CHEMISTRY LETTERS, pp. 1117-1120, 1986.

Crystal and Electronic Structures of δ-(BEDT-TTF)$_2$AuI$_2$

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The semiconducting salt of δ-(BEDT-TTF)$_2$AuI$_2$ crystallizes in the orthorhombic system with the lattice constants of a=6.802(2), b=14.822(8), c=33.387(9) Å. The BEDT-TTF molecules form a two-dimensional network parallel to (001). The origin of the semiconducting properties was discussed.

Recently, ambient-pressure superconductors of BEDT-TTF complexes with linear anions, such as I_3, IBr_2 and AuI_2 have been reported (BEDT-TTF=bis(ethylenedithio) tetrathiafulvalene).1-5) The most characteristic structural feature of the BEDT-TTF compounds is their polymorphism.6) The modifications of the AuI$_2$ salts ever reported are the β- and γ'-type ones found by Williams et al.4,7) In this paper, we will report the crystal and electronic structures of a new modification of the AuI$_2$ salt of BEDT-TTF (called hereafter δ-(BEDT-TTF)$_2$AuI$_2$).

The very thin plates of δ-(BEDT-TTF)$_2$AuI$_2$ were prepared electrochemically from the tetrahydrofuran solution. The crystal data of δ-(BEDT-TTF)$_2$AuI$_2$ are: $(C_{10}H_8S_8)_2AuI_2$, orthorhombic, Pbcm, a=6.802(2), b=14.822(8), c=33.387(9) Å, V=3366 Å^3, Z=4. The structure was solved by using 1315 reflections ($2\theta<55°$(Mo Kα), $|Fo|>3\sigma(|Fo|)$) and refined by the block-diagonal least-squares method to an R value of 0.090. The isotropic temperature factors were used for the carbon atoms. The final atomic coordinates are listed in Table 1. The unit cell structure is shown in Fig. 1.

The BEDT-TTF molecules are arranged to form two-dimensional(2D) sheet parallel to (001). The AuI^{2-} anions are located between BEDT-TTF sheets. Four BEDT-TTF molecules form a repeating unit along **b**. The mode of overlapping of BEDT-TTF's is shown in Fig. 2. Owing to the steric effect of the terminal ethylene groups of BEDT-TTF, the neighbouring molecules interrelated by two-fold axis rotate alternately around the b axis. Thus, two different orientations of BEDT-TTF appear every two molecules. Similar stacking mode of BEDT-TTF molecules has been first observed in β-(BEDT-TTF)$_2$PF$_6$.8) Many intermolecular short S···S contacts less than 3.70 Å (van der Waals distance) indicate a side-by-side arrangement of BEDT-TTFs along **a** (Fig. 3). There is no short S···S contact (<3.70 Å) along **b**.

The electrical resistivities (ρ) were measured by the d.c. four-probe ($\rho_{//\mathbf{a}}$) or two-probe ($\rho_{//\mathbf{c}}$) method. The gold wires with the diameter of 25 μm were bonded

Table 1. Atomic coordinates with their estimated standard deviations

Atom	$x(\times10^3)$	$y(\times10^4)$	$z(\times10^4)$	Atom	$x(\times10^3)$	$y(\times10^4)$	$z(\times10^4)$
Au	278(1)	4774(3)	2500	C(1)	176(8)	1216(40)	186(15)
I(1)	93(1)	6252(5)	2500	C(2)	122(8)	1260(42)	-215(15)
I(2)	465(1)	3308(6)	2500	C(3)	198(8)	943(37)	972(16)
S(1)	18(2)	1189(15)	578(4)	C(4)	388(9)	940(40)	832(16)
S(2)	430(2)	1170(15)	315(4)	C(5)	-79(9)	1365(42)	-881(17)
S(3)	-122(2)	1419(16)	-333(4)	C(6)	109(8)	1418(369	-974(15)
S(4)	288(2)	1392(16)	-589(4)	C(7)	316(10)	795(48)	1750(20)
S(5)	108(2)	838(12)	1431(4)	C(8)	493(13)	1003(56)	1626(24)
S(6)	597(2)	797(14)	1108(4)	C(9)	-186(8)	2051(40)	-1567(16)
S(7)	-288(2)	1467(12)	-1143(4)	C(10)	-10(8)	1597(39)	-1763(16)
S(8)	203(2)	1402(12)	-1456(4)				

to the elongated plate of δ-(BEDT-TTF)$_2$AuI$_2$ by gold conducting paint. Temperature dependence of $\rho_{//\mathbf{a}}$ shows a semiconducting behavior (Fig. 4), which is in contrast to the quasi-metallic behavior of β-(BEDT-TTF)$_2$PF$_6$ above room temperature. The room-temperature resistivity is 3 Ωcm and the activation energy is 0.25 eV. The anisotropy of the resistivities in (010) ($\rho_{//\mathbf{c}}/\rho_{//\mathbf{a}}$) is 10^4. The high resistivity along **c** is reasonable because the conduction pathway is interrupted by the anion sheets.

The band structure was examined on the basis of the simple tight-binding approximation. The transfer integrals(t) were assumed to be proportional to the intermolecular overlap integrals(S) of the highest occupied molecular orbital (HOMO)($t \simeq ES$, where E is the constant of the order of the orbital energy of HOMO ($\simeq$ -10 eV)). The A. O. parameters reported by Mori et al.$^{9)}$ were adopted. The overlap integrals are compared with those of β-(BEDT-TTF)$_2$PF$_6$$^{10)}$(Table 2). Despite the molecular stacking along **b**, the intermolecular overlap integral between the molecules interrelated by the inversion symmetry (S_2) is very small. This is due to the large intermolecular S···S distance (>3.9 Å) caused by the steric effect of the ethylene groups. Based on the overlap integrals in Table 2, the energy bands were calculated (Fig. 5). According to this simple band picture, there exists a Fermi surface indicating the system to be metallic, which is inconsistent with the results of the conduction experiments. By neglecting the interactions less than S_4, the approximate energy bands were easily deduced as,

$$\varepsilon(\mathbf{k}) = 2t_4\cos\mathbf{ka} \pm (t_1{}^2 + t_3{}^2 \pm 2t_1t_3\cos\mathbf{k}(\mathbf{b}/2))^{1/2} \qquad (1)$$

This energy band equation is essentially the same as simplified band of β-(BEDT-TTF)$_2$PF$_6$.$^{10)}$ The energy bands have four branches. They are separated into the two upper bands and the two lower bands. When $\mathbf{kb}/2 = \pi/2$, energy levels are degenerated (Fig. 5). The top of the lower bands is at $-2t_4+t_1-t_3$($=\varepsilon(\mathbf{a}^*/2)$) and the bottom of the upper bands is at $2t_4-t_1+t_3$($=\varepsilon(0)$). Therefore if $2t_4 > t_1 - t_3$ (or $2S_4 < S_1 - S_3$), there exists a energy gap between the lower and upper bands. When the energy bands of the 2:1 complex are separated by a gap at the middle of the band energy, the Fermi surface obtained by the simple tight-binding approximation is frequently artificial and the system becomes semiconductive, probably due to the effect of large on-site Coulomb repulsion.[6,11] When the intermolecular interaction along the transverse direction is large, the condition, $2S_4 < S_1 - S_3$ is not satisfied. In fact, β-(BEDT-TTF)$_2$PF$_6$ with large transverse interaction is in "quasi-metallic" state above room temperature.[8,10] The transverse interaction is very small in δ-(BEDT-TTF)$_2$AuI$_2$ and $2S_4$ is nearly equal to $S_1 - S_3$. Considering the roughness of the estimation of the transfer integrals, the condition of the formation of the mid-gap appears to be almost satisfied. Thus the semiconductive behavior of δ-(BEDT-TTF)$_2$AuI$_2$ seems to be reasonable.

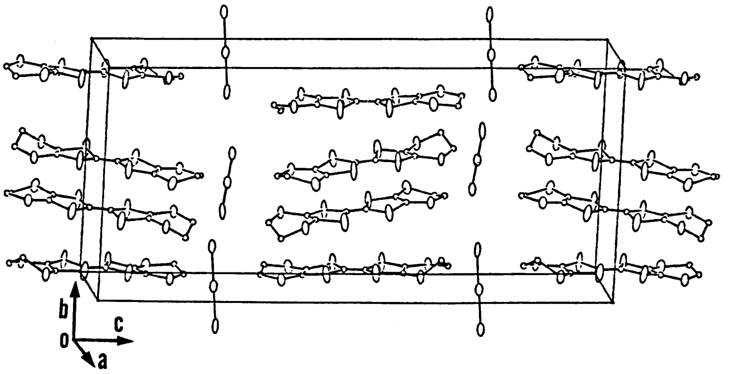


Fig. 1. Crystal structure of δ-(BEDT-TTF)$_2$AuI$_2$.

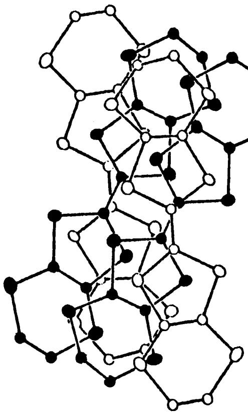
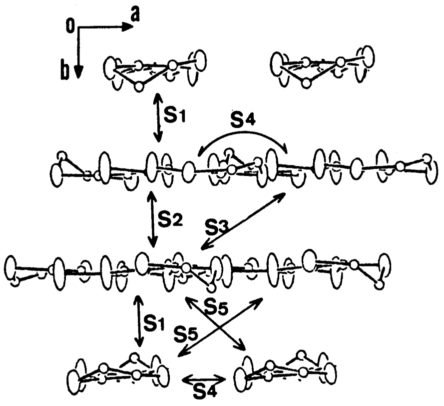


Fig. 2. Mode of intermolecular overlapping along **b**.

Table 2. Intermolecular overlap integrals ($S \times 10^3$) of HOMO of BEDT-TTF in δ-(BEDT-TTF)$_2$AuI$_2$ and β-(BEDT-TTF)$_2$PF$_6$



	δ-AuI$_2$	β-PF$_6$
S1	11.4	10.4
S2	0.7	-3.2
S3	6.5	14.2
S4	2.5	8.4
S5	0.8	2.8

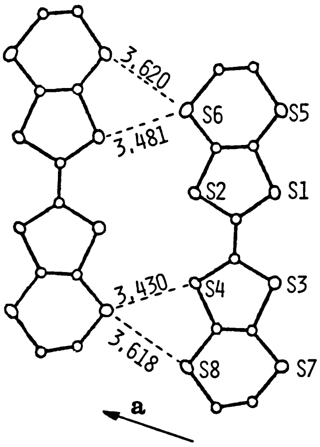


Fig. 3. Side-by-side arrangement of BEDT-TTF's.

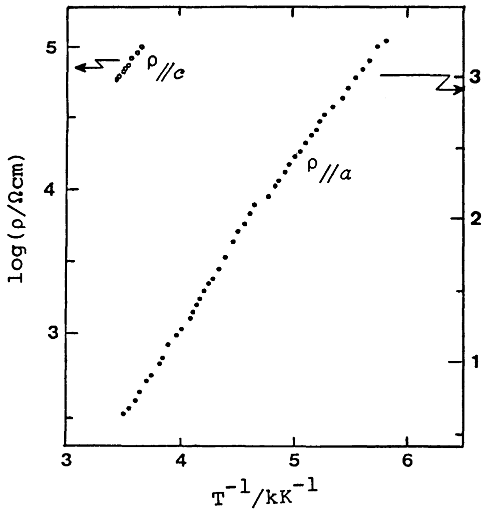


Fig. 4. Electrical resistivity of δ-(BEDT-TTF)$_2$AuI$_2$.

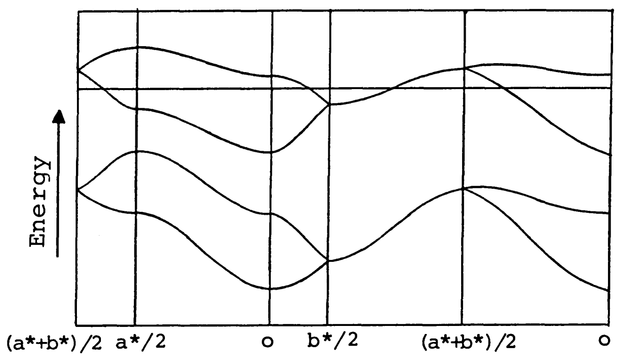


Fig. 5. Band structure of δ-(BEDT-TTF)$_2$AuI$_2$.

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(Received April 19, 1986)