Structures and Properties of (TMEO-ST-TTP)$_2$AsF$_6$

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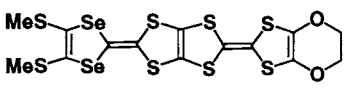
The title material, where TMEO-ST-TTP is 2-[4,5-bis(methylthio)-1,3-diselenol-2-ylidene)-5-(4,5-ethylendioxy-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, shows metallic conducting behavior down to 4.2 K. X-Ray structure analysis reveals it has the β-type array of donors in the BEDT-TTF salts. A tight-binding band calculation suggests the present salt has a quasi-one-dimensional Fermi surface.

For the development of organic molecular metals,[1] a bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP or simply TTP)[2] is of considerable interest because it has yielded a great number of metallic radical cation salts that are stable down to low temperatures (≤4.2 K).[3] Thanks to the ability of TTP framework to form two-dimensional molecular packing, its derivatives with various substituents are also promising to afford organic metals,[4] while chalcogene based substituents such as ethylenedithio group is needed for the TTF system.[5] Among the TTP derivatives prepared so far, 4,5-bis(methylthio)-4',5'-ethylendioxy-TTP (TMEO-TTP) has yielded many metallic radical cation salts down to ≤1.2 K with octahedral and linear anions.[6] However, their crystal structures have been less-characterized due to the poor quality of the crystals.[6,7] For the metallic TMEO-TTP salts, (TMEO-TTP)$_2$Au(CN)$_2$ is the only example whose crystal structure was determined.[6] It has the β"-type donor array in the BEDT-TTF salts, however, conducting behavior is distinct from the other metallic TMEO-TTP salts, namely the Au(CN)$_2^-$ salt showed metal to semimetal transition around 180 K, whereas the others exhibited simple metallic temperature dependence. Very recently we have found that a selenium analog of TTP, 2-(1,3-diselenol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (ST-TTP), empirically has a tendency to afford higher quality single crystals than TTP itself.[8] In this context, extension of this strategy for the other TTP derivatives is desirable to elucidate correlation between crystal structures and conducting properties in their conducting salts. We report herein structures and conducting properties of (TMEO-ST-TTP)$_2$AsF$_6$.



TMEO-ST-TTP

Synthesis of TMEO-ST-TTP will be reported in a separated paper.[9] Rectangle-like single crystals of (TMEO-ST-TTP)$_2$AsF$_6$ were harvested by use of an electrocrystallization technique at a controlled current method[10] in the presence of Bu$_4$NAsF$_6$ in chlorobenzene or 1,2-dichloroethane at 50 °C. The electrical conductivity was measured on a single crystal using a four-probe technique. Figure 1 shows its conducting behaviour. The conductivity is a high value of 40 S cm^{-1} at room temperature, and temperature dependence of resistivity was metallic down to 4.2 K. As observed in other TTP-based conductors, the ratio of resistivity R_{rt}/R_{min} was at most arount 4 owing to the comparatively poor crystallinity.

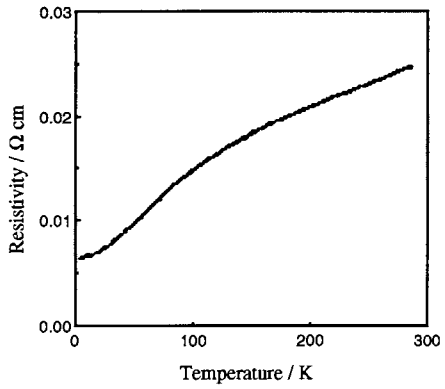


Figure 1. Conducting behavior of (TMEO-ST-TTP)$_2$AsF$_6$.

X-Ray structure analysis of (TMEO-ST-TTP)$_2$AsF$_6$ was carried out.[11] One donor molecule is located on a general position, while the AsF$_6^-$ anion lies on a center of inversion. The donors form conducting sheets along the *ac* plane, each of which is separated from the insulating anion layer (Figure 2). The array of the donors is classified as the β-type in the BEDT-TTF salts (Figure 3).[12] The overlap mode in the stack is ring-over-bond type (Figure 4), and the slip distances along the molecular long axis are about half of 1,3-dithiole ring for p1 (1.7

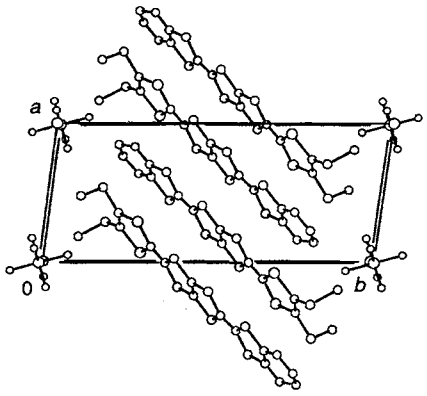


Figure 2. Crystal structure of (TMEO-ST-TTP)$_2$AsF$_6$ viwed onto the *ab* plane.

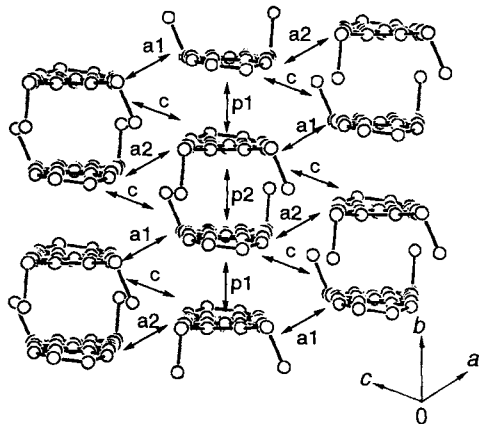


Figure 3. Donor sheet structure of (TMEO-ST-TTP)$_2$AsF$_6$. The intermolecular overlap integrals are p1 = 38.1, p2 = 16.9, a1 = -5.0, a2 = -4.1, c = -7.8 x 10^{-3}.

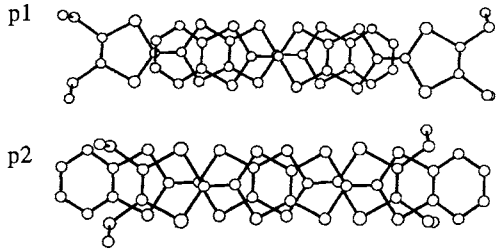


Figure 4. Overlap modes in the stack of (TMEO-ST-TTP)$_2$AsF$_6$.

Å), and one and half for p2 (5.0 Å), respectively. As a result, the donors are electronically dimerized along the stacking direction though interplanar distances are almost same (3.54 Å for p1 and 3.51 Å for p2, respectively) with each other. The ratio of the calculated overlap integrals (p1/p2) is 2.3. Figure 5 shows the band structure and the Fermi surface of (TMEO-ST-TTP)$_2$AsF$_6$ based on a tight binding calculation.[13] The two bands are completely separated due to strong dimerization along the stack. As a result, the upper band of the present salt is effectively half filled. Although there are comparatively strong interstack interactions (20-30% of p1), the calculated Fermi surface is open to this direction characteristic of one-dimensional metal. The interstack overlaps are 10-20% of the larger intrastack overlap. Thus, the calculated Fermi surface is closed along the stacking direction, but open along the interstack one as is observed in a quasi one-dimensional system.[14] However, interstack interactions are strong enough to suppress the metal to semiconductor transition at low temperature.

The donor array of the present salt is very closed to that of (TMEO-ST-TTP)2ClO4(1,2-dichloroethane)[9] though the space group is different from each other. In contrast with the metallic AsF_6^- salt, the ClO_4^- salt is a low conducting semiconductor even at room temperature (σ_{rt} = 0.07 S cm^{-1}, E_a = 0.05 eV). We think the ClO_4^- salt is a Mott insulator with a narrow effectively half-filled band because it has a narrow bandwidth (0.43 eV for the upper bands) and a large energy gap between the upper and lower bands (0.22 eV). In contrast, the bandwidth of the upper band of the present metallic salt (0.53 eV) is larger by 0.10 eV than that of the ClO_4^- salt. Furthermore, the energy gap

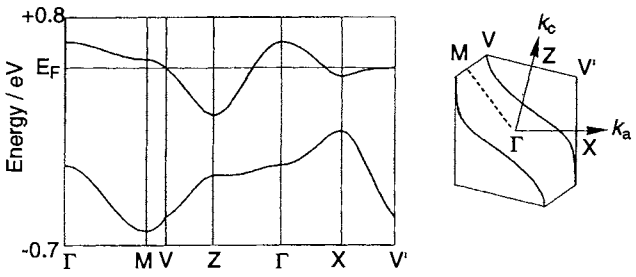


Figure 5. Energy band structure and Fermi surface of (TMEO-ST-TTP)$_2$AsF$_6$.

(0.08 eV) is about one-thirds of that of the ClO_4^- salt. Thanks to such relatively large bandwidth as well as a small energy gap, metallic conductivity is realized in (TMEO-ST-TTP)$_2$AsF$_6$.

The preparation of organic metals based on the other TMEO-ST-TTP salts is actively in progress. This work is partially supported by Grant-in-Aid for Scientific Research No. 09640687 from the Ministry of Education, Science, and Culture of Japan, and by Japan Society for the Promotion of Science Research for the Future Program (JSPS-RFTF96P00206).

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