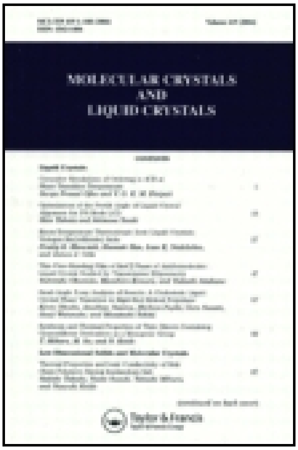

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Bis(ethylenedioxy)tetraselenafulva (BEDO-TSeF), A Late Newcomer to the World of Organic Conductors

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Bis(ethylenedioxy)tetraselenafulvalene (BEDO-TSeF), A Late Newcomer to the World of Organic Conductors

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Synthesis, crystal structure and physical properties of κ*-(BEDO-TSeF)*$_2$*I*$_3$*, (1) are reported. 1 is the first example of a cation radical salt based on BEDO-TSeF, which is the latest chalcogen analogue of BEDT-TTF.*

Keywords: crystal structures; electrical properties; magnetic properties; organic metals; tetraselenafulvalene

INTRODUCTION

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET [1]) is the most successful π-donor derived from TTF and several modifications of the ET skeleton have been reported. Among them, bis(ethylenedithio)tetraselenafulvalene (BETS [2]) and bis(ethylenedioxy) tetrathiafulvalene (BEDO-TTF or BO [3]) are two great results of these modifications. The former sought the enhancement of the chalcogen$\cdots$chalcogen intermolecular contacts by introducing selenium atoms in exchange for solubility towards common organic solvents, and the latter gained the hydrogen bonding ability and higher solubility by introducing the lightest group 16 element that may adversely affect the chalcogen interactions. Both BETS and BO have supplied a large number of organic metals including many superconductors and everyone in the field of organic conductors must have considered the hybrid of these two leading molecules, i.e., "BEDO-TSeF"

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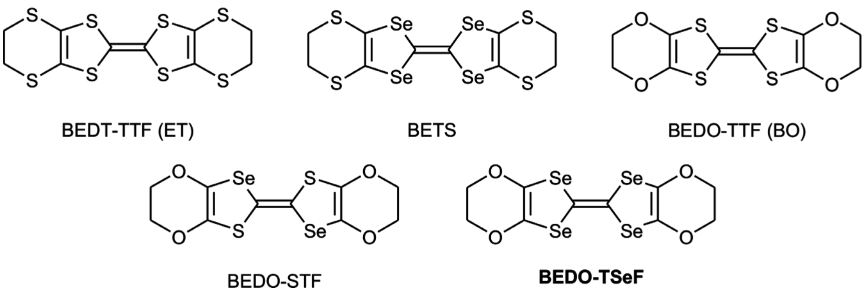

FIGURE 1 Molecular structures of BEDO-TSeF and related analogues.

(bis(ethylenedioxy)tetraselenafulvalene, Fig. 1) at least once. Nevertheless, the synthesis of BEDO-TSeF has not been reported for a long time. Since our early work on the synthesis of the half-selenated BO analogue BEDO-STF [4], we have long been pursuing a strategy for the synthesis of full-selenated BEDO-TSeF and finally achieved the first synthesis of BEDO-TSeF last year [5]. In this paper, we report synthesis, crystal structure and physical properties of κ-(BEDO-TSeF)$_2$I$_3$ (**1**) which is the first robust organic metal of BEDO-TSeF.

RESULTS AND DISCUSSION

Preparation of Crystals

The neutral molecule of BEDO-TSeF was synthesized by the reported method [5] and the I$_3$ salt was prepared by the galvanostatic oxidation of a chlorobenzene solution (20 ml) containing BEDO-TSeF (5–6 mg) and tetra-n-butylammonium triiodide (ca. 30 mg) as a supporting electrolyte. Platinum electrodes (1.0 mm ϕ) and standard H-shaped cells were employed and a constant current of 1.0 μA was applied at 20°C. Black plate crystals of **1** were harvested after 4–5 days.

X-ray Structure Analysis

X-ray structure analysis was performed on a single crystal using Bruker SMART-APEX CCD system [6]. Figure 2 shows the crystal structure viewed along the crystallographic c-axis. The donor-anion ratio is 2:1 and the donor molecules form dimers and the adjacent dimers are packed orthogonally giving rise to a typical κ-type two-dimensional structure. The terminal iodine atoms of the I$_3$ anion are out of the bc-plane and the anions are arranged in a zig-zag mode. Among the I$_3$-salts of the donors of the BEDT-TTF analogues, the

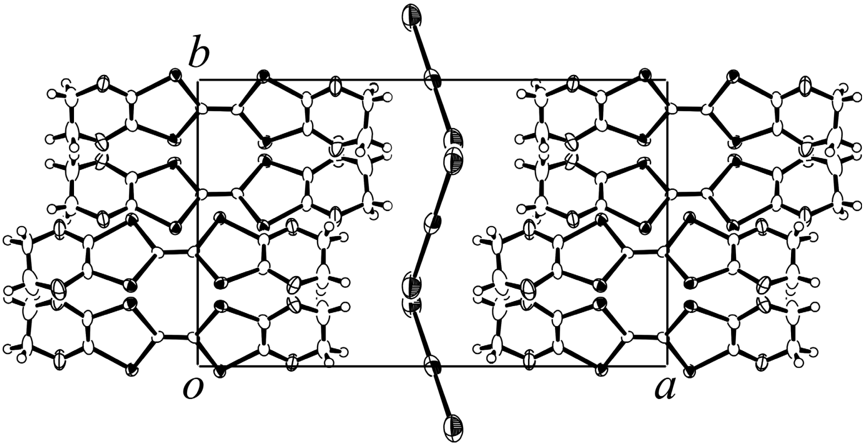

FIGURE 2 Crystal structure of **1** viewed along the c-axis.

molecular arrangement of κ-(BEDT-TTF)$_2$I$_3$ [7] is similar to the present I$_3$-salt. However, the I$_3$ anions of κ-(BEDT-TTF)$_2$I$_3$ are almost parallel to the *bc*-plane and the crystal structures of these two salts are not completely isomorphic. The crystal structure of the BO salts are dominated by CH···O type hydrogen bonding and the molecular arrangement of the donor layer tends to be a so-called β″-type [8]; however, the molecular arrangement of the BEDO-TSeF salt is a so-called

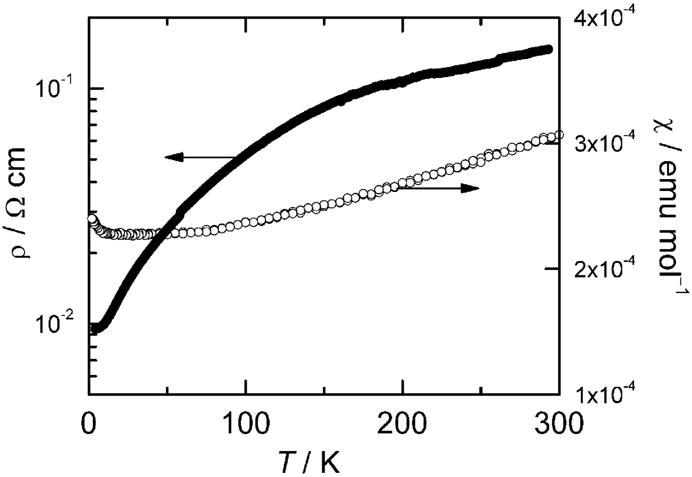

FIGURE 3 Temperature dependence of the electrical resistivity (closed circles) and magnetic susceptibility (opened circles) for **1**.

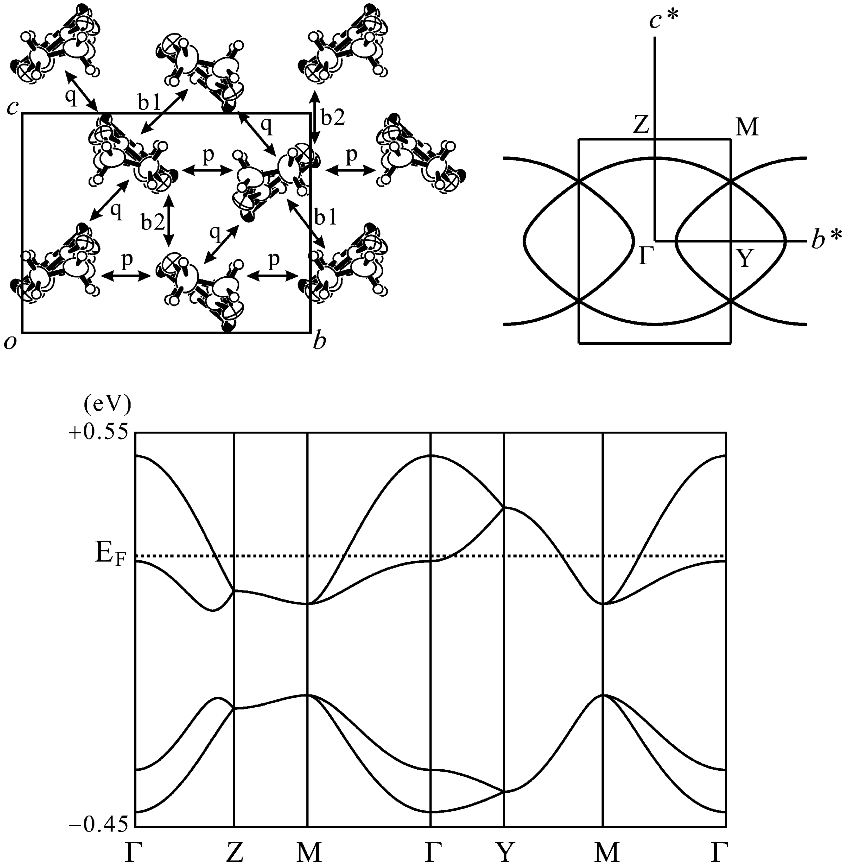

FIGURE 4 Calculated Fermi surfaces (top left), symbols of the overlap integrals (top right) and electronic band dispersions (bottom). Overlap integrals are ($\times 10^{-3}$): p = 4.68, q = 2.00, b1 = −23.7, b2 = −12.1.

κ-type and it is also different from the $(BETS)_2I_3$ which constructs the α-type packing motif [9]. It should also be stressed that no polytype was found for the present I_3-salt in contrast to that of BEDT-TTF.

Physical Properties

Figure 3 shows a plot of the electrical resistivity and magnetic susceptibility as a function of temperature for **1**. Temperature dependence of the resistivity is metallic down to 4.2 K and no sign of superconductivity was observed from the susceptibility measurement. Although there is sample dependence due to the fragility of the crystals, the typical value of the room temperature resistivity is 0.15 Ωcm and the residual resistivity ratio (*RRR*) is 15. The molar susceptibility χ is 3.1×10^{-4} emu mol^{-1} at room temperature and is dominated by temperature-independent Pauli paramagnetism down to 2 K. It is consistent with the metallic behaviour of the electrical resistivity in the same temperature range, and the relatively small value of χ suggests the weak correlation of the conducting electrons.

Electronic Band Calculation

Figure 4 shows the calculated Fermi surfaces and electronic band dispersions based on the tight-binding approximation using intermolecular overlap integrals calculated from the extended Hückel method [10]. Selenium 3d orbitals are not included for the calculations. There are four bands built from the HOMOs of the donor molecules, and the upper and the lower two bands are partially degenerated, respectively. The calculated Fermi surfaces are two-dimensional as expected from the κ-type molecular arrangement and the band width of the upper conduction band is about 50% wider than that of κ-(BEDT-TTF)$_2$I$_3$. These results are in accordance with the stable metallic behaviour of the electrical resistivity down to low temperatures.

CONCLUSION

Salt **1** is the first example of the cation radical salts of BEDO-TSeF and it is a stable metal down to low temperature. We expected to obtain the β''-type crystal of BEDO-TSeF because of the strong tendency of the BO molecule to construct β''-type molecular arrangement with the most common anions. However, the packing motif of the BEDO-TSeF salt is κ-type and the stoichiometry is in the ratios of whole numbers in contrast to the (BO)$_{2.4}$I$_3$ [11]. The κ-type structure is often observed for the BETS salts and the effect of the TSeF skeleton may have advantage over that of the oxygen atoms of BEDO-TSeF. A survey of cation radical salts with other counter anions is currently in progress in our laboratory.

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