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Optical and Magnetic Properties of $(DBTTF)_2(Cu_2Cl_6)$ and $(DBTTF)_2(Cu_2Br_6)$ Complexes

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Optical reflection and magnetic susceptibility measurements of $(DBTTF)_2(Cu_2Cl_6)$ and $(DBTTF)_2(Cu_2Br_6)$ complexes were carried out. The analysis of the reflection spectra of the single crystals of these complexes shows that the electronic structure of $DBTTF^+$ cation molecules is typical of the dimer type configuration. The magnetic susceptibilities of these complexes were measured over a temperature range of 2—300 K. The magnetic behavior conforms to a modified Bleaney-Bowers equation, indicating the existence of the spin coupling within the $Cu_2Cl_6^{2-}$ or $Cu_2Br_6^{2-}$ dimers and the antiferromagnetic spin interaction between $Cu_2Br_6^{2-}$ dimers.

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. After the discovery of the TTF–TCNQ complex, many compounds with fulvalene rings were synthesized to obtain the radical salts with highly electrical conductivity. Dibenzotetrathiafulvalene (DBTTF) is one of those compounds[1] and the direct oxidation of DBTTF by halogens and metal halides were reported to yield radical salts such as $(DBTTF)_2I_3$,[2] $(DBTTF)_8(SnCl_6)_3$,[3] and $(DBTTF)_3(SnBr_6)$.[3] Furthermore, we reported the crystal structure of $(DBTTF)_2(Cu_2Cl_6)$[4] and $(DBTTF)_2(Cu_2Br_6)$.[5] These complexes consist of the organic conducting stack and the inorganic magnetic stack and are supposed to have the interest properties of both the electrical conductivity and the magnetization. In the present paper, therefore, we report the optical and magnetic properties of $(DBTTF)_2(Cu_2Cl_6)$ and $(DBTTF)_2(Cu_2Br_6)$ complexes.

Experimental

The crystal of $(DBTTF)_2(Cu_2Cl_6)$ and $(DBTTF)_2(Cu_2Br_6)$ complexes was prepared by using the close system-evaporation crystallizer transfering DBTTF and $CuCl_2$ or $CuBr_2$ from solid sources to an acetonitrile solution.[6,7] The reflection spectra of the single crystal at the normal incidence were measured over the range of 5000—25000 cm^{-1} by means of a reflection spectrophotometer made in our laboratory and the temperature dependence of the magnetic susceptibility of the powder of the samples were recorded on a Oxford magnetic susceptibility instrument of the Instrument Center, Institute for Molecular Science, Okazaki. All calculations for the analysis of the experimental data were made on a FACOM M382 computer of Nagoya University.

Theoretical

For the dimer system of DBTTF cations, the Hamiltonian H can be written by the Hubbard approximation as follows,

$$H = -t\sum_{\sigma=\alpha,\beta}(a^+_{1,\sigma}a_{2,\sigma}+a^+_{2,\sigma}a_{1,\sigma}) + U\sum_{i=1,2}n_{i,\alpha}n_{i,\beta}, \tag{1}$$

where $a_{1,\sigma}$ and $a_{2,\sigma}$ are the annihilation operators of the π-electron occupying HOMO of the DBTTF molecule at the sites 1 and 2, σ represents the spin of π-electron, $n_{i,\sigma}=a^+_{i,\sigma}a_{i,\sigma}$, t is the electron transfer integral between the sites 1 and 2, and U is the intramolecular Coulomb integral. Then, the following ground and lower excited configuration functions are taken into account for the calculation of the electronic states of the dimer system.

$$\Phi_{T,1} = a_{1,\beta}a_{2,\beta}\Phi_{HF}, \tag{2}$$

$$\Phi_{T,0} = \frac{1}{\sqrt{2}}(a_{1,\beta}a_{2,\alpha}+a_{1,\alpha}a_{2,\beta})\Phi_{HF}, \tag{3}$$

$$\Phi_{T,-1} = a_{1,\alpha}a_{2,\alpha}\Phi_{HF}, \tag{4}$$

$$\Phi_{S,0} = \frac{1}{\sqrt{2}}(a_{1,\beta}a_{2,\alpha}-a_{1,\alpha}a_{2,\beta})\Phi_{HF}, \tag{5}$$

$$\Phi_{CT}(+) = \frac{1}{\sqrt{2}}(a_{1,\beta}a_{1,\alpha}+a_{2,\beta}a_{2,\alpha})\Phi_{HF}, \tag{6}$$

$$\Phi_{CT}(-) = \frac{1}{\sqrt{2}}(a_{1,\beta}a_{1,\alpha}-a_{2,\beta}a_{2,\alpha})\Phi_{HF}. \tag{7}$$

Here, Φ_{HF} means the Hartree-Fock wavefunction of the neutral dimer of DBTTF. Then, the secular equations are solved and the eigenfunctions and eigenvalues are obtained as follows, and the energy diagram of the cation dimer system is depicted in Fig. 1,

$$\left.\begin{aligned} \Psi_G &= c_1\Phi_{S,0} + c_2\Phi_{CT}(+), \\ E_G &= (U-\sqrt{U^2+16t^2})/2, \end{aligned}\right\} \tag{8}$$

$$\Psi_{T,i} = \Phi_{T,i}\ (i=-1,\ 0,\ 1),\quad E_{T,i} = 0, \tag{9}$$

$$\Psi_{CT}(-) = \Phi_{CT}(-),\qquad E_{CT}(-) = U, \tag{10}$$

$$\left.\begin{aligned} \Psi_{CT}(+) &= c_2\Phi_{S,0} - c_1\Phi_{CT}(+), \\ E_{CT}(+) &= (U+\sqrt{U^2+16t^2})/2, \end{aligned}\right\} \tag{11}$$

where the parameters c_1 and c_2 are expressed by the next equations,

$$c_1 = \frac{2t}{\sqrt{E_G^2+4t^2}} \quad \text{and} \quad c_2 = \frac{-E_G}{\sqrt{E_G^2+4t^2}}. \tag{12}$$

The optically allowed transition from Ψ_G to $\Psi_{CT}(-)$ has the transition energy given by,

$$\Delta E_{CT} = E_{CT}(-) - E_G = (U+\sqrt{U^2+16t^2})/2, \tag{13}$$

and the oscillator strength of the CT band can be expressed as follows,

$$\begin{aligned} f &= 3 \times 1.085 \times 10^{11}\Delta E_{CT}|\langle\Psi_G|r|\Psi_{CT}(-)\rangle|^2 \\ &= 3 \times 1.085 \times 10^{11}\frac{4t^2}{\sqrt{U^2+16t^2}}|R_{12}|^2, \end{aligned} \tag{14}$$

where R_{12} is the distance between the DBTTF molecules.

The magnetic susceptibility X_{DBTTF} of the cation dimer system is given as follows,

$$X_{DBTTF} = \frac{N(g_1\beta)^2}{k_BT} \times \frac{1}{3+\exp(J_1/k_BT)}, \tag{15}$$

where $J_1=(\sqrt{U^2+16t^2}-U)/2$, g_1 is the magnetic field splitting factor, β the Bohr magneton, N the Avogadro number, k_B the Boltzman constant, and T the absolute temperature.

For the $Cu_2X_6^{2-}$ ion, the ground state of a free Cu^{2+} ion is $^2D_{5/2}$ corresponding to the electronic configuration of $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^9$. The planar $Cu_2X_6^{2-}$ ion has D_{2h} symmetry and the symmetry orbitals can be obtained by group theoretical means from the 3d orbitals on the Cu^{2+} ion and the npσ and npπ orbitals on the halogen ion X^-. For the 3d orbitals on the Cu^{2+} ion, the fivefold degeneracy of the d orbital is completely removed under the D_{2h} symmetry.[8] The d_{xy} level is the highest one occupied by an electron and the other levels (d_{z^2}, $d_{x^2-y^2}$, d_{xz}, d_{yz}) are occupied by two electrons. As the result, the d-d transitions are expected to be located in the 10000—15000 cm^{-1} region. The charge transfer bands from the ligand to the d orbital may occur over the higher wavenumber region. However, these transitions are very weak and can be neglected for the analysis of the reflection spectra of the complex. On the other hand, the pairs of Cu^{2+} ions interact through exchange forces and each pair forms a lower singlet and an upper triplet state as is shown in Fig. 1. The exchange energy J_2 corresponds to the magnitude of the splitting between the singlet and triplet states and the magnetic susceptibility $X_{Cu_2X_6}$ of the $Cu_2X_6^{2-}$ dimer system is given by the modified Bleaney-Bowers equation,[9]

$$X_{Cu_2X_6} = \frac{N(g_2\beta)^2}{k_B(T-\Theta)} \times \frac{1}{3+\exp(J_2/k_BT)}, \tag{16}$$

where Θ is the Weiss constant that takes into account the spin interaction between the dimer ions.

The magnetic susceptibility $X(T)$ of the complex can be expressed by assuming that there is a separate contribution to the susceptibility from the DBTTF cation dimer, the $Cu_2X_6^{2-}$ anion dimer and the paramagnetic impurity,

$$X(T) = X_{DBTTF} + X_{Cu_2X_6} + \frac{N(g_3\beta)^2}{3k_BT}, \tag{17}$$

where the third term is the impurity term.

The optical reflectivity R can be expressed by the following equation,

$$R = \frac{1+|\varepsilon|-\sqrt{2(|\varepsilon|+\varepsilon_1)}}{1+|\varepsilon|+\sqrt{2(|\varepsilon|+\varepsilon_1)}}, \tag{18}$$

using the semiclassical Lorentz dielectric function,

$$\begin{aligned} \varepsilon(\omega) &= \varepsilon_{core} + \sum_j \frac{\Omega_j^2}{\omega_j^2-\omega^2-i\omega\gamma_j} \\ &= \varepsilon_1(\omega) + i\varepsilon_2(\omega), \end{aligned} \tag{19}$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function of the DBTTF cation dimers, and $|\varepsilon|=\sqrt{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)}$. The oscillator strength f is determined by using the equation,

$$f = \frac{m_e}{4\pi N_0 e^2}\Omega_j^2. \tag{20}$$

Here, m_e is the electron mass, and N_0 is the number density of DBTTF molecule.

By fitting the above-mentioned equations of the reflectivity R and the magnetic susceptibility $X(T)$ to

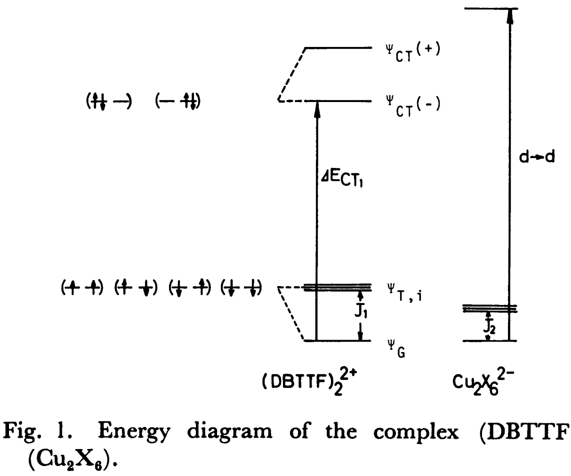

Fig. 1. Energy diagram of the complex $(DBTTF)_2$-(Cu_2X_6).

the observed values, the optical and magnetic parameters of the complexes, $(DBTTF)_2(Cu_2X_6)$, can be obtained and their energy structure can be determined.

Results and Discussion

$(DBTTF)_2$-(Cu_2Cl_6) Complex. The crystal of $(DBTTF)_2$-(Cu_2Cl_6) complex crystallizes in the form of the dark reddish plates (0.35X0.008X0.60 mm) and has the natural developed plane of (010). The space group is monoclinic *C*2/*m* and the unit cell dimensions are a=9.216, b=24.958, c=7.300 Å, and β=108.23°.[4,6] The projection of the complex onto the bc and ac planes are shown in Fig. 2. The stacking column of the cation molecules of DBTTF elongates along the c axis.

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 9000 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.[10] and the dispersion around 20000 cm^{-1} in the ⊥ c axis spectrum to the LE band of $DBTTF^+$ cation radical.[11] The best fit of Eq. 18 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, γ_j, and ε_{core}) are shown in Table 1 together with the oscillator strength determined by Eq. 20. Then, the experimental data (ΔE_{CT_1}=8700 cm^{-1}, f=0.75, and R_{12}=3.65 Å) give U=6500 cm^{-1}, t=2200 cm^{-1}, and J_1=2200 cm^{-1} as the spectroscopic values. Accordingly, the crystal of the complex has the semiconductive property as the dielectric function can be well expressed by the Lorentz equation without the Drude equation.

The temperature dependence of the magnetic susceptibility of the powder of the complex were measured over a temperature range of 2—300 K as is shown in Fig. 4. The best fit of Eq. 17 to the observed one is obtained and the calculated susceptibility is depicted in Fig. 4. The obtained parameters are J_1>1000 cm^{-1}, J_2=95 cm^{-1}, g_2=2.65, Θ=0, g_3=0.89.

$(DBTTF)_2$-(Cu_2Br_6) Complex. The crystal of the $(DBTTF)_2$-(Cu_2Br_6) complex crystallizes in the form of the dark reddish plates (0.13X0.05X0.20 mm) and

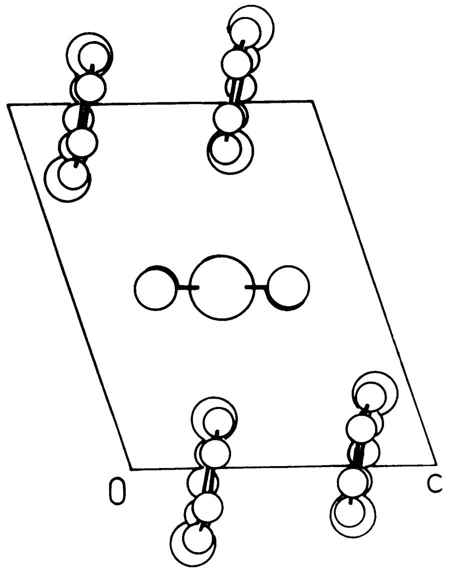

Fig. 2. The projection of the $(DBTTF)_2(Cu_2Cl_6)$ crystal onto the ac plane.

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	

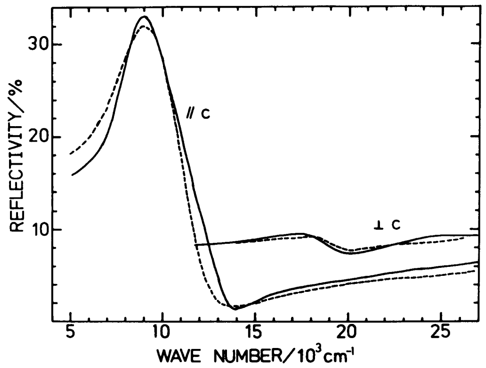

Fig. 3. The observed and calculated reflection spectra of the $(DBTTF)_2(Cu_2Cl_6)$ crystal. (——: Obsd, ----: Calcd)

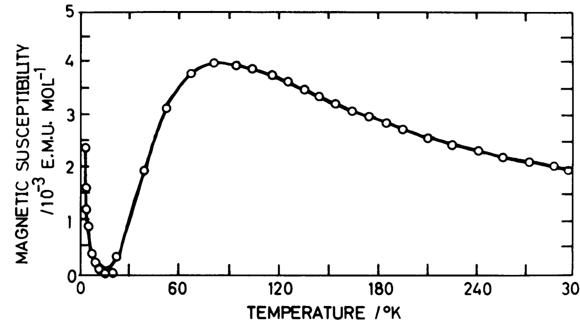

Fig. 4. The temperature dependence of the magnetic susceptibility of the powder of the complex $(DBTTF)_2$-(Cu_2Cl_6). (oooo: Obsd, ——: Calcd)

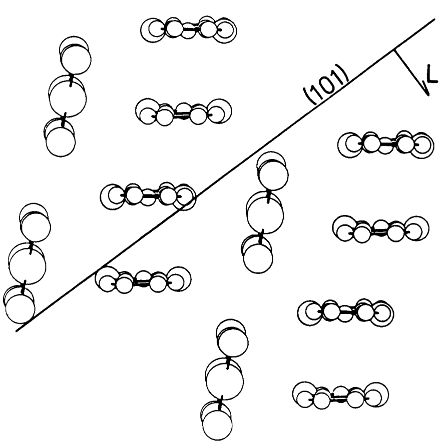

Fig. 5. The stacking of DBTTF molecules in the $(DBTTF)_2(Cu_2Br_6)$ crystal.

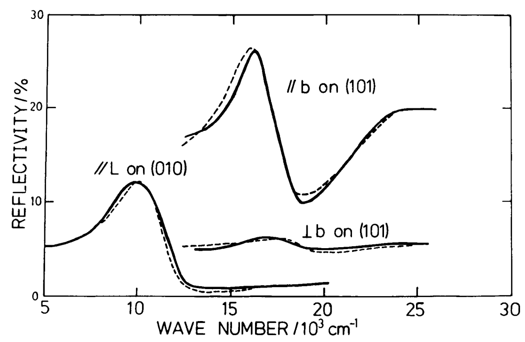

Fig. 6. The observed and calculated reflection spectra of the complex $(DBTTF)_2(Cu_2Br_6)$. (——: Obsd, ----: Calcd)

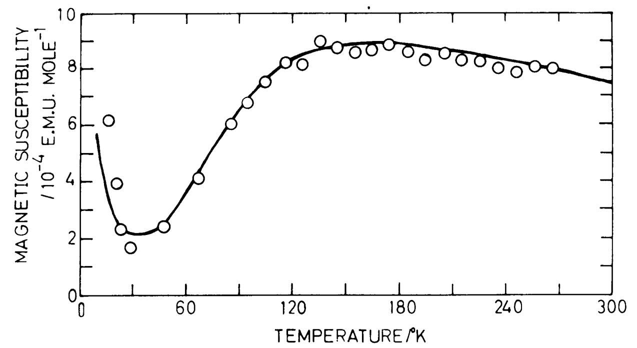

Fig. 7. The temperature dependence of the magnetic susceptibility of the powder of the complex $(DBTTF)_2$-(Cu_2Br_6). (oooo: Obsd, ——: Calcd)

has the natural developed planes of (010) and (101). The space group is triclinic, $P\bar{1}$ and the unit cell are dimensions a=9.982, b=12.122, c=7.893 Å, α=83.70, β=112.80, and γ=104.97°.[5,7] The stacking of DBTTF molecules is illustrated in Fig. 5. The stacking column of the $DBTTF^+$ cations elongates along the c axis with an interplanar distance of about 3.5 Å and two DBTTF molecules form the dimer system in the unit cell.

Table 2. 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	

The reflection spectra were observed for the polarization parallel and perpendicular to the b axis on the developed plane (101) and parallel to the L direction on the (010) plane as is shown in Fig. 6. The 10000 cm⁻¹ band in the L axis spectrum can be assigned to the CT_1 band[11] and the 16000 and 18000 cm⁻¹ bands in the spectra on the (101) plane to the LE bands of $DBTTF^+$ cation radical.[10] The best fit of Eq. 20 to the observed reflectivity is obtained and the calculated reflection spectra are depicted in Fig. 6 in order to compare with the observed ones. The obtained parameters (Ω_j, ω_j, γ_j, and ε_{core}) are shown in Table 2 together with the oscillator strength determined by Eq. 20. Then, the observed oscillator strength f_{obsd} on the (010) plane equals to the next equation,

$$f_{obsd} = f\cos^2\varphi. \qquad (21)$$

Here f is given by Eq. 14 and φ=52° is the angle between the L direction shown in Fig. 5 and the stacking axis (c axis) of DBTTF molecule. The experimental data (ΔE_{CT_1}=9900 cm⁻¹, f_{obsd}=0.27, and R_{12}=3.5 Å) give U=7700 cm⁻¹, t=2300 cm⁻¹, and J_1=2150 cm⁻¹ as the spectroscopic values. Accordingly, the crystal of the complex has the semiconductive property like $(DBTTF)_2$-(Cu_2Cl_6).

The temperature dependence of the magnetic susceptibility of the powder of the complex were measured over a temperature range of 2—260 K as is shown in Fig. 7. The best fit of Eq. 17 to the observed one is obtained and the calculated susceptibility is depicted in Fig. 7. The obtained parameters are J_1>1000 cm⁻¹, J_2=150 cm⁻¹, g_2=1.88, Θ=−83 K, g_3=1.23. The negative value for Θ indicates the presence of antiferromagnetic spin interaction between the anion dimers. Our result for J_2 and g_2 values is consistent with the conclusion observed in the majority of copper(II) complexes that the spin-exchange interaction is stronger through bromine ions than through chlorine ions.[9]

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