CHEMISTRY LETTERS, pp. 1753-1756, 1987. 

# Crystal Structure and Electrical Properties of $(BEDT\text{-}TTF)_3Br_2(H_2O)_2$

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A small anion, $Br^-$, forms a metallic 3:2 BEDT-TTF salt with an inclusion of water. In the crystal two water molecules and two bromide anions form a cluster which behaves as a dianion group. The measurement of the electric resistivity indicates that this material has a metal-insulator transition at 185 K.

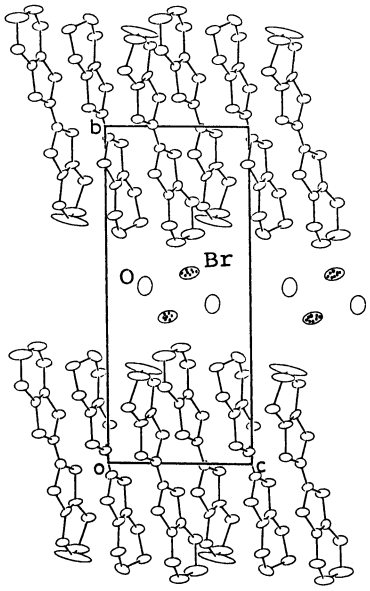
An organic donor BEDT-TTF is a unique molecule which gives a variety of packing modes in the complexes with comparing to other donors. For examples eleven phases of iodine complexes of BEDT-TTF have been reported so far: α-$(BEDT\text{-}TTF)_2I_3$,[1,2] β-$(BEDT\text{-}TTF)_2I_3$,[1,2] γ-$(BEDT\text{-}TTF)_3(I_3)_{2.5}$,[1,2] δ-$(BEDT\text{-}TTF)I_3\text{-}(C_2H_3Cl_3)_{0.333}$,[1,2] ε-$(BEDT\text{-}TTF)_4(I_3)_2(I_8)_{0.5}$,[1,2] ζ-$(BEDT\text{-}TTF)_2I_{10}$,[1] η-$(BEDT\text{-}TTF)I_3$[1], θ-$(BEDT\text{-}TTF)_2(I_3)_{1-x}(AuI_2)_x$,[3] and κ-$(BEDT\text{-}TTF)_2I_3$[4]. The way of BEDT-TTF's packing is the most important factor to determine the physical properties of the complexes. The packing ways are controllable to some extent with respect to anions of supporting electrolytes by changing the shape and size including the length of linear anion, employing mixed electrolytes, etc. Though the complexes with long linear anions have much interest because of the discoveries of several superconductors, there are still possibilities to search for good conductors with other anions. In the present paper, we report the crystal structure and electrical properties of BEDT-TTF complex with a quite small anion, $Br^-$.

Black plate-like crystals were obtained by electrical crystallization of BEDT-TTF in chlorobenzene and tetrahydrofuran by using tetra-n-butylammonium bromide as a supporting electrolyte during the course of 1-2 months. The sample crystal

had the shape of a distorted hexagon of the dimension, 0.43 x 0.35 x 0.02 $mm^3$. Reflection data were collected by the $\omega$-$2\theta$ scan technique with a Rigaku automated four-circle diffractometer with graphite monochromatized Cu $K_\alpha$ radiation($2\theta < 120°$). Absorption corrections were performed. Crystal data of $(BEDT\text{-}TTF)_3Br_2(H_2O)_2$ are: triclinic, space group $P\bar{1}$, a=16.167(2), b=18.125(3), c=7.718(1) Å, $\alpha$=91.05(2), $\beta$=94.09(2), $\gamma$=148.18(1)°, V=1176.0(4) $Å^3$, and Z=1. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method by using 2574 reflections ($|F_o| > 3\sigma(|F_o|)$). The final values of R and $R_w$ were 0.082 and 0.072, respectively. The hydrogen atoms were not included in the final refinement and the anisotropic thermal parameters were adopted for other atoms.

The crystal analysis indicates that this complex is composed of three BEDT-TTF, two bromine, and two $H_2O$ in a unit cell. The existence of $H_2O$ in the BEDT-TTF complex is also supported by the elemental analysis.[5] This bromine material is the first BEDT-TTF complex which contains $H_2O$ molecules.[6] Bromine and $H_2O$ molecules exist in the space between the sheet of the BEDT-TTF molecules as shown in Fig. 1. Two bromine anions and two oxygen atoms form a planar square. $Br^-\cdots O$ distances of 3.36 and 3.26 Å are a little bit longer than the van der Waals contact of a bromide anion and an oxygen, 3.22 Å. However, since the angle of Br··O ··Br, 111°, is comparable to that of H-O-H, 104°, the existence of the hydrogen bonds, Br··H-O-H, could be acceptable to form a dianion group containing two bromide anions and two water molecules. The accidental inclusion of water molecules from air moisture may result in the formation of the stable single crystals.

Two BEDT-TTF molecules are crystallographically independent. One is on the center of symmetry and the other is on the general position as shown in Fig. 1. The intramolecular bond distances and bond angles of two crystallographically independent BEDT-TTF molecules are shown in Fig. 2. The closely similar geometry of both BEDT-TTF molecules and the same distance of C=C bonds on the center of BEDT-TTF's, 1.37 Å,[7] suggest the geometry of $BEDT\text{-}TTF^{2/3+}$ and no charge separation. The BEDT-TTF molecules form a face-to-face stack along [11$\bar{1}$] with no short S···S contacts (> 3.6 Å). Along only one of two side-by-side directions, [112] and [221], short S··S distances (< 3.6 Å) are found and this complex has the strong transverse contacts along [221] (Figs. 3 and 4). Hence, though the anion is quite small, the crystal structure is isostructual to $(BEDT\text{-}TTF)_3(ClO_4)_2$,[8]



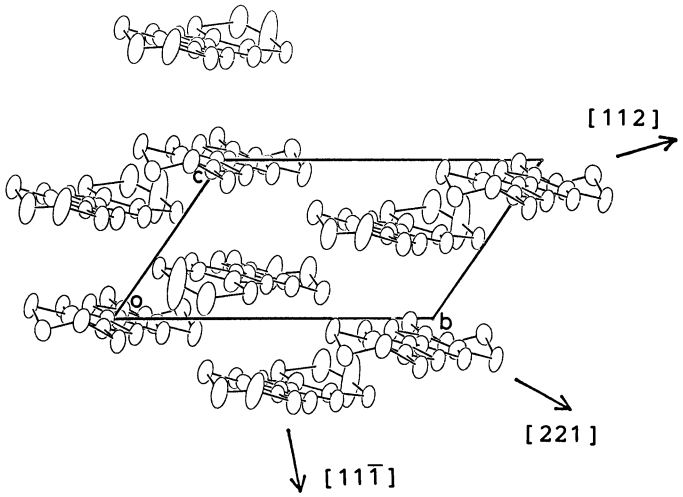
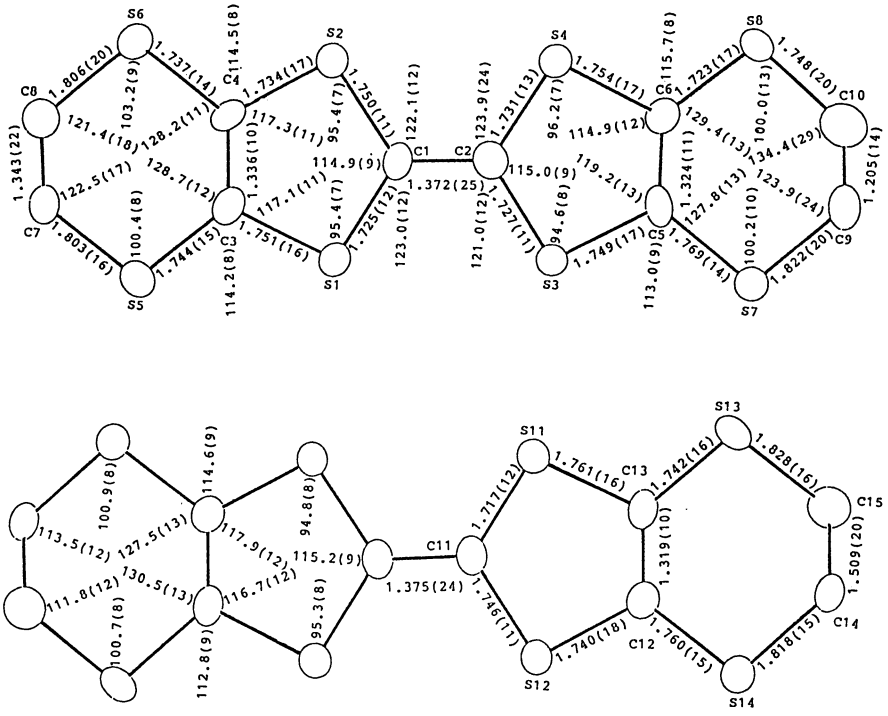




Fig. 3. The arrangement of the donor molecules in $(BEDT\text{-}TTF)_3Br_2(H_2O)_2$.

Fig. 1. Crystal structure of $(BEDT\text{-}TTF)_3Br_2(H_2O)_2$, projected on the bc plane.



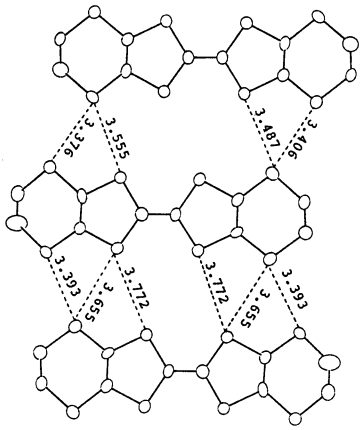



Fig. 4. Side-by-side arrangement of BEDT-TTF's.

Fig. 2. Molecular structure of BEDT-TTF's in $(BEDT\text{-}TTF)_3Br_2(H_2O)_2$.

$(BEDT\text{-}TTF)_3(FSO_3)_2$,[9] $(BEDT\text{-}TTF)_3(BF_4)_2$,[9] and $(BEDT\text{-}TTF)_3(IO_4)_2$, due to the formation of a dianion cluster of $(Br^{-}\cdot\cdot H_2O)_2$.[9]

The measurement of electric resistivity was performed by the conventional d.c. four-probe method. The contacts were applied by a gold paint and four gold wires of 20 μm thick were used as electrical leads. The electric resistivity ( ρ ) at room temperature is 0.013 Ωcm. The temperature dependence of ρ shows a weak metallic behavior above 185 K where the resistivity is 0.010 Ωcm (Fig. 5). Below that temperature the system transforms to semiconductor.

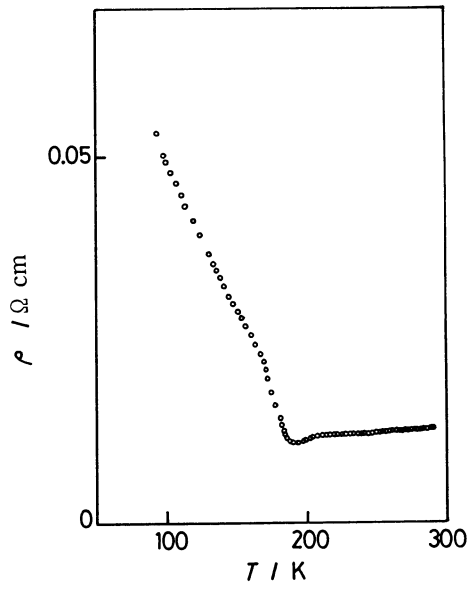



Fig. 5. Electric resistivities of $(BEDT\text{-}TTF)_3Br_2(H_2O)_2$.

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4) A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, Chem. Lett., 1987, 459.
5) Found: C, 26.69; H, 2.09%. Calcd for $Br_2C_{30}H_{28}O_2S_{24}$: C, 26.40; H, 1.97%.
6) The result of this water containing bromine complex of BEDT-TTF was presented at the symposium of Annual Meeting of Chemical Society of Japan, Tokyo, April 1987. During the preparation of this paper we have learned that another water containing BEDT-TTF complex with chlorine was synthesized by D. Chasseau, P. Day et al. We wish to thank Dr. Day for showing us the preprint: D. Chasseau, D. Watkin, M. Rosseinsky, M. Kurmoo, and P. Day, in press.
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9) S. S. P. Parkin, E. M. Engler, V. Y. Lee, and R. R. Schumaker, Mol. Cryst. Liq. Cryst., 119, 375(1985). Judging from the volume of the unit cell of the bromine complex reported by S. S. P. Parkin et al., their complex may not be $(BEDT\text{-}TTF)_3Br_2$ but $(BEDT\text{-}TTF)_3Br_2(H_2O)_2$.

( Received June 10, 1987 )