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Structural and Physical Properties of κ and θ-$(BEDT\text{-}TSeF)_2TaF_6$. Molecular Design Aimed Toward the Two-dimensional Metal

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Crystal structure analysis of cation radical salts κ- and θ-$(BEDT\text{-}TSeF)_2TaF_6$ indicates that BEDT-TSeF molecule has strong tendency to perform two-dimensional molecular packing. The κ salt is metallic down to 4.2 K. Temperature dependent resistivity of the θ salt shows minimum at 70 K and the ratio $\rho_{5\ K}/\rho_{70\ K}$ is ca. 30.

All the organic superconductors with T_c's exceeding 10 K are based on BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene).[1,2] It is essential that superconducting BEDT-TTF-based salts have two-dimensional electronic structure. Structural and electrical modification of BEDT-TTF is very significant for the purpose of improving solid state properties. In 1984, we have pointed out that replacement of the fulvene S atoms in BEDT-TTF with Se atoms could enhance two-dimensional intermolecular interaction.[3] Recently, we have found a reliable synthetic method of this BEDT-TSeF (bis(ethylenedithio)tetraselenafulvalene) molecule.[4] In this paper, we report structural and physical properties of two types of TaF_6 salts and discuss what our molecular design strategy has provided.

Single crystals of κ- and θ-$(BEDT\text{-}TSeF)_2TaF_6$ were prepared by galvanostatic (1 μA) oxidation of BEDT-TSeF in the presence of $(n\text{-}Bu)_4NTaF_6$ as the electrolyte. The κ form was mainly obtained from 1,1,2-trichloroethane solution at ca. 20 °C and the θ form from 1,1,2-trichloroethane solution containing 10% EtOH at 37 °C. Both of them are black thin plates. Crystal data are: The κ form, space group C2/c, a=35.163(4), b=8.362(1), c=11.636(2) Å, β=99.44(1)°, V=3374.9 Å^3, Z=4. The θ form, space group C2/c, a=37.93(3), b=4.240(3), c=11.596(9) Å, β=100.21(7)°, V=1835.3 Å^3, Z=2.

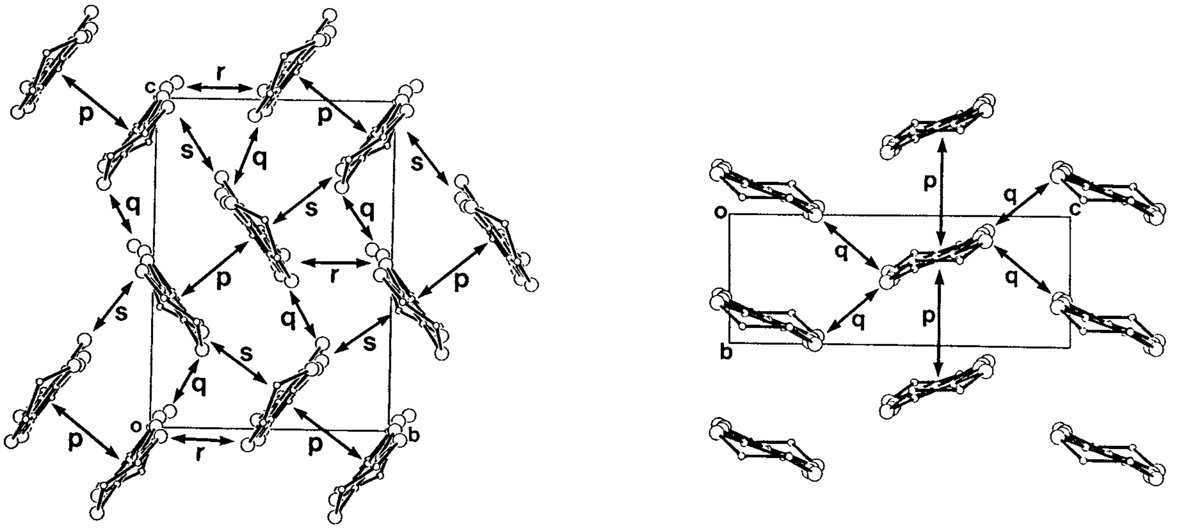
Intensity data were collected on a Rigaku automatic four-circle diffractometer with monochromated Mo-Kα radiation. The structures were solved by the direct method and refined by the block-diagonal least-squares method using reflections with $|F_O|>3\sigma(|F_O|)$. The final R values are 0.074 for the κ form and 0.15 for the θ form.

In the κ salt, two BEDT-TSeF molecules form a pair with a "ring over double bond" arrangement (Fig. 1a).$^{5)}$ The interplanar spacing is 3.6 Å. Each pair is arranged nearly orthogonally (76°) to one another in the bc plane. Many intra- and interpair chalcogen···chalcogen distances shorter than the van der Waals radii sum are observed. Carbon atoms in the ethylene groups exhibit positional disorder. The extent of interaction between adjacent donor molecules is examined in terms of their HOMO-HOMO overlap integral (S). The dimensionality of the electronic structure is mainly determined by the interpair interactions (**q**, **r**, and **s**, in Fig. 1a). As shown in Fig. 1a, the interactions **q** and **s** are distributed isotropically in the donor sheet. On the other hand, the interaction **r** runs along the b axis and has an anisotropic character. In this compound, the interaction **r** is larger than **q** and **s**, which results in the cylindrical Fermi surface stretched along the c* direction (Fig. 2a).

The θ salt is almost isostructural with θ-$(BMDT\text{-}TTF)_2AsF_6$.$^{6)}$ BEDT-TSeF units on the inversion centers repeat along the b axis (Fig. 1b). No short chalcogen···chalcogen distance is observed along this direction. On the other hand, there exist many short chalcogen···chalcogen distances between molecules interrelated by the screw axis symmetry. The dihedral angle between these molecular planes is 50.5°. This value is smaller than those for other θ type salts (80° for θ-$(BEDT\text{-}TTF)_2I_3$, 61° for θ-$(BMDT\text{-}TTF)_2AuBr_2$).$^{6)}$ The conformation of the ethylene group is disordered. The TaF_6 anions are located between the cation layers in the positionally disordered state. The calculated Fermi surface of the θ salt is cylindrical, which suggests two-dimensional nature of the electronic structure (Fig. 2b).

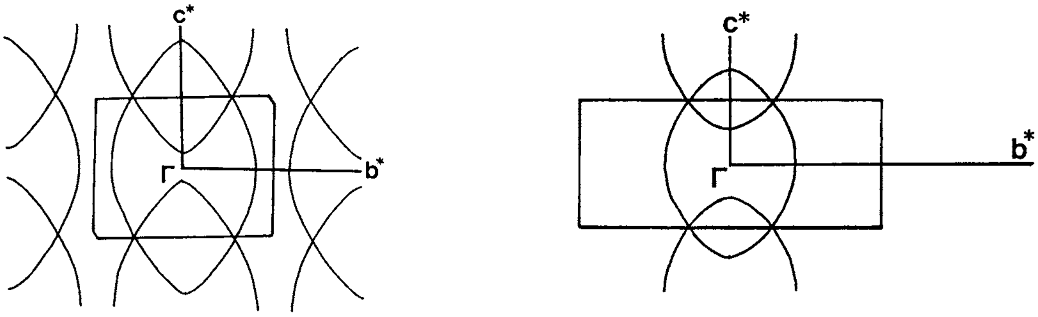
Temperature dependent resistivities of both salts is shown in Fig. 3. The κ salt is metallic down to 4.2 K ($\rho_{R.T.}=10^{-1}$ Ω cm). The anisotropy in the (100) plane (ρ_{max}/ρ_{min}; axes are not specified) is in the range of 3-4. The resistivity of the θ salt reaches its minimum at 70 K and then rises ($\rho_{R.T.}=10^{-1}$ Ω cm). It should be noted, however, that below 70 K the resistivity increased moderately and the ratio $\rho_{5\ K}/\rho_{70\ K}$ is ca. 30.

In the BEDT-TSeF molecule, the fulvene S atoms in the BEDT-TTF molecule are replaced by larger Se atoms. The expanse of the Se orbitals in the direction parallel to the molecular plane is almost the same with that of the S orbitals, that is, the peripheral "surface" of this molecule



a) b)

Fig. 1. Molecular arrangements of BEDT-TSeF molecules in a) κ- and b) θ-(BEDT-TSeF)$_2$TaF$_6$ viewed along the molecular long axis. Overlap integrals (S × 10^{-3}) of the HOMO are a) p;25.42, q;-5.25, r;10.83, s;0.39 b) p;-11.02, q;2.96.



a) b)

Fig. 2. Calculated Fermi surfaces of a) κ- and b) θ- (BEDT-TSeF)$_2$TaF$_6$.

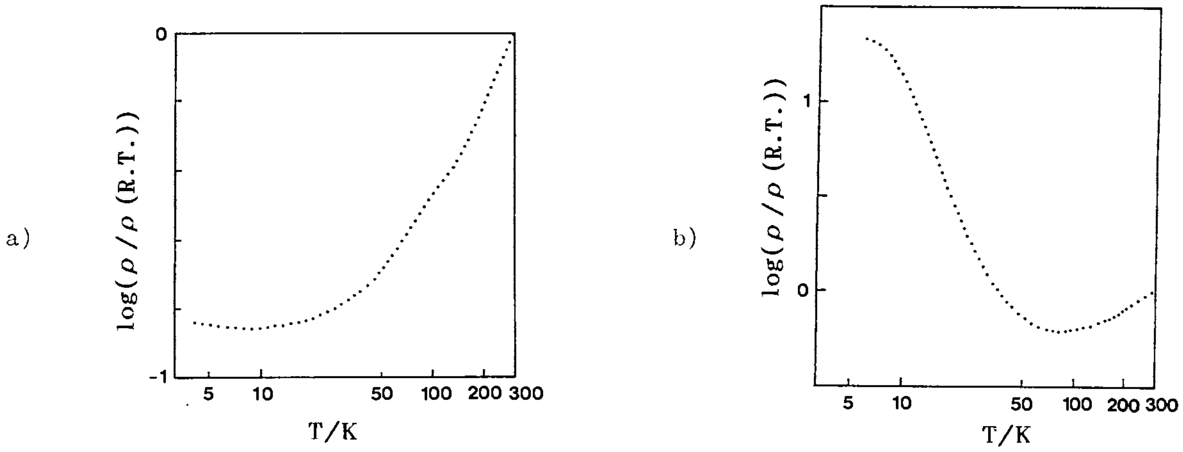


Fig. 3. Temperature dependent resistivities of a) κ- and b) θ- (BEDT-TSeF)$_2$TaF$_6$ in the (100) direction.

is almost flat. On the other hand, concerning the intermolecular interaction in the direction perpendicular to the molecular plane, the Se···Se distances determine the intermolecular spacing and additional short S···S and S···Se intermolecular distances are prevented by the "bulkiness" of the Se atoms. Our wide research on the BEDT-TSeF salts with various counter anions suggests that the pertinent molecular arrangements for the BEDT-TSeF molecule are α, κ, and θ types, all of which contain the chalcogen···chalcogen contacts almost parallel to the molecular plane.4) In these types of molecular arrangement, the BEDT-TSeF molecules with the flat peripheral "surface" are expected to exhibit tight chalcogen···chalcogen contacts.3) It should be noted that we have observed no β type molecular arrangement which is often observed in the BEDT-TTF salts. In the β type salt, the donor molecules are arrayed to form the "corrugated" sheets, and a given donor molecule is positioned parallel to and between the planes of two adjacent donor molecules. As a consequence, there is no intermolecular chalcogen···chalcogen contact parallel to the molecular planes. Such a feature distinguishes the β type from other two-dimensional molecular arrangements and should be closely related to the reason why the β type molecular arrangement is not found in the BEDT-TSeF salts. The fact that the BEDT-TSeF molecule prefers two-dimensional arrangements to the one-dimensional column structure indicates that our molecular design by means of engineering the intermolecular chalcogen···chalcogen contacts is available to the research of the two-dimensional molecular metal.

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