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Structural and Electrical Properties of $(BEDT\text{-}TTF)_3CuBr_3$

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An organic conductor $(BEDT\text{-}TTF)_3CuBr_3$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) crystallizes in the monoclinic space group $P2_1/c$, a = 16.937(3), b = 10.123(1), c = 14.178(4) Å, β= 102.59(2)°, V = 2372.2(9) Å^3, and Z = 2. The donors form a two-dimensional network, in which a charge separation takes place as $(D^{3/4+}D^{3/4+}D^0)_2CuBr_2^-CuBr_4^{2-}$. The resistivity at room temperature is 0.6 Ωcm and semiconductive.

Since the discovery of an organic superconductor β-$(BEDT\text{-}TTF)_2AuI_2$,$^{1)}$ a considerable number of halogenoaurate salts of BEDT-TTF have been prepared, and their crystal structures and physical properties have been investigated.$^{2)}$ These investigations have developed the possibility that mixing of (more than) two valence states in the anions containig transition metals realizes new types of donor arrangements and resulting conducting properties, which would be impossible by use of simple anions.$^{3)}$ In the present paper, we report the crystal structure and the electrical properties of a new Cu-containing salt, $(BEDT\text{-}TTF)_3CuBr_3$.

Black plate-like crystals were grown by electrochemical crystallization of BEDT-TTF in 1,1,2-trichloroethane by using tetra-n-butylammonium·$CuBr_2$ as a supporting electrolyte. The crystal structure was solved by the direct method and refined by using 3470 independent reflections (Mo Kα , $2\theta < 60^\circ$, $|F_o| > 3\sigma(|F_o|)$) to an R value of 0.079. Thermal parameters were anisotropic for all non-hydrogen atoms and isotropic for hydrogen atoms.

The atomic parameters are listed in Table 1. Figures 1 and 2 show the crystal structure. The unit cell contains two crystallographically independent BEDT-TTF molecules (molecules A and B). The center of the molecule B is on the inversion center. The donors BEDT-TTF are stacked as AABAAB... along the c axis with their molecular planes almost parallel to each other (Fig. 1). The molecules belonging to the adjacent stacks are inclined with a dihedral angle of ω= 67 - 72°. The donor arrangement is almost the same as that in $(BMDT\text{-}TTF)_3ClO_4(C_2H_4Cl_2)$ (BMDT-TTF: bis(methylenedithio)tetrathiafulvalene).$^{4)}$ There are, however, some unimportant differences: inclusion of the solvent, orthorhombic crystal system, and a smaller dihedral angle ω= 57 - 58° in the BMDT-TTF salt. Inclined arrangements of the donors have been found also in some BEDT-TTF salts: α-$(BEDT\text{-}TTF)_2I_3$ (ω= 59

- 70^o) and θ-(BEDT-TTF)$_2$I$_3$ (ω= 80^o). In general, such inclined arrangements appear when the interactions between donors are highly two-dimensional.

The donor sheets parallel to the (100) plane (Fig. 1) are separated from each other by the anions (Fig. 2). The copper atom is present on an inversion center, and surrounded by four bromine atoms. However, the population of the bromine atoms is about 0.75; the refinement with the Br polulation 1.0 or 0.5 brought much poorer results. Thus the anions are considered to be composed of (about) 1:1 mixture of linear CuBr$_2^-$ (Cu(I), d^{10}) and square planar CuBr$_4^{2-}$ (Cu(II), d^9). This is the first well-characterized BEDT-TTF salts including a divalent anion.

In Table 2 the bond lengths of the TTF skeleton are compared with those in other BEDT-TTF salts. The B molecule can be regarded as neutral. The A molecule is placed between D$^+$ and D$^{1/2+}$; its charge is probably about +0.75. Then the charge in the crystal is distributed as (A$^{3/4+}$A$^{3/4+}$B^0)$_2$CuBr$_2^-$ CuBr$_4^{2-}$.

The electrical resistivity and the thermoelectric power are shown in Fig. 3. The resistivity is about 0.6 Ωcm at room temperature, and its activation energy is 0.17 eV above room temperature, and 0.05 eV below 200 K. The thermoelectric power is also activated with an activation energy of about 0.1 eV, and changes its sign at 350 K.

Table 1. Atomic Coordinates (x 10^4)

Atom	X	Y	Z	B$_{eqv}$
Cu	5000	5000	0	2.8
Br(1)	4801(1)	3312(1)	1093(1)	3.1
Br(2)	4748(1)	6642(1)	1112(1)	3.3
S(1)	8336(1)	982(3)	2892(2)	2.9
S(2)	10191(1)	963(3)	3932(2)	3.1
S(3)	8543(1)	-1348(3)	1768(2)	3.2
S(4)	10474(1)	-1348(3)	2831(2)	3.3
S(5)	6582(1)	1197(3)	2183(2)	3.8
S(6)	11857(1)	1211(3)	5056(2)	3.2
S(7)	6811(1)	-1644(3)	837(2)	3.1
S(8)	12205(1)	-1588(3)	3737(2)	3.3
SS(1)	8937(1)	3754(3)	4973(2)	3.3
SS(2)	9162(1)	6252(3)	3987(2)	3.4
SS(3)	7177(1)	3583(3)	4192(2)	3.2
SS(4)	7452(2)	6583(3)	3033(2)	3.5
C(1)	8999(5)	-204(9)	2618(6)	2.7
C(2)	9799(5)	-203(9)	3069(6)	2.5
C(3)	7457(5)	345(9)	2136(7)	2.7
C(4)	11171(5)	337(9)	4179(6)	2.2
C(5)	7558(5)	-747(9)	1609(6)	2.3
C(6)	11299(5)	-716(9)	3674(7)	2.5
C(7)	5823(5)	15(11)	1660(7)	3.3
C(8)	12738(5)	141(10)	5260(7)	3.1
C(9)	5947(5)	-515(10)	697(7)	3.0
C(10)	12949(6)	-400(10)	4345(7)	2.9
CC(1)	9616(5)	4991(10)	4782(7)	2.8
CC(2)	8085(5)	4480(9)	4257(7)	2.7
CC(3)	8182(5)	5617(9)	3810(7)	2.6
CC(4)	6518(5)	4347(10)	3139(7)	3.0
CC(5)	6497(6)	5812(10)	3163(7)	3.3

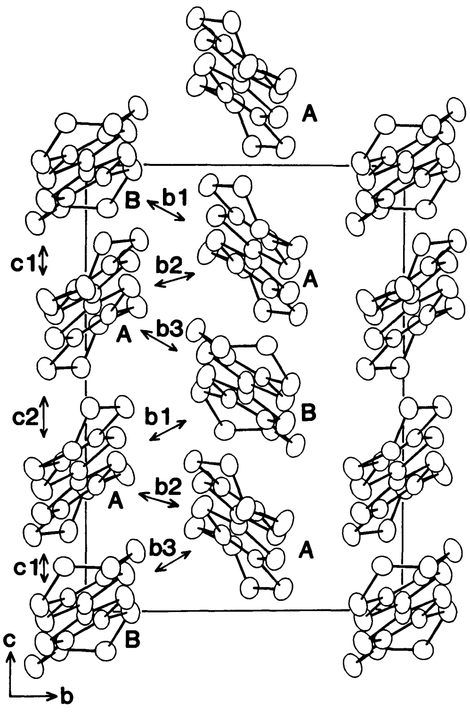

Fig. 1. Donor arrangement of (BEDT-TTF)$_3$CuBr$_3$, projection along the a axis.

The overlap integrals calculated by a simple molecular orbital calculation are listed in Table 3.[5)] The interactions along the stack, especially c2, are smaller than the transverse interactions. These transverse interactions form a two-dimensional network, and lead to a two-dimensional energy band. Because a

Table 2. A comparison of averaged bond lengths (Å) (mmm molecular symmetry).

	D^0	B	$D^{1/2+}$	A	D^+
C(1)-C(2)	1.319	1.31	1.365	1.37	1.38
C(1)-S(1)	1.757	1.76	1.740	1.73	1.72
C(3)-S(1)	1.754	1.74	1.763	1.75	1.73
C(3)-C(4)	1.332	1.34	1.329	1.35	1.37

D^0: neutral BEDT-TTF, $D^{+1/2}$: α-(BEDT-TTF)$_2$PF$_6$, and D^+: (BEDT-TTF)ReO$_4$(THF)$_{0.5}$.[5)]

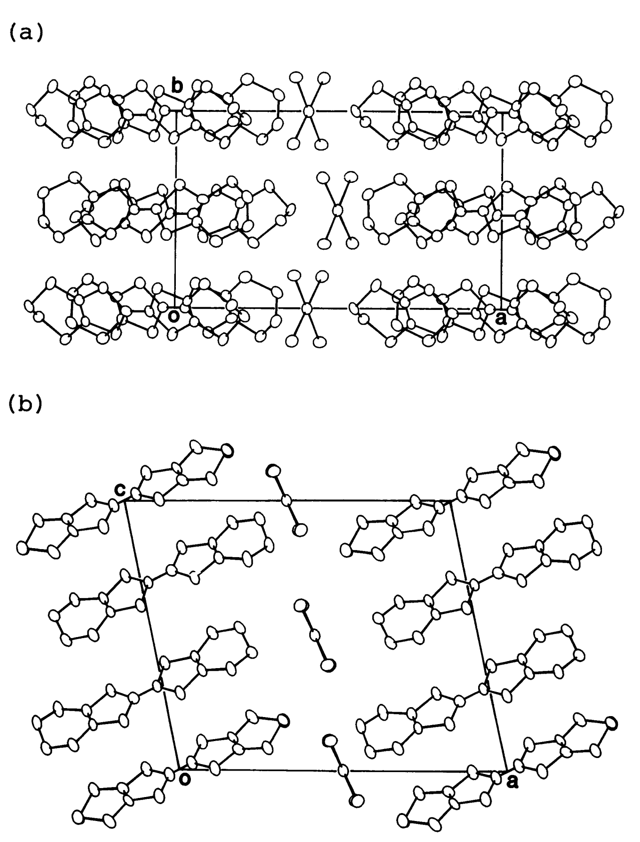

Fig. 2. Crystal structure of (BEDT-TTF)$_3$-CuBr$_3$, projection along (a) the c axis and (b) the b axis.

Table 3. Calculated overlap integrals of HOMO (x 10^3). The symbols of the interactions are designated in Fig. 1.

c1	4.4	b1	-6.3
c2	0.7	b2	7.8
		b3	12.2

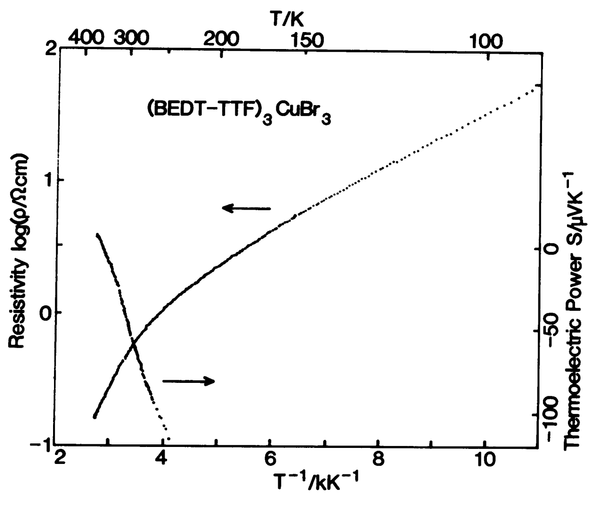

Fig. 3. Electrical properties.

unit cell contains six BEDT-TTF molecules, the conduction band consists of six energy bands. These six are separated by a small energy gap to three pairs of energy bands due to the essentially three-fold periodicity of the molecular arrangement (Fig. 1). Since three electrons (in a unit cell) are present on the conduction band, the conduction band is half-filled. Thus the middle pair of the energy band is half-filled. If there were no charge separation, the band structure would be semimetallic. The charge separation, however, induces a small gap between the central pair of the energy bands. This simple model agrees well with the moderately high conductivity and the change of sign in thermoelectric power.

There was some ambiguity in the estimation of both the charge separation and the Br population. If the Br population were 1.0 and the charge on the molecule A were 1+, the charge distribution would be $(A^+A^+B^0)CuBr_4^{2-}$. This case would afford a 1/3-filled conduction band and an inherently insulating energy band even without the charge separation (a kind of Peierls structure). This model clearly conflicts with the observed electrical properties. Like this way, however, the Br population is strongly correlated with the positive charge on BEDT-TTF. There may remain some possibility that the Br population and the charge on the molecule A are somewhat deviated from 0.75.

The charge separation has been also observed in $(BMDT\text{-}TTF)_3ClO_4(C_2H_4Cl_2)$.$^{4)}$ It should be, however, pointed out that the positive charge is distributed in the opposite way; the centrosymmetric molecule is charged in the BMDT-TTF salt. (The definition of A and B molecules are opposite in Ref. 4 and the present paper). In addition, the positive charge is fractional (3/4+) in the present salt. The crystal structure type of these salts is obviously associated with the 3:1 (donor:anion) composition. Generally BEDT-TTF prefers 1/2+ (∿1+) charge and 2:1 composition. The averaged charge on the BEDT-TTF in the present salt is actually 1+. Thus the realization of the present structure type is related to the inclusion of the divalent anion, $CuBr_4^{2-}$. This observation suggests the further possibilities of forming new structure types by the proper use of divalent anions.

References

1) H. H. Wang, M. A. Beno, U. Geise, M. A. Firestone, K. S. Webb, L. Nunez, G. W. Crabtree, K. D. Carlson, J. M. Williams, L. J. Azevedo, J. F. Kwak, and J. E. Schirber, Inorg. Chem., 24, 2466 (1985).

2) T. Mori, F. Sakai, G. Saito, and H. Inokuchi, Chem. Lett., 1986, 1589, and references therein.

3) T. Mori and H. Inokuchi, Solid State Commun., in press.

4) R. Kato, H. Kobayashi, A. Kobayashi, and Y. Sasaki, Chem. Lett., 1984, 1693: R. Kato, H. Kobayashi, T. Mori, A. Kobayashi, and Y. Sasaki, Solid State Commun., 55, 387 (1985).

5) H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, and H. Inokuchi, Chem. Lett., 1984, 183.

6) T. Mori, A. Kobayashi, Y. Sasaki, R. Kato, and H. Kobayashi, Solid State Commun., 53, 627 (1985).

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