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Structure and Electrical Properties of θ- and κ-Type BEDT-TSeF Salts with Bromomercurate Anions

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Four types of the crystals of BEDT-TSeF ("BETS") salts with bromomercurate anions were synthesized electrochemically. The salts with θ- and κ-type molecular arrangements retain high conductivity down to 4 K.

In the course of the research for the two-dimensional organic conductors with stable metallic states, a new efficient synthetic route of BEDT-TSeF (BETS) has been developed.1) A number of BETS salts have turned out to be more stable metals than the corresponding BEDT-TTF salts.1) In this letter we report some BETS salts with bromomercurate anions.

The crystals were prepared by electrochemical method at room temperature. There are at least four modifications. Let us number them from #1 to #4 for simplicity. The solvent was either chlorobenzene(#1,#3) or 1,1,2-trichloroethane(#2,#4), both of which included 10 %(vol.) of ethanol. The supporting electrolytes were the mixture of $(n\text{-}C_4H_9)_4NBr$, $HgBr_2$ and [K(18-crown-6)]Br or $\{(n\text{-}C_4H_9)_4N\}_2HgBr_4$.

One of these phases (#1) is obtained as a black hexagonal platelet. The conductivity at room temperature is 10 $S\cdot cm^{-1}$. Anomalously small temperature dependence of the resistivity (Fig. 1) will not be an intrinsic nature of the system but possibly related to lattice defects. X-Ray structural analysis gave the stoichiometry, BETS : $HgBr_4$: C_6H_5Cl =4:4:0.25. The crystal data are as follows: θ-$(BETS)_4HgBr_4(C_6H_5Cl)_x$ (x≃0.25), tetragonal, $I4_1/a$, a=9.742(1), c=75.68(1) Å, V=7182.5(2.1) $Å^3$. Figure 2 shows the crystal structure. BETS molecules form conducting layers normal to (001), while $HgBr_4^{2-}$ anions are located on the two-fold axes between the BETS layers (Fig. 2). The Hg-Br length is 2.59(1) Å and the bond angle of Br-Hg-Br is 109.5(2)°. The difference Fourier synthesis revealed the inclusion of the heavily disordered solvent molecules (C_6H_5-Cl). The content of the solvent molecules included were roughly estimated from the occupancy probability of the Cl atom ($x \simeq 0.25$). The gradual loss of the luster of the crystal surface will be related to the loss of the crystal solvent. Every BETS molecule is surrounded by six BETS molecules. The dihedral angle between adjacent donor molecules (A and B in Fig. 3) is 74°. The extended Hückel tight-binding band calculation gave a two dimensional (2D) Fermi surface, whose general feature is essentially the same as that of the organic superconductor θ-ET_2I_3.[2)]

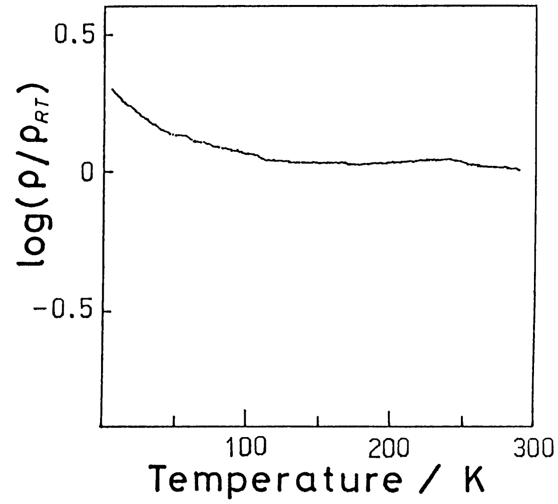

Fig. 1. Electrical resistivity of θ-$(BETS)_4HgBr_4(C_6H_5Cl)_x$.

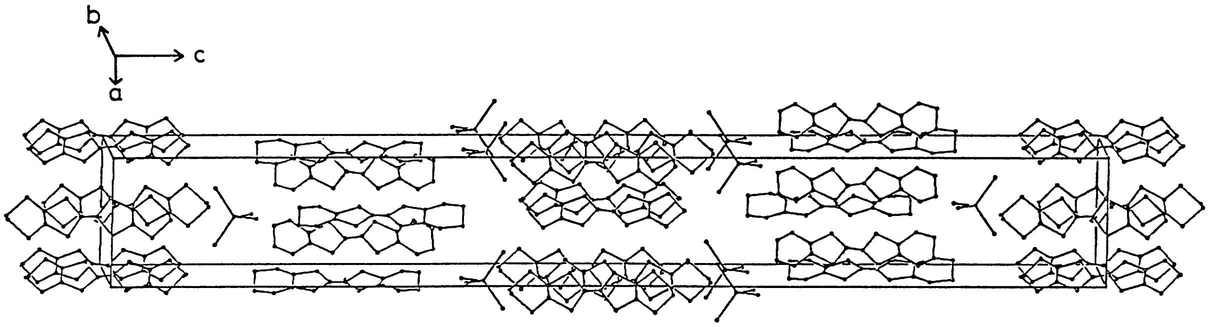

Fig. 2. Crystal structure of θ-$(BETS)_4HgBr_4(C_6H_5Cl)_x$. The positions of C_6H_5Cl are omitted.

The second phase (#2) yielded a black needle. The crystal data are : triclinic, $P\bar{1}$ (or P1), a=17.200(7), b=22.331(7), c=12.015(4) Å, α=110.81 (2), β=110.51(3), γ=64.01(3)° , V=3772.0(2.6) $Å^3$. The ratios of the numbers of atoms in this salt determined by EPMA (electron probe micro analysis) are: S/Br=2.5-3.5, Se/Br=2.5-3.5 and Br/Hg=4.0-5.5. The resistivity is almost constant down to 100 K, below which it increases gradually ($\rho/\Omega\cdot$cm ≃ 2 (RT-100 K), 87 (4 K)).

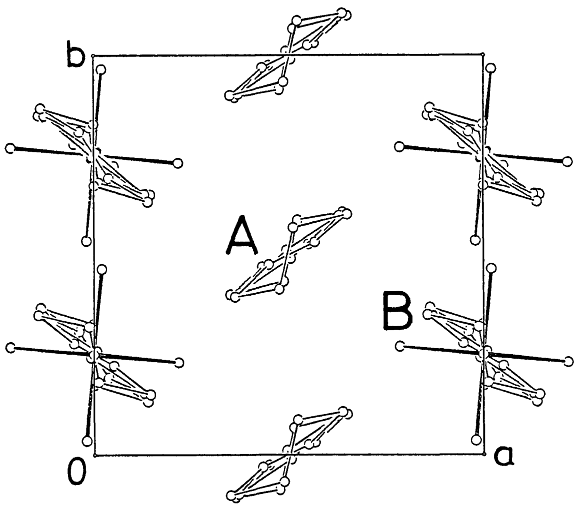

Fig. 3. The θ-type molecular arrangement of BETS' in θ-(BETS)$_4$HgBr$_4$(C$_6$H$_5$Cl)$_x$.

The third phase(#3) exhibits a sharp metal-to-insulator transition at 100 K. The poor quality of the crystal prevented us from the X-ray structural analysis. X-Ray photogragh gave strong diffuse scatterings.

The fourth phase (#4) was harvested as black platelets. Consecutive X-ray photograghs demonstrated that the crystal gradually collapsed presumably by giving off the crystal solvent molecules. So the behavior of the electrical resistivity strongly depends upon the deterioration of the samples (Fig. 4). In one fresh sample, the resistivity seemed to drop around 5 K(d), though we have not yet been able to reconfirm the same behavior. The crystal belongs to the monoclinic system with space group C2/c and the lattice constants of a=39.064(15), b=8.654(4), c=11.516(5) Å, β=106.13(3) ,V=3739.9(2.7) Å^3 . The Br/Hg ratio (3.7-5.3) obtained from EPMA seems to suggest the existence of HgBr$_4^{2-}$ anion. Though the arrangement of BETS molecules was easily deduced and refined, the positions of Hg and Br atoms could not be determined definitely due to their heavy disorderness. The mode of the arrangement of BETS molecules is that of the typical κ-type organic superconductors originally discovered in κ-ET$_2$I$_3$(Fig. 5).$^{3)}$ The intradimer distance between BETS molecules is 3.50 Å. The dihedral angle between the dimers interrelated by the screw axis is 80.3°.

Considering the crucial importance of the disorder in the low-temperature transport properties of the organic conductors, much effort remains to be required to improve the quality of the crystal.

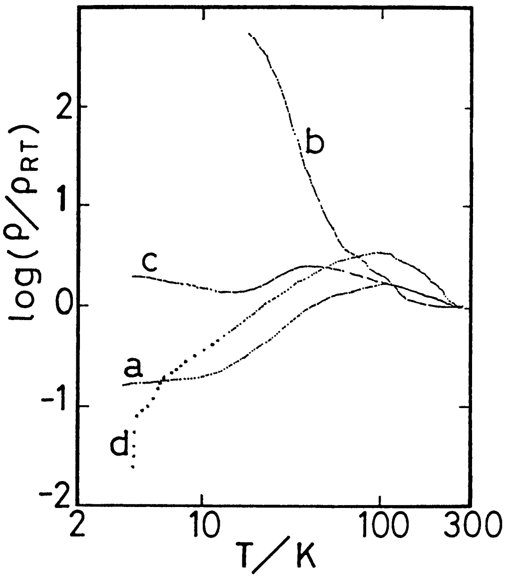

Fig. 4. Sample dependence of the electrical resistivities of the crystals of monoclinic modification (κ-type). (a) A fresh sample. (b) An old sample. (c) After stored in the vapor of the proper solvent, the old sample recovered metallic propety to some extent. (d) One fresh sample showing the resistivity drop around 5 K.

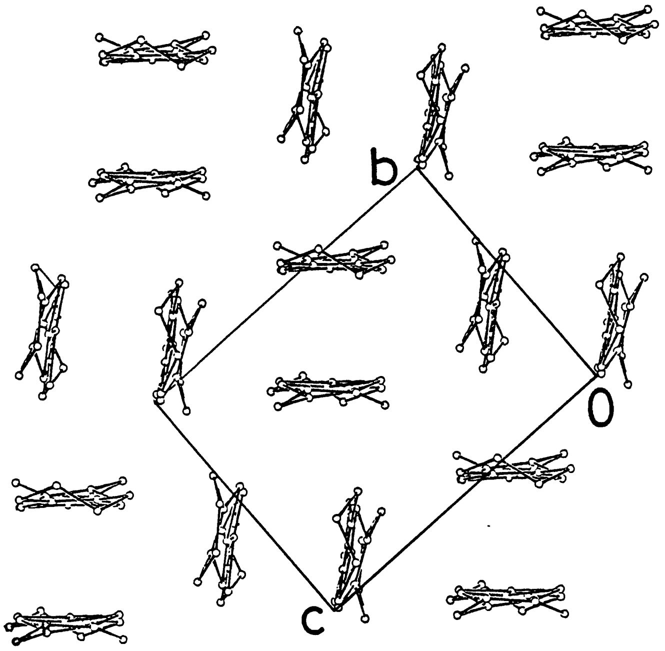

Fig. 5. The κ-type molecular arrangement of BETS' in the monoclinic modification.

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