CHEMISTRY LETTERS, pp. 1211-1214, 1988.

Crystal Structure and Physical Property of $(BEDT\text{-}TTF)_2(IBr_2)_2(1,1,2\text{-Trichloroethane})_{0.5}$

Hideki YAMOCHI, Hatsumi URAYAMA, Gunzi SAITO,*
Kokichi OSHIMA,+ Atsushi KAWAMOTO,++ and Jiro TANAKA++
Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minato-ku, Tokyo 106
+Cryogenic Center, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113
++Department of Chemistry, Faculty of Science, Nagoya University,
Chikusa-ku, Nagoya 464

The title complex which is isostructural to ε-$(BEDT\text{-}TTF)_2I_3(I_8)_{0.5}$ changes its conducting property from semiconductive to metallic by tempering with the loss of its weight. This metallic state retains down to 0.5 K and this product is regarded as being different from α- and β-$(BEDT\text{-}TTF)_2IBr_2$.

BEDT-TTF has become one of the intensely investigated electron donors since it gives several ambient pressure organic superconductors.[1] This donor is also well known to give many complexes of different modifications with the same anion. Among them, α-$(BEDT\text{-}TTF)_2I_3$[2] and ε-$(BEDT\text{-}TTF)_2I_3(I_8)_{0.5}$[3] exhibit the transformation from one modification to the other by tempering the crystals. This paper describes preparation, crystal structure and unusual conducting properties of a modification of the IBr_2 salts; $(BEDT\text{-}TTF)_2(IBr_2)_2$ $(1,1,2\text{-trichloroethane})_{0.5}$ which exhibits the transformation from a semiconductor to a metal by tempering the crystals.

The crystals were prepared by the electrocrystallization in 1,1,2-trichloroethane (TCE). 130 to 150 mg of $Bu_4N{\cdot}IBr_2$ as a supporting electrolyte was added to the solution of 100 ml of TCE containing ca. 30 mg of BEDT-TTF. Microcrystals of the cation radical salts tend to precipitate spontaneously even before the electrodes are connected when the ammonium salt was added. Constant current electrocrystallization (2 μA) for 1 to 2 months gave dark green crystals on the Pt electrodes.[4] The outlooks of these crystals are rich in variety (distorted hexagonal plates, thin plates, broken shell-like masses, and so on), however all of them showed the same behavior during the melting point measurements. These crystals change their color to brown at 180 to 182 °C followed by the decomposition at 224 to 225 °C when heated at the rate of 4 K/min.[5] On the other hand, the diffusion method[6] in TCE gave mainly this modification with α- and/or β-$(BEDT\text{-}TTF)_2IBr_2$ as minor products.

The crystal structure was analyzed on a broken shell-like crystal. The unit cell parameters are; monoclinic, space group $P2_1/c$, a = 18.767(3), b =

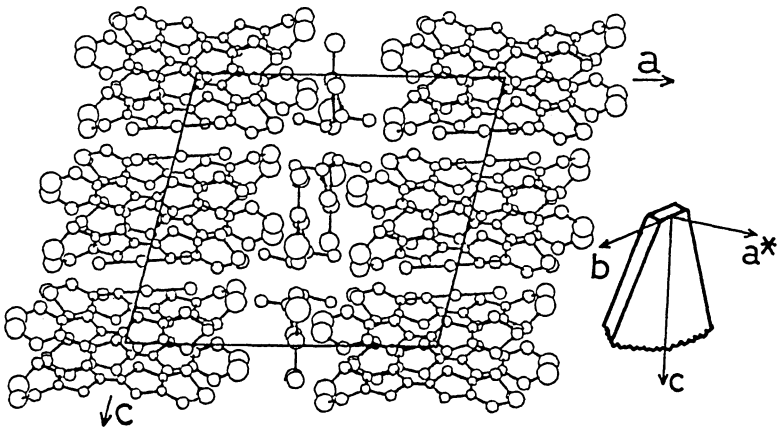

Fig. 1. Crystal structure of $(BEDT\text{-}TTF)_2(IBr_2)_2(TCE)_{0.5}$. Left; Projection along the b-axis. Right; Crystal habit.

13.859(1), c = 17.133(2) Å, β = 103.7(1)°, V = 4329.3(8) Å^3, Z = 4 for the formula of $(BEDT\text{-}TTF)_2(IBr)_2(TCE)_{0.5}$, D_m = 2.14, and D_c = 2.162 g/cm^3. These data differ not only from those of semiconductive α-modification [7,8] and ambient pressure superconductor, β-salt (T_c = 2.0 to 2.7 K)[8] but also from that of γ-salt[7] of which the crystal structure has not been solved. The crystal structure was solved by direct method and were refined on F^2 by the full-matrix least-squares program using the 6142 independent reflections ($|Fo| > \sigma(|Fo|)$). The final R-value is rather high (0.1084) due to the poor quality of the crystal and the disorders of the anion site. Figure 1 shows the packing pattern and the relation between the crystallographic axes and the outlook of the crystal. The cation-anion layers of the composition $(BEDT\text{-}TTF)_2IBr_2$ alternate with the anion-solvent layers along the a-axis. The total packing pattern is isostructural to ε-$(BEDT\text{-}TTF)_2I_3(I_8)_{0.5}$.[3]

Regarding the cation-anion layers, a couple of crystallographically independent BEDT-TTFs form a dimeric pair with the molecular plane almost parallel to each other (Fig. 2a). Within the dimer, the BEDT-TTF molecules overlap almost directly on each other (dihedral angle = 4.49°) and short S•••S contacts using each inner four sulfur atoms (3.36 to 3.60 Å) are found. The carbon atoms of one of the terminal ethylene groups have big temperature factors (B_{eq} = 10.51 to 14.34 Å^2) and these ethylene groups locate on the same side in the dimer. Also short inter-

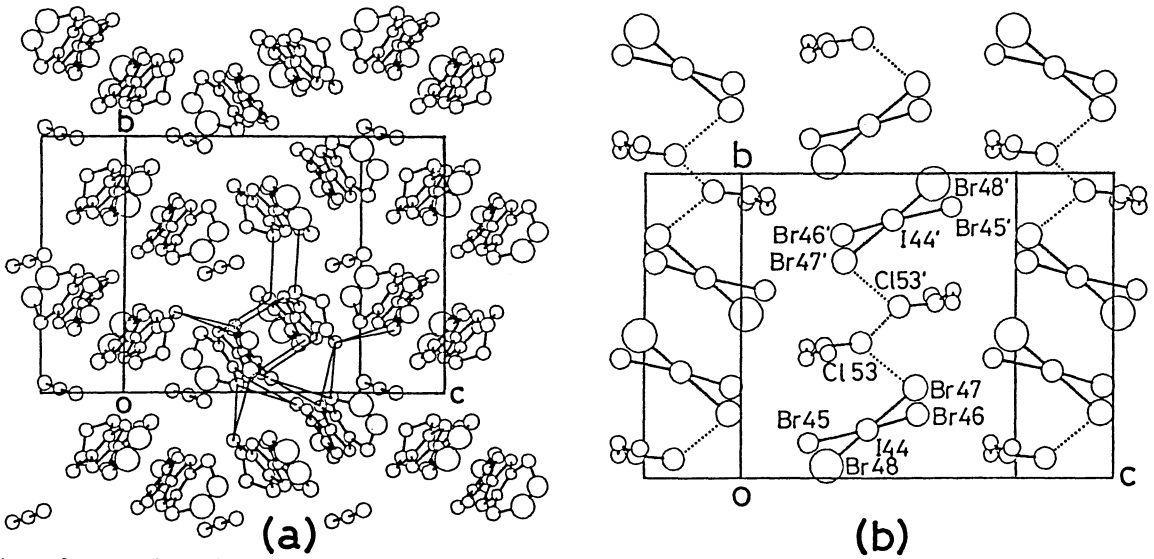

Fig. 2. Projection onto the bc-plane. (a) x= 0, typical intermolecular S•••S contacts shorter than 3.61 Å are drown by solid lines. (b) x = 0.5.

dimer S•••S contacts are observed ($\geq$ 3.47 Å). Consequently, two dimensional S•••S network is formed parallel to the bc-plane and IBr_2^- ions penetrate to this sheet.

In the anion-solvent sheet (Fig. 2b), the occupancies of carbon, chlorine, and bromine atoms are 50%, respectively, and the layer is composed of [IBr_2(TCE)IBr_2] as a unit cluster. There are two assignments of atomic positions which avoid intermolecular halogen-halogen atomic contacts shorter than the sum of van der Walls radii in the cluster. One is the set of atoms at Br48, Br47, Cl53', Br46', and Br45'. The other is Br45, Br46, Cl53, Br47', and Br48'. It is reasonable to consider that these two types of clusters have 50% of possibilities to appear at each site.

To the best of our knowledge, this complex is the first example of the ε-I_3 type BEDT-TTF complex other than the I_3 complex where the I_3 and I_8 anions are replaced by IBr_2^- and [IBr_2(TCE)IBr_2] unit, respectively, so the present complex can also be expressed as $(BEDT\text{-}TTF)_2IBr_2[IBr_2(TCE)IBr_2]_{0.5}$. With regard to the conducting properties of ε-I_3 complex, Shibaeva et al. reported that the semiconductive ε-I_3 salt becomes an ambient pressure superconductor β-$(BEDT\text{-}TTF)_2I_3$ by tempering.[3] One can expect that the present IBr_2 complex shows the similar behavior from the view point of the crystal structure.

The direct current resistivities were measured by four-probe method using gold wires and gold paste before and after the tempering as mentioned below. Before the tempering, the resistivities in the bc-plane are almost isotropic and reveal 2 to 5 x 10^3 Ω cm in the bc-plane (Ea = 0.28 eV; Fig. 3, insert), however the resistivity along the a^*-axis is ca. 10^6 Ω cm. Using the thermogravimetric apparatus, the crystals were heated at 140 °C for 30 hours under the reduced pressure of 1 to 5 mmHg. The crystals change the color to brown and loose 32% of their original weight while the shapes are still unchanged. The brown crystals show the room temperature resistivities of ca. 0.1 Ω cm and metallic behavior down to 0.5 K (Fig. 3). In the infrared spectrum (KBr disk), rather sharp vibrational absorption bands in the original crystals almost disappeared and a broad intense one appeared. This band covers almost all the measured range (4000 to 400 cm^{-1}) and indicates that the fully ionized complex changed to a mixed-valence compound.

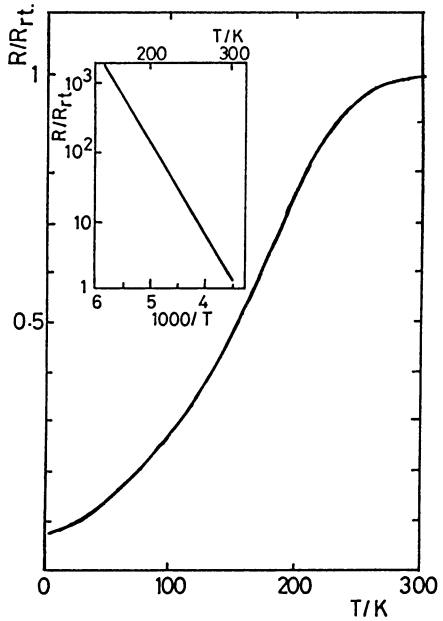

Fig. 3. Temperature dependencies of resistivity of $(BEDT\text{-}TTF)_2(IBr_2)_2(TCE)_{0.5}$ before (insert) and after tempering.

The most interesting and important subject is how the crystals transform and what the product is. As to the known metallic IBr_2 salts, β-$(BEDT\text{-}TTF)_2IBr_2$ has been well analyzed, however γ-salt gave only the unit cell parameters and conducting property (metallic down to 1.3 K).[7] The characterization of the samples which lost ca. 30% of their original weight have been carried out. The elemental analyses (C, H, N, S, I) never gave the comfortable values as β-modification. On the other hand, the mass spectral

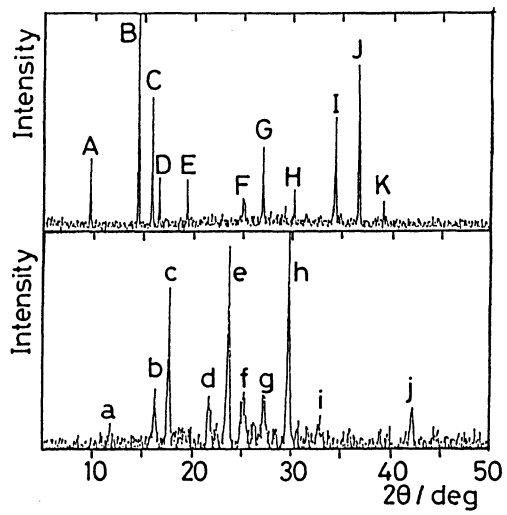

Fig. 4. X-Ray diffraction pattern of the powdered samples before (upper) and after (lower) tempering.

measurements showed that the metallic product contains BEDT-TTF and IBr_2 species but the signals arisen from TCE could not be detected. Since the number of reflections having significant intensities were so little on each single crystals, the X-ray diffraction measurements were carried out on the powdered samples (Fig. 4). It is obvious that the crystal structure of the tempered sample differed from that of the virgin one. The crystals tend to break into mica-like thin plates by grinding both before and after the tempering. In our experiments, this situation enhances the peak intensities arisen from the reflection plane parallel to the most developed face.[9] The peaks c, e, and h of the tempered sample can be indexed as (003), (004), and (005), respectively, however the total feature of the diffraction pattern does not agree with the simulated pattern of the β-$(BEDT\text{-}TTF)_2IBr_2$. The actual mechanism of the transformation and the structure of the tempered crystals are not clear for us at present. Further studies are in progress in order to obtain a decisive evidence whether the tempered saple is γ-modification or hitherto unknown new modifications.

This work was partly supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 62604014). One of the authors (H. Y.) thanks Professor Shibaeva for her kind informations on the ε-I_3 complex.

References

1) H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett., 1988, 55; H. Urayama, H. Yamochi, G. Saito, S. Sato, A, Kawamoto, J. Tanaka, T. Mori, Y. Maruyama, and H. Inokuchi, ibid., 1988, 463 and references cited in.
2) G. O. Baram, L. I. Buravov, L. S. Degtyarev, M. E. Kozlov, V. N. Laukhin, E. E. Laukhina, V. G. Onishchenko, K. I. Pokhodnya, M. K. Sheinkman, R. P. Shibaeva, and E. B. Yagubskii, JETP Lett., 44, 376(1986); D. Schweitzer, P. Bele, H. Brunner, E. Gogu, U. Haeberlen, I. Hennig, I. Klutz, R. Swietlik, and H. J. Keller, Z. Phys. B, 67, 489(1987)
3) R. P. Shibaeva, R. M. Lobkovskaya, E. B. Yagubskii, and E. E. Kostyuchenko, Sov. Phys. Crystallogr., 31, 267(1986).
4) Preliminarily reported in G. Saito, Physica, 143B, 296(1986).
5) Under the same condition, α-$(BEDT\text{-}TTF)_2IBr_2$ crystals crack in the range of about 145 to 220 °C and decompose at around 225 to 235 °C without foaming. The crystals of β-modification remain unchanged up to 280 °C.
6) G. Saito, T. Sugano, H. Yamochi, M. Kinoshita, K. Oshima, M. Suzuki, C. Katayama, and J. Tanaka, Chem. Lett., 1985, 1037.
7) E. B. Yagubskii, I. F. Shchegolev, R. P. Shibaeva, D. N. Fedutin, L. P. Rozenberg, E. M. Sogomonyan, R. M. Lobkovskaya, V. N. Laukhin, A. A. Ignat'ev, A. V. Zvarykina, and L. I. Buravov, JETP Lett., 42, 206(1985).
8) J. M. Williams, H. H. Wang, M. A. Beno, T. J. Emge, L. M. Sowa, P. T. Copps, F. Behroozi, L. N. Hall, K. D. Carlson, and G. W. Crabtree, Inorg. Chem., 23, 3840(1984).
9) For the non-tempered sample, peaks A, B, E, and J are enhanced comparing to the simulated pattern of the completely non-oriented sample.

(Received May 11, 1988)