angle between the L direction shown in Fig.2 and the stacking axis(c axis) of DBTTF molecules. The experimental data ($\Delta E_{CT_1} \simeq$ 9900 cm^{-1} and $f_{obsd} \simeq$ 0.27) give U = 7700 cm^{-1} and t = -2300 cm^{-1} as the spectroscopic values.

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