Structures and Conducting Properties of CPTM-TTP Salts

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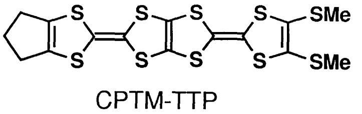
The title donor, CPTM-TTP (4,5-cyclopenteno-4',5'-bis-(methylthio)-2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) has produced metallic cation radical salts with octahedral and linear anions. Among them, $(CPTM\text{-}TTP)_4AsF_6$ has a two-dimensional "β-type" arrangement of donor molecules and a closed Fermi surface.

A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP),[1,2] is a promising π-electron framework for construction of two-dimensional (2D) metals because it has so called "a ladder-like array" of sulfur atoms similar to BEDT-TTF.[3] Thus, the parent BDT-TTP forms cation radical salts retaining metallic conductivity down to liquid helium temperature regardless of counter anions, in which the donors are arranged in 2D fashion.[2] In this connection, BDT-TTPs having substituents such as alkyl, benzo and/or methylthio groups which usually give one-dimensional conductors in TTF system[4] are also available in the search for 2D metals and superconductors. In this communication we report structures and conducting properties of cation radical salts based on 4,5-cyclopenteno-4',5'-bis(methylthio)-BDT-TTP (CPTM-TTP).



CPTM-TTP

CPTM-TTP was prepared by a similar method to methyl substituted BDT-TTP derivatives.[1c,5] The cyclic voltammogram of CPTM-TTP exhibited four pairs of single-electron redox waves at +0.46, +0.69, +0.98 and +1.13 V (vs. SCE, in PhCN at 25 °C). Its cation radical salts were prepared by electrochemical oxidation in the presence of the corresponding tetra-*n*-butylammonium salts under a constant current of 0.3-1 $\mu A cm^{-2}$ in chlorobenzene or 1,2-dichloroethane at 50 °C. The conducting properties measured by four-probe technique on single crystals are summarized in Table 1. All of salts obtained so far show relatively high conductivity of 10^0-10^2 S cm^{-1} at room temperature. The salts with tetrahedral anions (ClO_4, BF_4 and $GaCl_4$) are semiconductor with activation energy of 0.031-0.061 eV. In contrast, octahedral (PF_6, AsF_6 and SbF_6) and linear ($Au(CN)_2$) anions gave metallic salts. Among them, the SbF_6 salt showed metal to semiconductor transition around 50 K. On the other hand, conducting behavior of the other metallic salts is somewhat tricky. In the cooling run, the resistivity decreased monotonically down to 100-200 K, below of which it increased about 1 order as large as the room temperature value accompanied with several jumps. However, temperature dependence of resistivity was not semiconductive around liquid helium temperature. In the heating run the PF_6 and AsF_6 salts showed metallic behavior in the low temperature region, and a broad maximum of resistivity around 80 K (Figure 1). On the other hand, resistivity of the $Au(CN)_2$ salt decreased as the temperature increased. However, its temperature dependence was very weak, and not semiconductive. These are characteristic of metal to metal (or semimetal) transition as is observed in $(BDT\text{-}TTP)_2X$ (X = ClO_4, BF_4 and ReO_4)[2b] and $(TMEO\text{-}TTP)_2Au(CN)_2$,[1d] where TMEO-TTP is 4,5-bis(methylthio)-4',5'-ethylenedioxy-BDT-TTP.

Table 1. Composition and electrical conductivity of CPTM-TTP salts ($CPTM\text{-}TTP{\cdot}A_x$)

Anion	x[a]	σ_{rt}/Scm^{-1} [b]	E_a/eV
ClO_4	0.52(Cl)	2	0.031
BF_4	- c	4	0.038
$GaCl_4$	1.5(Ga)	4	0.061
PF_6	0.25(X)	110	Metallic
AsF_6	0.25(X)	66	Metallic
SbF_6	0.28(Sb)	7	T_{MI} = 50 K
$Au(CN)_2$	0.68 (Au)	40	Metallic

[a] Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. X designates the value determined from X-ray structure analysis. [b] Room temperature conductivity measured by four-probe technique on a single crystal. [c] The contents of light elements such as B and F were not reliably determined by EDS.

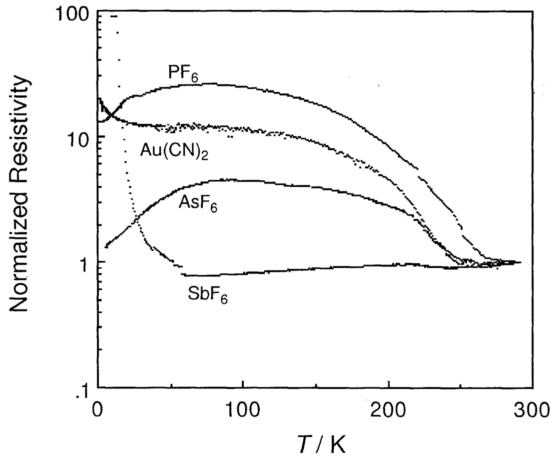


Figure 1. Conducting behavior of CPTM-TTP salts in the heating run.

X-Ray structure analysis was carried out for AsF_6 salt.[6] The unit cell contains two crystallographically independent donor molecules (molecules A and B). On the other hand, the AsF_6 anion lies on the center of inversion, therefore, the ratio of donor and anion is to be 4:1. In the molecule A, one of the methyl groups overhangs perpendicularly to the molecular plane, and the other projects outside of the molecular long axis. On the other hand, both methylthio groups in the molecule B hang over the molecular plane. Because no large difference of the bond

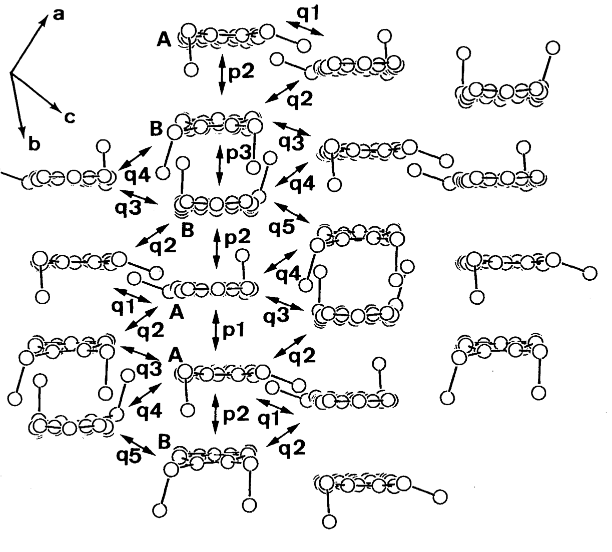


Figure 2. Donor arrangement in $(CPTM\text{-}TTP)_4AsF_6$. Projection along the molecular long axis.

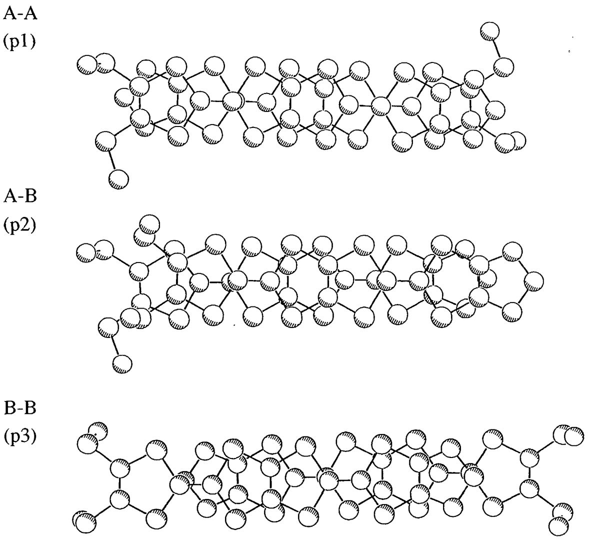


Figure 3. Overlap modes of donor molecules in $(CPTM\text{-}TTP)_4AsF_6$. Projection onto the molecular planes.

distances in molecules A and B is observed, we think that there is no significant difference in the formal charge. The arrangement of donors in the conducting sheet is similar to the β-type BEDT-TTF salts (Figure 2).[7] The donors are stacked with a four-folded period as AABB. Thus, there are three overlap modes of donor molecules (Figure 3). The donor molecules are stacked in a head-to-tail manner in A-A (p1) and B-B (p3), while they are stacked in a head-to-head manner in A-B (p2). The interplanar distances are 3.58, 3.61 and 3.40 Å for p1, p2 and p3, respectively. All of overlap modes are ring-over-bond type, however, the slip distance along the molecular long axis D of p3 (4.73 Å) is larger than those of p1 (1.55) and p2 (1.68 Å). Because BDT-TTP is about twice longer than TTF, the large D value of p3 does not affect overlap integral so much. Thus, the overlap of p3 (18.1×10^{-3}) is smaller by only ca. 20% than those of the other intrastack interactions. Such a weak tetramerization results in a large band width of 1.1 eV. On the other hand, there are relatively large interstack interactions (q2 and q4). As a result, the Fermi surface calculated by tight-binding method is a typical eclipse which is characteristic of 2D metals as is observed in $\beta\text{-}(BEDT\text{-}TTF)_2I_3$ (Figure 4).[7b] The further investigations on physical properties of the present salts are in progress.[8]

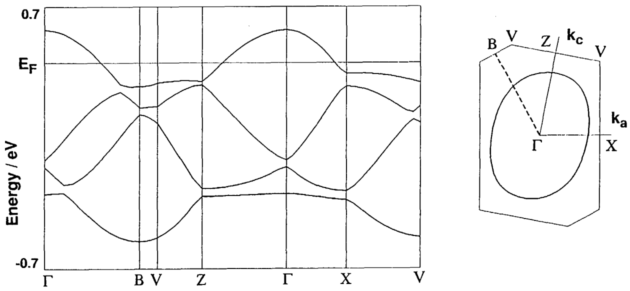


Figure 4. Energy band structure and Fermi surface of $(CPTM\text{-}TTP)_4AsF_6$; p1= 22.6, p2 = -22.0, p3 = 18.1, q1 = 1.4, q2 = 7.4, q3 = -0.5, q4 = 6.6, q5 = -0.1 ($\times 10^{-3}$).

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5 The details of synthesis will be reported in a separated paper.

6 Crystal data of $(CPTM\text{-}TTP)_4AsF_6$: triclinic, space group $P\ \bar{1}$, a = 11.80(3), b = 21.11(7), c = 8.40(3) Å, α = 92.7(3), β = 100.7(2), γ= 91.6(3)°, V = 2054(11) $Å^3$, Z = 1, ρ_{calcd} = 1.811. The data were collected on a Rigaku AFC-7R diffractometer with graphite monochromatized Mo $K\alpha$ radiation. Anisotropic thermal parameters were adopted for all non-hydrogen atoms. The final R (Rw) value is 0.045 (0.044) for independent 3858 reflections ($|I| > 3\sigma(I)$). The PF_6 salt is also isostructural with the present salt.

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