CHEMISTRY LETTERS, pp. 1589-1592, 1986.

Crystal Structure and Electrical Properties of an Organic Conductor δ-(BEDT-TTF)$_2$AuBr$_2$

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The crystal structure of a novel organic conductor δ-(BEDT-TTF)$_2$AuBr$_2$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) is determined by X-ray analysis. This salt is essentially isostructural with δ-(BEDT-TTF)$_2$AuI$_2$ and one-dimensional along the adjacent stacks. Along this direction a two-fold superlattice is present at room temperature. The resistivity and the thermoelectric power exhibit anomalies above 320 K.

Since the discovery of superconductivity in β-(BEDT-TTF)$_2$AuI$_2$,[1] several dihalogenoaurate salts of BEDT-TTF have been investigated in an attempt to develop a new organic superconductor.[2-5] As for $AuBr_2^-$ salts, α'-(BEDT-TTF)$_2$AuBr$_2$, which is isostructural with $Au(CN)_2^-$ and $Ag(CN)_2^-$ salts,[4] and β''-(BEDT-TTF)$_2$AuBr$_2$, which is regarded as a modification of the superconductive β-form,[5] have been reported so far. In the present paper, we report the crystal structure, the band calculation, and the electrical properties of δ-(BEDT-TTF)$_2$AuBr$_2$, and discuss its relation to other BEDT-TTF salts from the structural point of view.

Black rod-like crystals were grown by electrochemical crystallization of BEDT-TTF in benzonitrile using tetra-n-butylammonium dibromoaurate(I) as a supporting electrolyte. Crystal data: orthorhombic, space group Pbcm, a=6.798(2), b=14.837(6), c=32.624(5) Å, V=3290(3) Å^3, and Z=4. The detail of the structure analysis followed the description in Ref. 5. By using 2479 independent reflections ($|F_o|>3\sigma(F)$), the structure was refined to an R value of 0.065.

The atomic parameters are listed in Table 1, and the crystal structure is shown in Fig. 1. The anion is present on a mirror plane at z=1/4. The donors form a conducting sheet parallel to the (001) plane, and the sheets are separated from each other by the anions. The molecular arrangement within this donor sheet is shown in Fig. 2. In a donor stack along the b axis, a two-fold axis along the a axis relates the donor pairs connected by the interaction b1, and an inversion center is present on the interaction b2. These symmetry elements determine the modes of intermolecular overlap as depicted in Fig. 3: twisted for b1 and parallel for b2. Such a molecular arrangement is similar to the β-(BEDT-TTF)$_2$PF$_6$ series of salts.[6] In Table 2, the salts with analogous crystal structures are summarized. Although the space group varies depending on the symmetry of the anion and on the

interrelation of the different donor sheets, these salts have the following common structural characteristics:
(1) Along the stacking direction (the b axis in Fig. 2), the donors are related by two-fold axes and inversion centers, alternately.
(2) Along these two-fold axes (the a axis), the donors form a uniform side-by-side array.
The present δ-$AuBr_2^-$ salt is considered to be essentially isostructural with the δ-AuI_2^- salt,[3] with respect to the space group and the anion site as well as the donor arrangement (Table 2). However, the crystal shape is quite different; the δ-AuI_2^- salt has been reported to be very thin plates. It is noteworthy that if all donors in a stack were related by two-fold axes, the structure would be that of α'-$(BEDT\text{-}TTF)_2X$ ($X=AuBr_2^-$, $Au(CN)_2^-$, and $Ag(CN)_2^-$) (Ref. 4). On the other hand, in

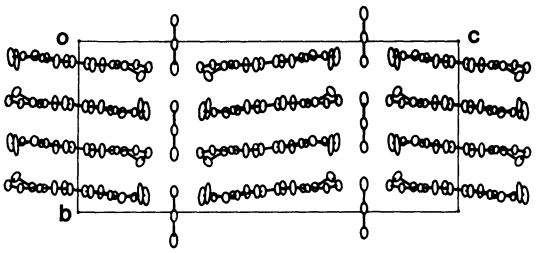

Fig. 1. Crystal sturcture of δ-$(BEDT\text{-}TTF)_2AuBr_2$, projected on the bc plane.

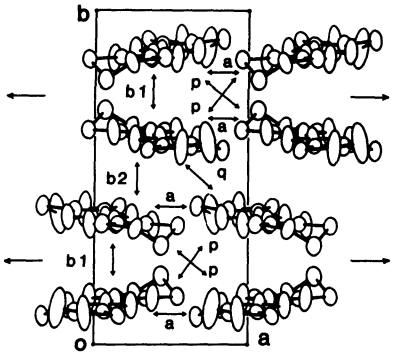

Fig. 2. Molecular arrangement in the donor sheet, projected on the ab plane.

Table 1. Atomic parameters ($\times 10^4$) of δ-$(BEDT\text{-}TTF)_2AuBr_2$

Atom	X	Y	Z	B_{eq}
Au	2145(1)	208(1)	2500	4.7
Br(1)	3866(3)	-1196(1)	2500	5.5
Br(2)	464(3)	1616(2)	2500	7.1
S(1)	790(4)	3824(3)	4679(1)	5.1
S(2)	2188(4)	3604(3)	5617(1)	5.8
S(3)	4903(4)	3821(3)	4415(1)	5.3
S(4)	6293(4)	3597(3)	5355(1)	5.6
S(5)	-839(4)	4146(2)	3861(1)	4.1
S(6)	2993(4)	3619(2)	6498(1)	3.7
S(7)	4065(4)	4143(2)	3544(1)	3.2
S(8)	7916(4)	3559(2)	6193(1)	3.6
C(1)	3248(14)	3792(9)	4825(3)	4.4
C(2)	3830(15)	3680(9)	5216(3)	4.6
C(3)	1235(14)	4030(7)	4165(3)	3.4
C(4)	3985(14)	3622(7)	6000(3)	3.0
C(5)	3127(14)	4020(7)	4043(3)	2.8
C(6)	5848(14)	3619(7)	5878(3)	3.1
C(7)	149(21)	3918(16)	3378(3)	10.9
C(8)	5144(16)	3469(8)	6820(3)	4.2
C(9)	1862(17)	4069(14)	3238(4)	8.5
C(10)	6842(16)	2953(8)	6617(3)	4.5

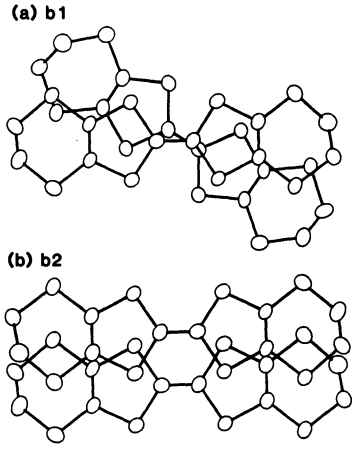

Fig. 3. Modes of intermolecular overlap along the stacking direction.

Table 2. Space group, lattice constants, and anion site of the β-(BEDT-TTF)$_2$PF$_6$ series of salts. The space group and the lattice constants are transformed for a simple comparison with δ-(BEDT-TTF)$_2$AuBr$_2$

Salt	Space group	a /Å	b /Å	c /Å	Anions on	Ref.
β-(BEDT-TTF)$_2$PF$_6$	Pbnn	6.66	14.96	32.64	2	6
(BEDT-TTF)$_2$AsF$_6$	I2/a	6.72	15.10	33.23	$\bar{1}$	7,8
(BEDT-TTF)$_2$SbF$_6$	I2/a	6.70	14.93	33.56	$\bar{1}$	7
γ'-(BEDT-TTF)$_2$AuI$_2$	(Bbcm)[a]	(6.42)[a]	(15.48)[a]	34.16	2/m	2
δ-(BEDT-TTF)$_2$AuI$_2$	Pbcm	6.80	14.82	33.39	m	3
δ-(BEDT-TTF)$_2$AuBr$_2$	Pbcm	6.80	14.84	32.62	m	this work

a) Original B-centered lattice corresponds to (2a, b/2, c).

Table 3. Overlap integrals of the HOMO, the parameter φ: the angle between the molecular plane and the interaction direction, and D: the slip distance along the molecular long axis [9]

Direction	Overlap /10^{-3}	φ /°	D /Å
b1	9.2		
b2	-5.7	62	0.1
a	8.7	2	2.0
p	1.8		
q	8.9	36	1.9

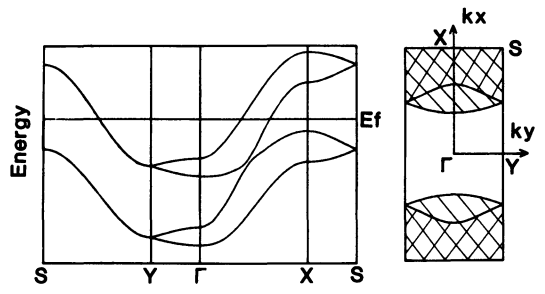

Fig. 4. Energy band structure of δ-(BEDT-TTF)$_2$AuBr$_2$. The shaded regions indicate hole-like parts.

the β-I_3^- series of salts, all donors are related by inversion centers.[5]

The overlap integrals of the HOMO and the band structure are calculated by the procedure of Ref. 9 (Table 3 and Fig. 4). Like β-(BEDT-TTF)$_2$PF$_6$, the band structure is one-dimensional along the adjacent stacks. As discussed in Ref. 9, this is due to the uniform molecular arrangement along the side-by-side array and the dimer structure along the face-to-face stacks. The one-dimensional nature along the a axis again contrasts with the δ-AuI_2^- salt, where the a axis dispersion is comparatively small.[3] This probably originates in the small difference of the donor arrangement.

A preliminary X-ray diffraction study revealed the presence of superlattice reflections corresponding to (2a, b, c) at room temperature. This agrees well with the one-dimensional nature of the band structure in Fig. 4. The structure determination in the present work should be recognized as the average structure which neglected this two-fold modulation. The presence of the modulated structure

allowed us to expect that a metal-insulator (Peierls) transition would take place above room temperature.

Figure 5 shows the resistivity and the thermoelectric power of δ-(BEDT-TTF)$_2$-AuBr$_2$. Below room temperature the resistivity is semiconducting with an activation energy of E_a=0.18 eV. As the temperature is increased, the resistivity decreases abruptly between 320 K and 335 K, but above this temperature region the resistivity is again activated with E_a= 0.4 eV. This activation energy is twice as large as that of the low-temperature phase. Metallic temperature dependence was not found up to 400 K.

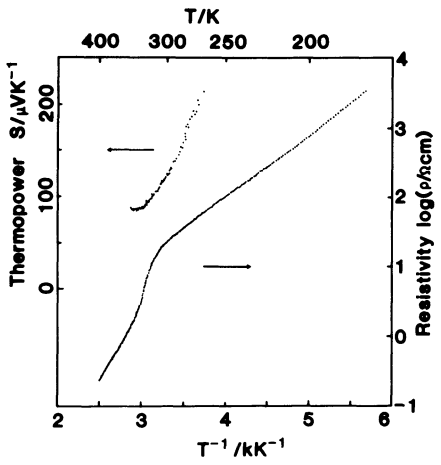

Fig. 5. Electrical resistivity and thermoelectric power of δ-(BEDT-TTF)$_2$AuBr$_2$.

The thermoelectric power is also activated, with E_a=0.2 eV, but becomes almost constant above 330 K. The nature of the phase transition around 330 K and its relation to the two-fold modulation are problems to be resolved in the future.

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(Received July 7, 1986)