$(ET)_3(Br_3)_5$: A Metallic Conductor with an Unusually High Oxidation State of ET (ET = Bis(ethylenedithio)tetrathiafulvalene)

Hiromi Minemawari, Toshio Naito, and Tamotsu Inabe*
Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810

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Electrochemical oxidation of ET with Br^- in methanol/$CHCl_3$ yields a metallic crystalline product, $(ET)_3(Br_3)_5$, in which the bromine chemical species is all Br_3^- and the formal charge of ET becomes an unusually high value (5/3+).

ET (bis(ethylenedithio)tetrathiafulvalene) is known as an excellent donor component to a number of organic conductors and superconductors. Most of these conductors have the following stoichiometry, $(ET)_2X$ (X = monovalent anion). In addition to such a 1/2+ formal charge of ET, it is known that there are metallic conductors with different formal charges such as 2/3+ and 5/6+.[1] These partially oxidized salts are thought to consist of a mixed-valence state of ET^0 and ET^{1+}. On the other hand, one can imagine a partially oxidized salt with higher oxidation states, since ET can be oxidized up to ET^{2+}. Such a conducting salt, having a mixed-valence state of ET^{1+} and ET^{2+}, has only been reported for $(ET)_6(AuBr_2)_6Br(TIE)_3$ (TIE = tetraiodoethylene).[2] The formal charge of ET in this salt is 7/6+, only slightly higher than 1+, and its conductivity shows weakly temperature-dependent metallic behavior down to 50 K. Another such partially oxidized conducting salt reported thus far is the TTM-TTP salt (TTM-TTP = 2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene). Since TTM-TTP demonstrates a four-step reversible redox process,[3] high oxidation states are easily accessible. Therefore, in the partially oxidized salt of $(TTM\text{-}TTP)(I_3)_{5/3}$, the 5/3+ formal charge of TTM-TTP has been achieved.[4] In the present study, we have identified a novel metallic ET conductor with a formal charge of 5/3+ for ET. Such a high oxidation state for ET is rather surprising, because ET only shows a two-step reversible redox process. In this communication, we present the crystal growth, structure, and physical properties of the crystal, $(ET)_3(Br_3)_5$.

Crystal growth was achieved by a galvanostatic oxidation process with a constant current of 4.0–7.0 μA.[5] Electrolysis in a mixed solvent consisting of methanol/$CHCl_3$ using the electrolyte of TPP•Br or PTMA•Br (TPP = tetraphenylphosphonium, and PTMA = phenyltrimethylammonium) was found to give brownish-black platelets for $(ET)_3(Br_3)_5$. The mixing ratio of the solvent affected the electrolysis; when the methanol/$CHCl_3$ ratio was in the range of 1/5–2/1 by volume, $(ET)_3(Br_3)_5$ was found to be obtained as the major product, whereas different unidentified microcrystals grew simultaneously when the ratio is higher than 1/1 by volume. Significant effects on the crystal growth were observed when the solvent system was altered. Ethanol instead of methanol was found to give $(ET)_3(Br_3)_5$, whereas substituting acetonitrile for methanol gave completely different crystals; the anionic species in the crystal was found to consist only of Br^-.[6]

The crystal structure of $(ET)_3(Br_3)_5$ is shown in Figure 1.[7] The crystallographically independent unit consists of three ET molecules and fifteen bromine atoms. All the bromine atoms exist as discrete Br_3 units,[8] with no anomalies in the temperature factors under the assumption of the occupancy being 1.0. Since the intraunit Br–Br bond lengths were found to be 2.5–2.6 Å, all the Br_3 units can be unambiguously assigned as Br_3^-.[9] Therefore, the formal charge of ET becomes 5/3+ based on the composition. The geometries of three crystallographically independent ET molecules suggest that the charge is almost equally distributed in the three ET molecules.[10,11]

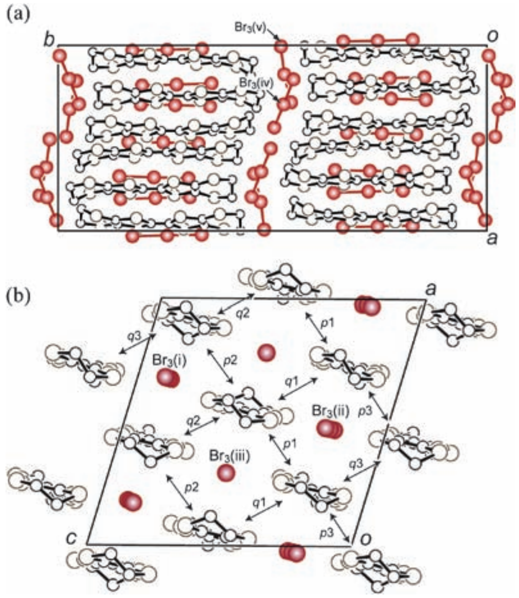

Figure 1. Crystal structure of $(ET)_3(Br_3)_5$. View along the *c* axis (a) and view along the *b* axis (b). Brown spheres represent bromine atoms. The HOMO–HOMO overlap integrals ($\times 10^3$) between the ET molecules are as follows; *p*1: 16.9, *p*2: 4.7, *p*3: −18.6, *q*1: 6.5, *q*2: 20.1, and *q*3: −6.0.

The ET molecules are aligned in the *ac* plane with their long axis nearly parallel to the *b* axis. Three of the five Br_3^- anions (Br_3(i), Br_3(ii), Br_3(iii)), also located in the same plane with their long axis parallel to the *b* axis, form the anion-incorporated ET layer. The remaining two Br_3^- anions (Br_3(iv), Br_3(v)) are located between these layers.

The *b*-axis projection of the anion-incorporated ET layer shown in Figure 1b indicates that the ET···ET contacts are only partially interrupted by Br_3^- anions. The HOMO–HOMO overlap integrals calculated by the extended Hückel method[12] indicate that the electronic interactions are rather two-dimensionally extended in the layer; the band structure calculated is shown in Figure 2. This is primarily due to a number of S···S short contacts between ETs. In addition, there are many notably short Br···S contacts in this layer.

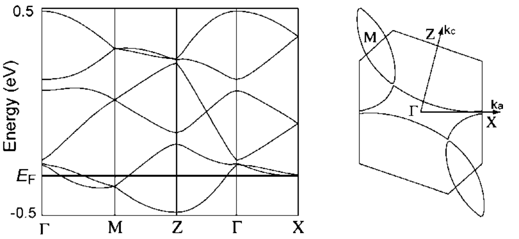

Figure 2. Calculated band structure of $(ET)_3(Br_3)_5$.

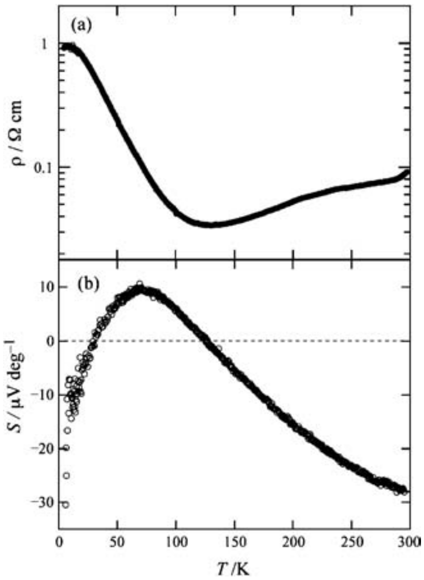

Figure 3. Temperature dependence of the electrical resistivity (a) and the thermoelectric power (*S*; b) of $(ET)_3(Br_3)_5$ along the *c* axis.

Since the crystals were primarily elongated along the *c* axis, the charge-transport properties were measured along the *c* axis. Figure 3a shows the temperature dependence of the resistivity measured by the four-probe method using a carbon paste as the electrical contact between the gold lead wires ($\phi = 10\,\mu m$) and the crystal. The resistivity with a room temperature value of 0.09 Ω cm decreases with decreasing temperature, down to 120 K, showing clear metallic behavior. Below this temperature, the resistivity gradually increases. On the other hand, the thermoelectric power (TEP) shows a large negative value ($-28\,\mu V\,deg^{-1}$) at room temperature, as shown in Figure 3b. The negative value is consistent with the fact that the HOMO band is 1/6-filled, and electrons may be the major charge carrier. The TEP almost correlates linearly with temperature down to 80 K, indicating its metallic nature. The TEP shows a broad positive maximum around 70 K and gradually decreases at lower temperatures. The deviation from the linear correlation is thought to correspond to charge-localized behavior at low temperature. The magnetic susceptibility measured by a SQUID susceptometer at 2–300 K showed a small positive value (about $6.1 \times 10^{-4}\,emu\,mol^{-1}$) over almost the entire temperature range.[10,13] This behavior is considered to show Pauli-like susceptibility, at least in the high-temperature region. However, the constant paramagnetism at low temperature is thought to be inconsistent with the transport behavior, and further investigation is required in order to explore the low-temperature nature of this compound.

In conclusion, we have determined that partial oxidation of ET with a formal charge higher than 1+ can be realized by adjusting the electrolysis conditions. The obtained salt, $(ET)_3(Br_3)_5$, has been found to possess metallic charge-transport properties. Thus far, many ET superconductors have been found in partially oxidized salts with formal charges less than 1+. This study suggests that even with ordinary anions one can expand the variation of the conductors with higher oxidation states by modifying the solvent system and electrolyte composition of the electrochemical crystal growth.

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References and Notes

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13 Very small additional Curie tailing (about 0.16%) was observed at low temperatures.