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CRYSTAL STRUCTURE AND REFLECTION SPECTRA OF $(DBTTF)_2$-(Cu_2Cl_6) COMPLEX

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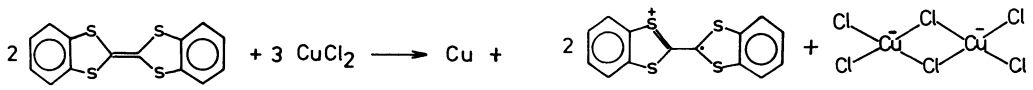
X-Ray and optical reflection measurements of $(DBTTF)_2$-(Cu_2Cl_6) single crystals were carried out. The single crystal of the complex consists of stacking columns of the cation molecules $DBTTF^+$. The analysis of the reflection spectra of $(DBTTF)_2$-(Cu_2Cl_6) single crystals shows that the electronic structure of $DBTTF^+$ cation molecules 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. Dibenzotetrathiafulvalene(DBTTF) is one of these compounds and the preparation of its complexes with high conductivity was extensively attempted.[2] In the present paper, we report the crystal structure and the reflection spectra of the single crystal of $(DBTTF)_2$-(Cu_2Cl_6) complex.

The crystal of $(DBTTF)_2$-(Cu_2Cl_6) complex was prepared by the diffusion of DBTTF and $CuCl_2$ molecules in acetonitrile and DBTTF seems to be oxidized according to the following reaction.



The complex crystallizes in the form of the dark reddish plates and the space group is monoclinic C2/m. The unit cell dimensions are a=9.216, b=24.958, c= 7.300 Å and β=108.23°. The projections of the complex onto the bc and ac planes

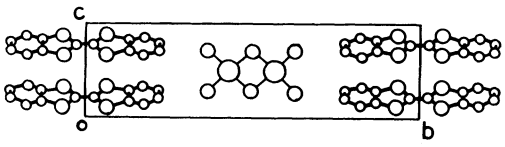


Fig. 1. Projection of $(DBTTF)_2(Cu_2Cl_6)$ crystal onto the bc plane.

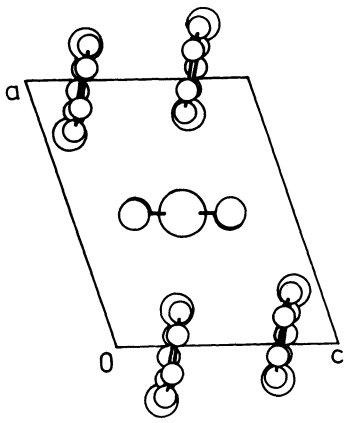


Fig. 2. Projection of $(DBTTF)_2(Cu_2Cl_6)$ crystal onto the ac plane.

are shown in Figs. 1 and 2. The stacking column of the cation molecules of DBTTF elongates along the c axis and the S atoms in $DBTTF^+$ cation make the coordination bond of S··Cu··S with the Cu atoms in Cu_2Cl_6 dianion. All calculations for the x-ray analysis were made on a FACOM M382 computer of Nagoya University.

The reflection spectra were observed for the polarizations parallel and perpendicular to the c axis on the ac plane as is shown in Fig. 3. The reflectivity R can be expressed 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

$$f = \frac{m_e}{4\pi^2 N e^2} \int \omega\, \varepsilon_2(\omega)\, d\omega .$$

Here, m_e is the electron mass and N is the number density of DBTTF cation molecule ($N=2.5\times10^{21}$ cm^{-3}).

The 8700 cm^{-1} band in the c axis spectrum can be assigned to the CT_1 band of a dimer type system classified by Tanaka, *et al.*[3] and the 20000 cm^{-1} band in the $\perp$ c axis spectrum to the LE band of $DBTTF^+$ cation radical.[4] For the dimer type system, the singlet ground (Φ_G) and CT_1 (Φ_{CT_1}) configration functions are given as follows,

$$\Phi_G = a_{1,m}\, a_{2,m}\, |HF\rangle$$

and $$\Phi_{CT_1}(\pm) = \frac{1}{\sqrt{2}}\,(a_{1,m}{}^2 \pm a_{2,m}{}^2)\,|HF\rangle.$$

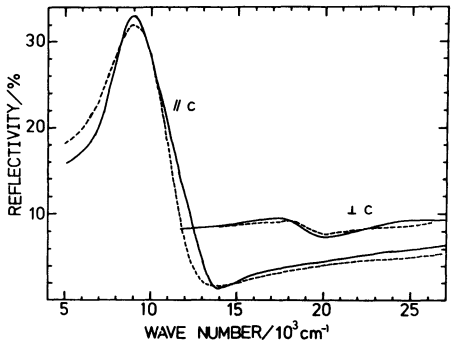


Fig. 3. Reflection spectra of $(DBTTF)_2(Cu_2Cl_6)$ crystal (——: obsd, ---: calcd).

Here, $|HF\rangle$ means the Hartree-Fock wavefunction of the neutral dimer of $(DBTTF)_2$. $a_{1,m}$ and $a_{2,m}$ are the annihilation operators of the π-electron occupying HOMO ($\phi_{1,m}$ and $\phi_{2,m}$) of the molecules 1 and 2 in the dimer. The wavefunctions and the energies of the ground state (Ψ_G) and the $CT_1(\pm)$ states ($\Psi_{CT_1}(\pm)$) are given as the solution of the modified Hubbard Hamiltonian,[3]

$$\Psi_G = c_1\,\Phi_G + c_2\,\Phi_{CT_1}(+) \qquad E_G = \frac{U - \sqrt{U^2 + 16\,t^2}}{2}$$

$$\Psi_{CT_1}(-) = \Phi_{CT_1}(-) \qquad E_{CT_1}(-) = U$$

$$\Psi_{CT_1}(+) = c_2\,\Phi_G - c_1\,\Phi_{CT_1}(+) \qquad E_{CT_1}(+) = \frac{U + \sqrt{U^2 + 16\,t^2}}{2}$$

where t is the transfer integral and U is the Coulomb interaction term, and the parameters c_1 and c_2 are expressed by the next equations,

$$c_1 = \frac{2t}{\sqrt{E_G{}^2 + 4\,t^2}}, \text{ and } c_2 = \frac{E_G}{\sqrt{E_G{}^2 + 4\,t^2}}.$$

Table 1. Dielectric Parameters of the Lorentz Fits of Reflectivity Data for $(DBTTF)_2$-(Cu_2Cl_6)

	// c spectrum	⊥ c spectrum	
ε_{core}	2.83	3.17	
Ω_j / cm^{-1}	13520	4000	90000
ω_j / cm^{-1}	8660	19000	30000
γ_j / cm^{-1}	2900	2500	2500
f	0.75	0.15	

Then, the allowed transition from Ψ_G to $\Psi_{CT_1}(-)$ has the transition energy given by,

$$\Delta E_{CT_1} = E_{CT_1}(-) - E_G = \frac{U + \sqrt{U^2 + 16\,t^2}}{2} \quad .$$

Furthermore, the oscillator strength of the CT_1 band can be expressed as

$$f = 3\times1.085\times10^{11}\ \Delta E_{CT_1}\ |\langle\Psi_G|r|\Psi_{CT_1}(-)\rangle|^2$$

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

where R_{12}=3.65 Å is the distance between the cation molecules of DBTTF. Then, the experimental data ($\Delta E_{CT_1} \simeq 8700$ cm^{-1} and $f \simeq 0.75$) give U = 6500 cm^{-1} and t = -2200 cm^{-1} as the spectroscopic values.

References

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