Structures and Electrical Properties of $(EO\text{-}TTP)_2AsF_6$

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The title material, where EO-TTP is 2-(4,5-ethylenedioxy-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, shows metallic conducting behavior down to 1.5 K. X-Ray structure analysis reveals it has the so-called β-type array of donors.

In the development of new organic molecular metals and superconductors,[1] control of molecular packing is one of the most important subjects because the band structure and conducting properties strongly depend on the molecular array as well as the band-filling in the materials.[2] We have demonstrated that fusion of two π-electron donors is a promising strategy to prepare radical cation salts showing metallic conductivity down to low temperature.[3-5] For example, a bis-fused tetrathiafulvalene (TTF), 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP) has afforded many metallic radical-cation salts stable down to ≤1.2 K regardless of shape and size of counter anions.[4] Furthermore, $(DTEDT)_3Au(CN)_2$, where DTEDT is 2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene, was found to show superconductivity below 4 K.[5] Though TTP itself has a tendency to yield the so-called β-type array of donors, 4,5-cyclohexeno-TTP (CH-TTP) affords the κ-type I_3^- salt.[6] In this context, radical cation salts based on TTP derivatives fused with other six-membered rings is of interest to elucidate correlation between molecular structure and its packing pattern in the TTP type conductors. TTP fused with dehydro-1,4-dioxane, in other words, ethylenedioxy-TTP (EO-TTP) is a promising candidate because ethylenedioxy substituted TTP derivatives EOET-TTP[7] and CPEO-TTP[8] have yielded κ-type metals. Though EO-TTP itself has been prepared in several years before,[7] no detailed investigation on structure and properties of its conducting salts has been performed. Thus, we have reinvestigated on preparation of single crystals of EO-TTP salts, and report herein their structures and transport properties.

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

Acceptor	Form[a]	x[b]	σ_{rt}/Scm^{-1} [c]	Conductiivity[d]
ClO_4^-	P	0.33(Cl)	860	M down to 4.2 K
BF_4^-	P	-	380	M down to 4.2 K
PF_6^-	P	0.39(P)	1300	M down to 1.5 K
AsF_6^-	P	0.50(X)	600	M down to 1.5 K
$Au(CN)_2^-$	N	0.72(Au)	3.4	$E_a = 0.14$ eV

[a] P = Plate; N = Needle. [b] Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. X designates X-ray structure analysis. [c] Room temperature conductivity measured on a single crystal using the four-probe technique. [d] M = Metallic

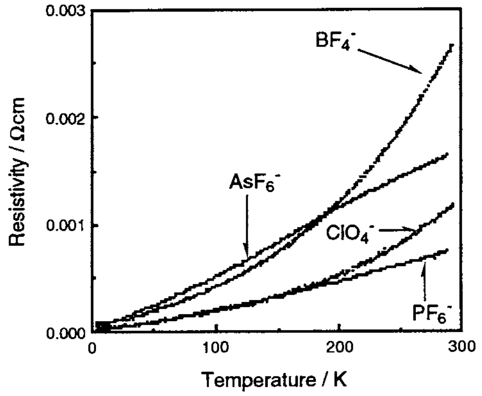
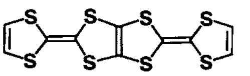
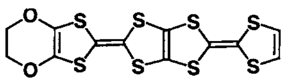


Figure 1. Conducting behaviour of EO-TTP salts in the heating runs.

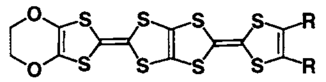
The radical cation salts were prepared by means of an electrocrystallization technique in 1,2-dichloroethane containing 5% (v/v) ethanol at 50 °C. The electrical conductivity was measured on a single crystal using a four-probe technique. Their electrical properties are summarized in Table 1.[9] The salts with tetrahedral (ClO_4^- and BF_4^-) and octahedral (PF_6^- and AsF_6^-) anions obtained as plate-like crystals showed quite high conductivity of 10^2 - 10^3 S cm^{-1} at room temperature. All of them exhibited metallic temperature dependence down to 1.2-4.2 K. The ratio of resistivity R_{rt}/R_{min} is 10-20. In contrast, the $Au(CN)_2^-$ salt obtained as needle crystal is a rather low conductive ($\sigma_{rt} = 10^0$ S cm^{-1}) semiconductor with a large activation energy (0.14 eV).



TTP



EO-TTP



2R = $-S(CH_2)_2S-$, EOET-TTP
2R = $-(CH_2)_3-$, CPEO-TTP

Figure 2 shows thermoelectric power of the AsF_6 salt. The room temperature value (14 μVK^{-1}) is comparable to that of $(TTP)_2ClO_4$,[4b] indicating a large bandwidth (>1 eV). They are positive in the whole temperature region in correspondence with hole conduction. The AsF_6^- salt exhibited almost *T*-linear temperature dependence towards zero thermoelectric power, which is characteristic of normal metals. A small anomaly observed below 50 K might be due to phonon drag.

An X-ray structure analysis of the AsF_6^- salt was achieved.[10] One donor molecule is located on a general position, while the AsF_6^- anion lies on a center of inversion. The ratio of the donor to anion was determined to be 2:1 because population analysis of

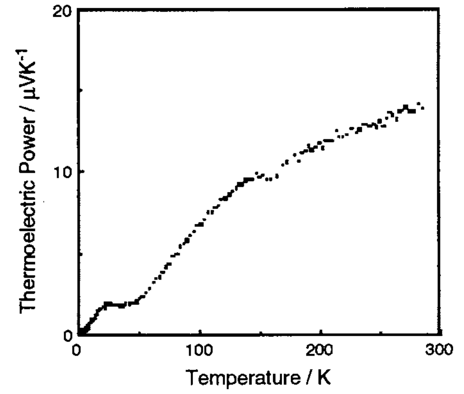


Figure 2. Thermoelectric power of (EO-TTP)$_2$AsF$_6$.

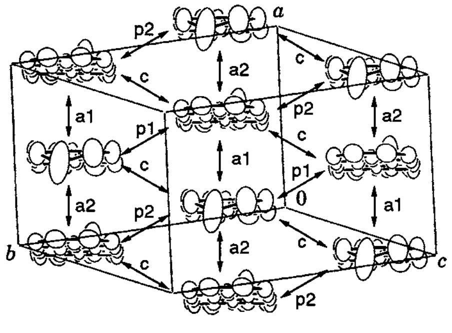


Figure 3. Donor sheet structure of (EO-TTP)$_2$AsF$_6$ projected along the donor long axis.

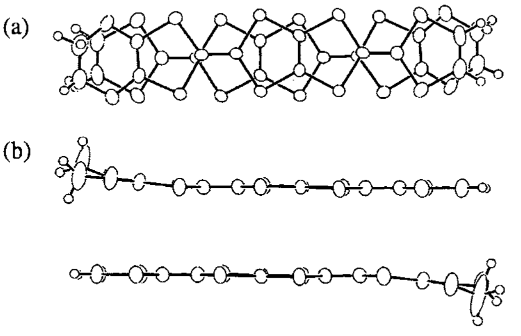


Figure 4. (a) Overlap mode in the stack of (EO-TTP)$_2$AsF$_6$ and (b) the side view.

the As atom indicates no significant lack of the anion. The array of donors resembles that of (TTP)$_2$SbF$_6$,[4a] which is classified as the β-type (Figure 3).[11] The unsymmetrical EO-TTP molecules are stacked alternately, and are slightly dimerized with the interplanar distances of 3.47 and 3.52 Å, respectively. The both overlap modes in the stack are the so-called ring-over-bond type (Figure 4), and the slip distance along the molecular long axis is 1.5 Å. The TTF moiety substituted with ethylenedioxy group adopts a boat conformation bent at the sulfur atoms in each 1,3-dithiole ring with the dihedral angles of 7.3°, while the unsubstituted TTF one is completely planar. The torsion angle around the ethylene bridge is 37°, which is about two thirds of that in (CH-TTP)(I$_3$)$_{0.31}$ (57°).[6] Such a smaller dihedral angle as well as less hydrogen atoms in the dehydrodioxane ring compared with the cyclohexene ones may favor the stacking β-type structure rather than the strongly dimerized κ-type one. A tight binding band calculation[12] indicates that this salt has a closed Fermi surface similar to (TTP)$_2$SbF$_6$ (Figure 5) though one-dimensional character is still strong owing to large overlaps along the stacking direction.

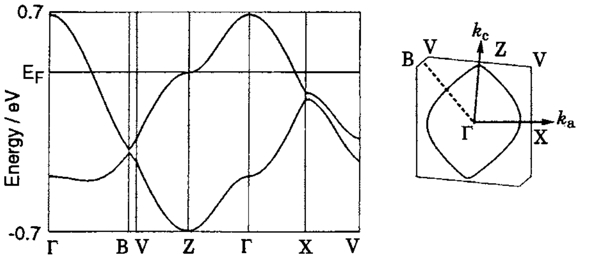


Figure 5. Energy band structure and Fermi surface of (EO-TTP)$_2$AsF$_6$. The intermolecular overlap integrals are a1 = 26.9, a2 = 25.2, p1 = 0.47, p2 = 0.11, c = -9.07 x 10^{-3}.

The preparation of radical-cation salts based on the other ethylenedioxy substituted TTPs is actively in progress. This work is partially supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

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9 The result of a preliminary conductivity measurement for the PF$_6^-$ salt (σ_{rt} = 1.5 S cm^{-1}, E_a = 0.026 eV on a compressed pellet) has been reported.[7]

10 Crystal data for (EO-TTP)$_2$AsF$_6$: AsC$_{24}$F$_6$H$_{12}$O$_4$S$_{16}$, M = 1066.22, triclinic, space group $P\,\bar{1}$, a = 7.60(1), b = 16.917(6), c = 7.091(2) Å. α = 96.84(2), β = 96.79 (5)°, γ = 77.41(6)°, V = 879(1) Å^3, Z = 1, R = 0.052, R_w = 0.051 for 2079 observed ([$I \geq 3\sigma(I)$]) reflections from 4035 unique data.

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