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# Structural and Electrical Properties of $(BEDT\text{-}TTF)_3Cl_2(H_2O)_2$

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An organic conductor $(BEDT\text{-}TTF)_3Cl_2(H_2O)_2$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) has been prepared by using $[(C_2H_5)_4N]_2CoCl_4$ as an electrolyte. This complex shows as high a conductivity as $\sigma_{rt}$ = 500 S $cm^{-1}$, and undergoes a metal-semiconductor transition around 100 K.

The discovery of an organic superconductor, β-$(BEDT\text{-}TTF)_2I_3$ has aroused much interest in the halogen complexes of BEDT-TTF.[1)] So far BEDT-TTF complexes have been obtained with $I_2Br^-$, $IBr_2^-$, $IBrCl^-$, and $ICl_2^-$.[2-4)] It is, however, very difficult to directly prepare crystals of bromine or chlorine complexes of BEDT-TTF which do not contain iodine. Very recently Urayama et al. have succeeded in the preparation and the crystal structure analysis of $(BEDT\text{-}TTF)_3Br_2(H_2O)_2$.[5)] In the course of studying halogeno-transition metal complexes, we have unexpectedly obtained a highly conductive chlorine complex, $(BEDT\text{-}TTF)_3Cl_2(H_2O)_2$. In the present letter, we report the crystal structure, the transport properties, and the electronic band structure of this complex.[6)]

Black plate-like crystals were grown by electrochemical crystallization of BEDT-TTF in benzonitrile by using $[(C_2H_5)_4N]_2CoCl_4xH_2O$ as a supporting electrolyte.[7)] The anion $CoCl_4^{2-}$ was not included in the crystal, and instead the chlorine complex was obtained. Crystal data: triclinic, space group $P\bar{1}$, a=13.905(2), b=15.929(2), c=11.228(1) Å, α=109.22(1), β=97.08(1), γ=94.67(1) °, V=2310.5(5) $Å^3$, and Z=2. The crystal structure was solved by the Patterson method and the succeeding Fourier syntheses and refined by using 5000 independent reflections (Mo Kα, $2\theta < 60^\circ$, $|F_o| > 3\sigma(|F_o|)$) to an R value of 0.041. Thermal parameters were anisotropic for all non-hydrogen atoms and isotropic for hydrogen atoms.

The crystal structure is depicted in Figs. 1-4. There are three crystallographically independent BEDT-TTF molecules, A, B, and C. The examination of the intramolecular bond lengths of the donors shows no charge separation; all donors are uniformly charged as 2/3+. Table 1 shows the parameters which describe the configuration of the neighboring donor molecules;[8)] φ is the angle between the molecular plane and the interaction direction, and D is the slip distance along the molecular long axis. Though the donor molecules seem to be stacked along the a axis, Fig. 4 shows that there is no true face-to-face ( $\phi=90^\circ$) interaction (Table 1 and Fig. 4); along the a axis the donors are arranged by $\phi = 60^\circ$ interactions. The $30^\circ$ interactions along the c axis and the $0^\circ$ interactions along the [203] direction have many short sulfur-to-sulfur contacts. Such a donor arrangement as consists of the $0^{\circ}$-$30^{\circ}$-$60^{\circ}$ interactions, is similar to those of (BEDT-TTF)$_2$ClO$_4$(C$_2$H$_3$Cl$_3$)$_{0.5}$, (BEDT-TTF)$_3$(ClO$_4$)$_2$, α-(BEDT-TTF)$_3$(ReO$_4$)$_2$, and β"-(BEDT-TTF)$_2$AuBr$_2$.$^{8-10)}$

Like other BEDT-TTF complexes, the donors form a conducting sheet parallel to the ac plane, and the conducting sheets are separated from each other by the anions. The anion sheets are composed of Cl$_4$(H$_2$O)$_4$ unit (Fig. 3). Around an inversion center, two Cl(2) atoms are connected with two O(2) atoms through hydrogen bonds. The rectangle of this part has close resemblance to the Br$_2$(H$_2$O)$_2$ unit in (BEDT-TTF)$_3$Br$_2$(H$_2$O)$_2$.$^{5)}$ In the present chlorine complex, however, additional Cl(1) and O(1) are attached to this unit by using hydrogen bonds. Thus the size of the anion unit is twice of the bromine complex. This is the reason why the unit cell volume of the chlorine complex is twice of the bromine complex. The structure of the present chlorine complex is, roughly speaking, regarded as the doubled analog of the 3:2 (ClO$_4^-$ etc.) structure.

For better understanding of the intermolecular interaction, the intermolecular overlap integrals of the donor HOMO are calculated on the basis of extended Hückel molecular orbital calculation (Table 1).$^{8)}$ The magnitudes of the overlap integrals are closely correlated with the direction of the interaction:

(1) The largest interactions are the c interactions with $\phi = 30^{\circ}$.

(2) The second largest group is the p interactions which are formed by the $\phi = 0^{\circ}$, side-by-side arrangements. The magnitudes of these interactions are more than half of the first group.

(3) The third group is the $\phi = 60^{\circ}$ interactions. These are in the order of one third of the first group in magnitude.

Because the difference of these interactions is so small, we can expect a

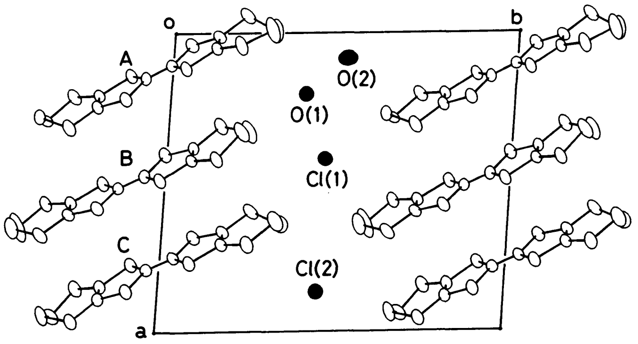

Fig. 2. Crystal structure, projected onto the ab plane.

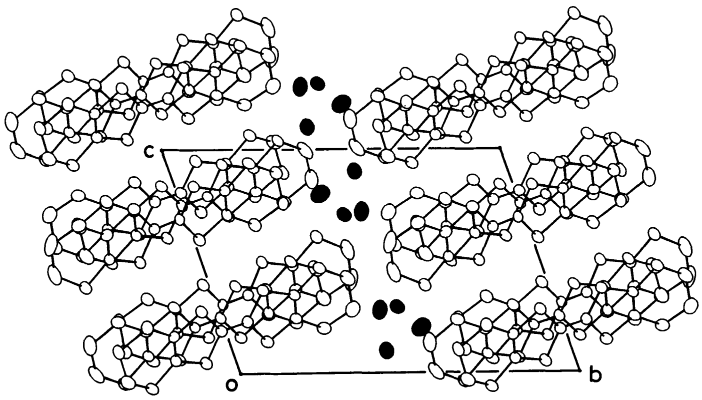

Fig. 1. Crystal structure, projected onto the bc plane.

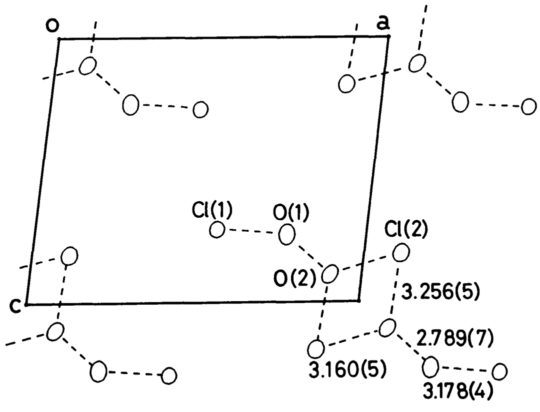

Fig. 3. Structure of the anion sheet, projected onto the ac plane.

Table 1. Overlap integrals of the HOMO and the parameters describing the configuration of the neighbor molecules [8)]

| Direction | Overlap $/10^{-3}$ | $\phi$ /° | D /Å |
|---|---|---|---|
| a1 | 5.8 | 62 | 3.1 |
| a2 | 3.5 | 64 | 3.3 |
| a3 | 4.9 | 63 | 0.3 |
| c1 | 16.0 | 33 | 1.6 |
| c2 | 16.0 | 35 | 1.4 |
| c3 | 13.7 | 35 | 1.4 |
| c4 | 12.6 | 37 | 1.5 |
| p1 | -7.6 | 4 | 1.5 |
| p2 | -9.5 | 4 | 1.7 |
| p3 | -7.0 | 1 | 4.4 |
| p4 | -9.9 | 4 | 1.8 |

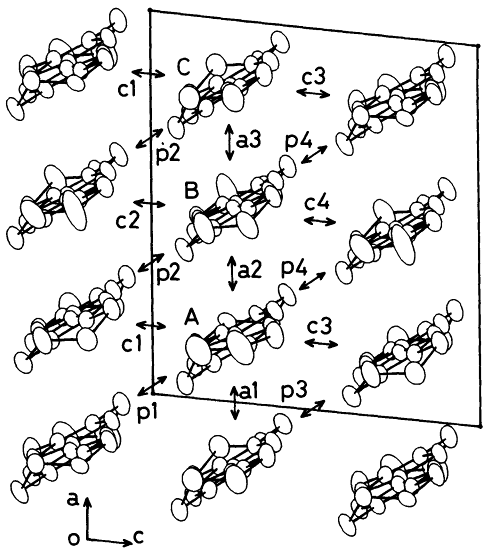

Fig. 4. Crystal structure viewed along the molecular long axis.

two-dimensional electronic structure. Figure 5 shows the electronic band structure calculated by the tight-binding method by using the overlap integrals in Table 1. From the six donors in a unit cell, there appear six energy levels. Since the bands are 2/3-filled as a whole, the lower four levels are occupied. Then the band structure is either semiconductive or semimetallic. Figure 5 gives a semimetallic band structure; this is consistent with the metallic transport properties in this complex (vide infra). It is obvious from Fig. 5 that there are comparable energy dispersions along both the a and the c axes.

The electric resistivity and the thermoelectric power are shown in Fig. 6. The room-temperature conductivity is as high as 500 S $cm^{-1}$. Since the conductivities of BEDT-TTF complexes are ordinarily low (<100 S $cm^{-1}$), this is one of the highest room-temperature conductivity in the BEDT-TTF complexes. In the present chlorine complex, because the volume fraction occupied by the anion is comparatively small, the carrier concentration is larger than the other BEDT-TTF complexes. This may be associated

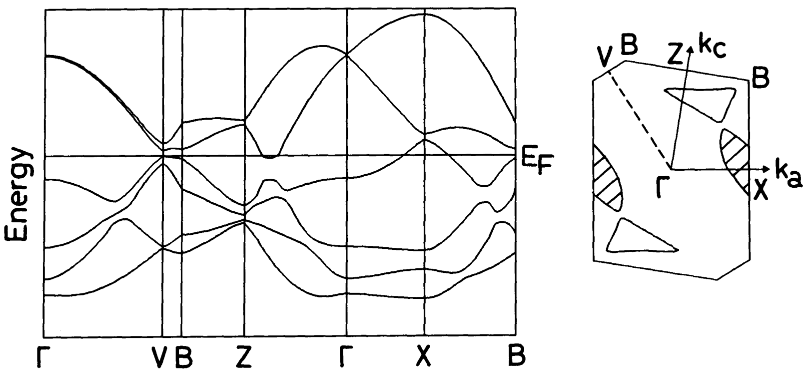

Fig. 5. Energy band structure and Fermi surface. The shaded region indicates hole-like parts.

with the high conductivity. However, one should be somewhat critical of this too naive consideration, because it is not completely consistent with the semimetallic nature of the band structure. The anisotropy of the resistivity is roughly estimated to be $\rho_c : \rho_a : \rho_b = 1:7:1000$.

This complex undergoes a metal-semiconductor transition around 100 K. This is also clear in the thermoelectric power. It is worth noting that the thermoelectric power changes its sign around 220 K; this is the evidence of the semimetallic nature of the band structure.

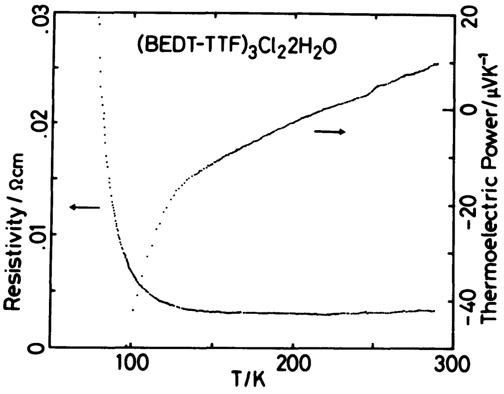

Fig. 6. Electric resistivity and thermoelectric power.

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