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THE CRYSTAL STRUCTURES AND ELECTRICAL RESISTIVITIES OF $(BEDT\text{-}TTF)_3(ClO_4)_2$ AND $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$

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The crystal structures of $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$ and $(BEDT\text{-}TTF)_3(ClO_4)_2$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) were determined. In both crystals, BEDT-TTF molecules are arranged side-by-side. The former is a semiconductor with the room-temperature resistivity of 1 Ω cm. The 3:2 salt undergoes a sharp metal-insulator transition at 170 K.

The dimensionality of a system plays an essential role to determine the electrical properties of an organic conductor. Most of the molecular metals are composed of the planar π-donor and/or acceptor molecules. In one-dimensional(1-D) metal, Fermi surface is composed of two pieces of the planes and its metallic state is easily broken by the nesting of the Fermi surface. In 2-D system, the Fermi surface is distorted and the metallic state becomes more stable.

The most prominent feature of the crystal structures of the organic conductors based on the donor molecule, BEDT-TTF(bis(ethylenedithio)tetrathiafulvalene), is the side-by-side array of the molecules. If the transverse intermolecular interaction is large enough, it may be possible that the system becomes metallic along the direction parallel to the molecular plane. In β-$(BEDT\text{-}TTF)_2PF_6$, the electrical conductivity is largest in the transverse direction and a metal-insulator transition occurs at 297 K.[1] The $4k_F$-lattice modulation wave develops below 297 K and the lattice spacing is doubled along the direction parallel to the side-by-side array of BEDT-TTF.[2] On the other hand, $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ shows 2-D metallic properties.[3-5] The electrical conductivity is maximum (10^3 S cm^{-1}) at 16 K and the system retains high conductivity even at 1.4 K (600 S cm^{-1}).[3] The band structure calculation suggests the 2-D properties of the compound.[5]

In this paper, the crystal structures and electrical resistivities of $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$ and $(BEDT\text{-}TTF)_3(ClO_4)_2$ are presented.

The crystals of $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$ were prepared electrochemically from the mixed solution of dioxane and 1,1,2-trichloroethane. The dioxane molecules are included in the crystals. The other compound, $(BEDT\text{-}TTF)_3(ClO_4)_2$ was obtained from the dichloromethane solution.

Crystal data: $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$, $(C_{10}H_8S_8)_2ClO_4(C_4H_8O_2)$, monoclinic, space group, P2/c, a=8.242(3), b=6.677(2), c=32.998(6) Å, β=92.71(3)°, V=1814 Å^3, Z=2; $(BEDT\text{-}TTF)_3(ClO_4)_2$, $(C_{10}H_8S_8)_3(ClO_4)_2$, triclinic, space group, $P\bar{1}$, a=16.463(2), b=9.498(2), c=7.613(2) Å, α=95.91(2), β=87.17(1), γ=90.84(1)°, V=1182 Å^3, Z=1.

Intensities were measured on a Rigaku automated four-circle diffractometer with Mo Kα radiation up to 2θ=60°. Numbers of the independent reflections ($|F_o|>3\sigma(|F_o|)$) are 2074 for $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$ and 4545 for $(BEDT\text{-}TTF)_3(ClO_4)_2$. The structures were solved by the direct method and refined to conventional R values of 0.100 for $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$ and 0.048 for $(BEDT\text{-}TTF)_3(ClO_4)_2$.

The crystal structures are shown in Figs. 1 and 2. In the crystal of $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$, BEDT-TTFs are stacked along the a axis. The long axes of the adjacent molecules are not parallel to each other but rotate mutually in order to reduce the intermolecular steric repulsion between ethylene groups. The ClO_4 anions and dioxane molecules are on the centers of symmetry. They exhibit large thermal motions. Since ClO_4 is a tetrahedral anion, its orientation is disordered. Despite of the apparent stacking structure of BEDT-TTF, there is almost no short intermolecular contact along the a axis: the shortest S···S distance of 3.69 Å is approximately equal to the van der Waals distance of S···S(3.70 Å). As shown in Fig. 3, much shorter S···S contacts are found along the b axis. BEDT-TTF molecules are arranged side-by-side. The electrical resistivities show semiconductive

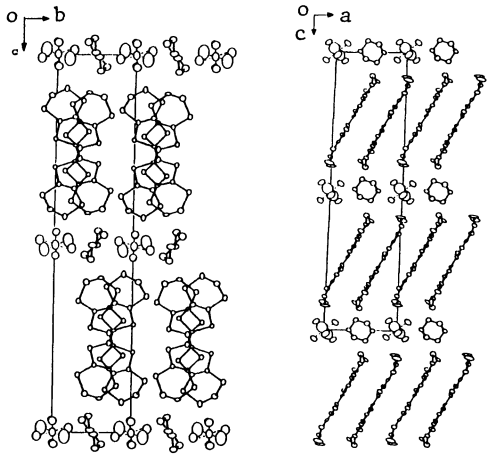


Fig. 1. The crystal structure of $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$.

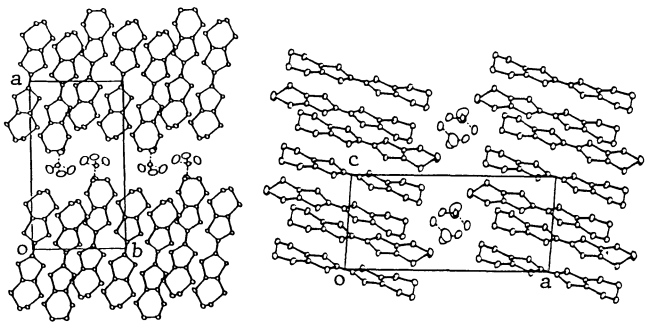
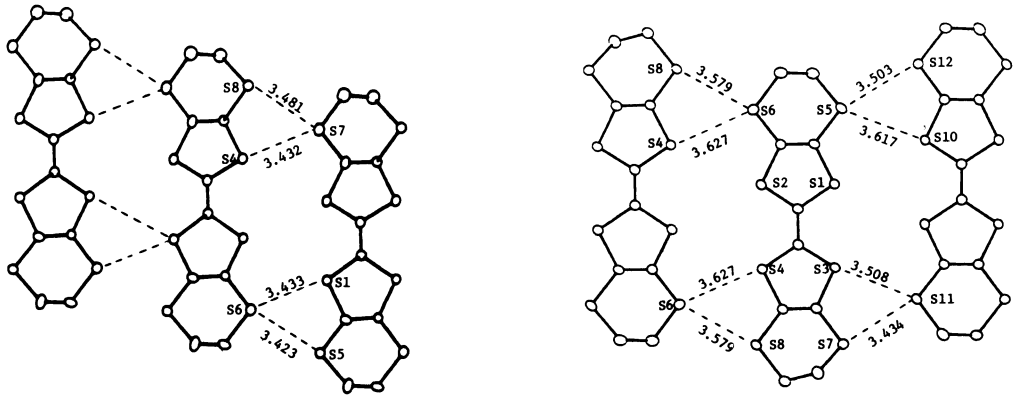


Fig. 2. The crystal structure of $(BEDT\text{-}TTF)_3(ClO_4)_2$.



(a) $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$ (b) $(BEDT\text{-}TTF)_3(ClO_4)_2$

Fig. 3. Side-by-side arrangement of BEDT-TTF.

behavior with an activation energy of 0.3 eV. The anisotropy of the resistivity is very small (≈1) in the ab plane with the room-temperature resistivity of 1 Ω cm but the resistivity along the c axis is 10^5 times larger than those in the ab plane.

In the crystal of $(BEDT\text{-}TTF)_3(ClO_4)_2$, two BEDT-TTF molecules are crystallographically independent (see Fig. 2). One is on the general position and the other is on the center of symmetry. Figure 4 shows that BEDT-TTFs appear to stack along [0$\bar{1}$1]. However, there is no short intermolecular contact along this direction. The short S···S contacts suggest that BEDT-TTFs are arranged side-by-side along [021] (see Figs. 3b and 4). Similar transverse array of BEDT-TTF has been found in several compounds such as $(BEDT\text{-}TTF)_2ClO_4(C_3H_3Cl_3)_{0.5}$,[4] α-$(BEDT\text{-}TTF)_2PF_6$,[6] β-$(BEDT\text{-}TTF)_2PF_6$[1] and $(BEDT\text{-}TTF)_2ClO_4(C_4H_8O_2)$ (this work). Some short S···S contacts can be also observed along [012]. The molecular arrangement of BEDT-TTF closely resembles that found in $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$, which has 2-D band structure. Undoubtedly, suppression of the Peierls instability in $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ is due to the 2-D intermolecular interaction.[5,7]

Contrary to this, the metallic state of $(BEDT\text{-}TTF)_3(ClO_4)_2$ becomes unstable and a metal-insulator transition occurs at 170 K (Fig. 5). The resistivity measurements were made along two directions: one is parallel to (100) ($\rho_{//}$) and the other is perpendicular to it ($\rho_{\perp}$). The room-temperature values of $\rho_{//}$ and $\rho_{\perp}$ are 0.02 Ω cm and 300 Ω cm, respectively. Above 170 K, $\rho_{//}$ decreases slowly with decreasing temperature but $\rho_{\perp}$ is constant over the

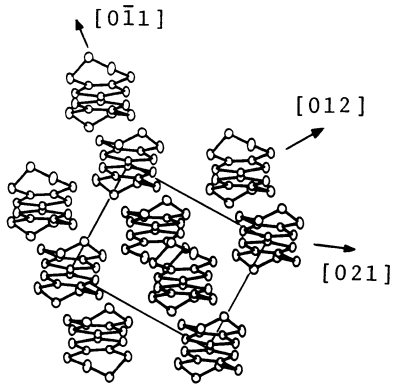


Fig. 4. The molecular arrangement of BEDT-TTF in (100) plane of $(BEDT\text{-}TTF)_3(ClO_4)_2$.

temperature range of 300-170 K.

We calculated the band structure parameters of $(BEDT\text{-}TTF)_3(ClO_4)_2$ and obtained the following results.[2)]

(1) The intermolecular transfer integrals of the highest occupied molecular orbital of BEDT-TTF indicate the 1-D band structure: t[012] ≫ t[021] > t[0$\bar{1}$1], where t[ijk] is the transfer integral between BEDT-TTFs arranged along [ijk] (see Fig. 4)).

(2) Although t[021] is not zero, the band structure is essentially the same as that of 1-D metallic system with regular chain along [012].

(3) If this band picture is true, the system should transform into an insulator without any change in the lattice constants, because of the triad units of BEDT-TTF along [012]. In fact, preliminary low-temperature X-ray studies showed no serious change in the lattice constants.

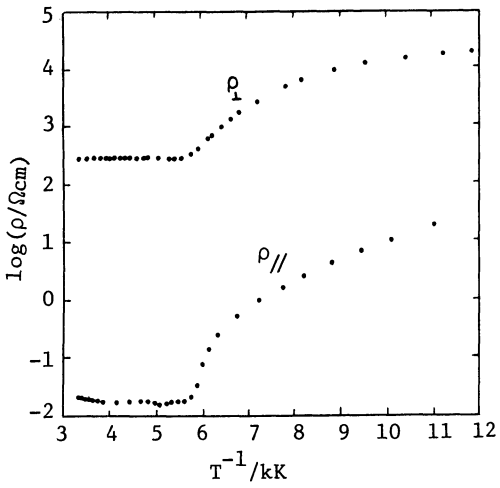


Fig. 5. Electrical resistivity of $(BEDT\text{-}TTF)_3(ClO_4)_2$. The resistivities $\rho_{//}$ and $\rho_{\perp}$ are those parallel and perpendicular to the (100) plane, respectively.

Since the thermal parameters of ClO_4 anion indicate the large thermal motion, there might be some possibilities that the rotational phase transition of ClO_4 anions and the metal-insulator transition take place cooperatively.

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