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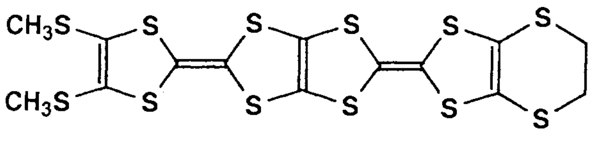
Structure and Conducting Properties of TMET-TTP Radical-Cation Salts

Takehiko MORI,* Hiroo INOKUCHI, Yohji MISAKI,† Hiroyuki NISHIKAWA,†
Tokio YAMABE,† Hatsumi MORI,†† and Shoji TANAKA††
Institute for Molecular Science, Okazaki 444
†Department of Hydrocarbon Chemistry and Division of Molecular
Engineering, Kyoto University, Yoshida, Kyoto 606
††International Superconductivity Technology Center, Mutsuno, Nagoya 456

Radical cation salts of TMET-TTP (2-(4',5'-bis(thiomethyl)-1',3'-dithiol-2'-ylidene)-5-(4",5"-ethylenedithio-1",3"-dithiol-2"-ylidene)-1,3,4,6-tetrathiapentalene) with various anions show high electrical conductivity. Many of them have a similar structure with two-dimensional donor arrangement.

All component molecules of organic superconductors so far known have ladder-like array of sulfur (selenium and sometimes oxygen) atoms.[1] This seems to be an indispensable requirement for constructing two-dimensional network of the component molecules in a crystal. If one attempts to extend the skeleton of the component molecules with keeping this structural concept, one can imagine a molecule as shown below, where two TTF (tetrathiafulvalene) molecules are fused, or in other words a TTP (tetrathiapentalene) unit is inserted into the central double bond of a TTF molecule. Though the preparation of this kind of molecules had been attempted for a long time,[2] they had not been realized generally due to their synthetic difficulty. Recently, however, Misaki *et al.* have developed a general synthetic route to these TTF/TTP conjugated molecules.[3,4] Because these TTF/TTP molecules do not generally show high solubility in organic solvents, we investigated the conducting and structural properties of radical cation salts of TMET-TTP, whose solubility is considerably improved by the presence of the methylthio parts.



TMET-TTP

The donor molecule, TMET-TTP, was prepared as has been previously reported.[3,4] This molecule is as much soluble in organic solvents as BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene). Electrochemical crystallization in 1,1,2-trichloroethane, THF, or benzonitrile in the presence of tetrabutylammonium salts of various anions gave plate- or needle-like crystals of the radical cation salts.[4] The temperature-dependent resistivity of some representative salts are shown in Fig. 1. Many salts, (TMET-TTP)A_x with tetrahedral (ClO_4, IO_4(x=0.13-0.22), ReO_4(0.35), BF_4), octahedral (PF_6(0.27)), linear (AuI_2(0.20), $AuBr_2$(0.20), $AuCl_2$(0.20), $Au(CN)_2$(0.38)), planar

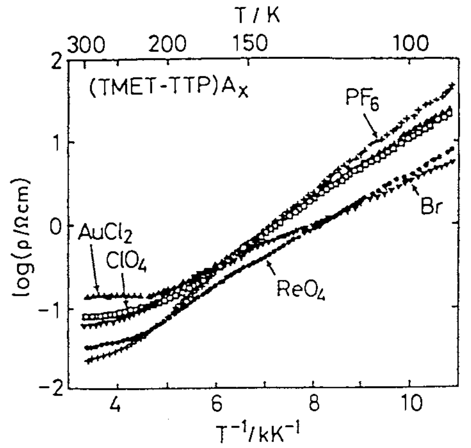


Fig. 1. Electrical resistivity of TMET-TTP salts.

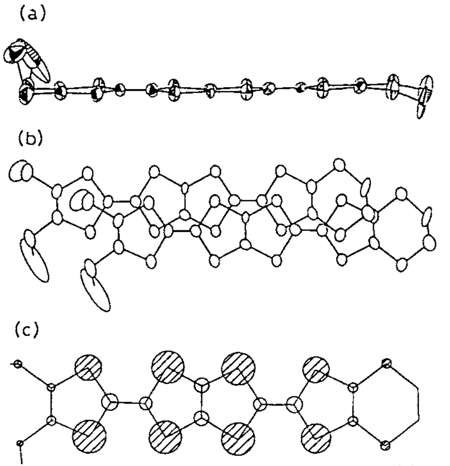


Fig. 2. (a) Molecular structure, (b) stacking mode, and (c) HOMO of TMET-TTP.

($HgBr_3$(0.25)), and monoatomic (Cl, Br(0.34)) anions show quite similar conducting behavior; the conductivity is 10-30 Scm^{-1} at room temperature, almost flat down to about 200 K, and behaves like a semiconductor below this temperature. X-ray photography indicates these salts have essentially the same lattice constants. The anion content x, however, varies from salt to salt, and is very small (0.13-0.38). This exhibits a striking contrast with the usual TTF salts, where usually x=0.5-0.67. This is still more surprising because the present donor has more steps of redox abilities and larger molecular size.[3,4] Though this phase appears quite generally for various anions, there are a few exceptions:[4] AsF_6 (x=0.34, metal down to 0.6 K), SbF_6 (x=0.37, including 1,1,2-trichlorothenane), and $HgBr_3$ (needle-like, x=0.42, T_{MI}=80 K). These salts will be discussed in a separate paper.

Lattice constants of some salts are listed in Table 1. In spite of the diversified composition, the lattice constants are quite similar for many salts. Single-crystal X-ray structure analyses were performed for the PF_6 and ReO_4 salts. The donor molecules are planer except the two methyl groups of the thiomethyl parts (Fig. 2(a)); the S-CH_3 bonds extend almost perpendicularly to the molecular plane. The donor molecules are "stacked" along the crystallographic c axis (Fig. 3(a)), with keeping the methylthio groups in the same side to avoid their steric hindrance, but in the "stack", the molecules are slipped not only along the molecular long axis but also along the molecular short axis (Fig. 2(b)). On the contrary there are many "side-by-side" short S-S contacts along the b axis, and the donors form a conducting sheet along the bc-plane. The donor arrangement of this conducting sheet (Fig. 3(b)) is similar to the θ-type BEDT-TTF salt .[5] It is remarkable that in spite of the presence of the methylthio groups, TMET-TTP makes a two-dimensional molecular network like a BEDT-TTF salt.

The anions are sandwiched by the donor sheets. The anion sites are not fully occupied, but occupied in the probability of 0.54 for PF_6 and 0.64 for ReO_4. Moreover, the ReO_4 anion is distributed in three different sites near an inversion center. Preliminary structure analysis of the AuI_2 salt indicates the linear AuI_2 anion is parallel to the c axis, and exists in the probability of 0.50. Because the anion length (9.4 Å) is longer than the lattice constant c, there

Table 1. Lattice Constants of (TMET-TTP)A_x

A =	AuI2	PF_6[6)]	ReO_4[7)]	IO_4	ClO_4
x(Anal.)[a)]	0.20(Au) 0.23(I)		0.35(Re)	0.13 -0.22(I)[b)]	
x(Struc.)	0.25	0.27	0.34		
a (Å)	39.62(2)	40.351(4)	40.348(6)	40.10(2)	39.79(1)
b (Å)	11.097(3)	11.108(4)	11.015(6)	11.114(4)	10.987(3)
c (Å)	4.993(6)	5.008(5)	4.981(6)	4.989(4)	5.016(1)
b (°)	93.36(6)	93.50(5)	93.42(1)	92.89(5)	93.01(2)
V (Å^3)	2192(3)	2240(2)	2210(3)	2221(2)	2190(1)
Space G.	$P2_1/n$	$P2_1/n$	$P2_1/a$		($P2_1$)

a) Determined from the energy dispersion spectroscopy from the ratio of sulfur and the elements designated in the parentheses. b) Microscopically large scatter was observed in x.

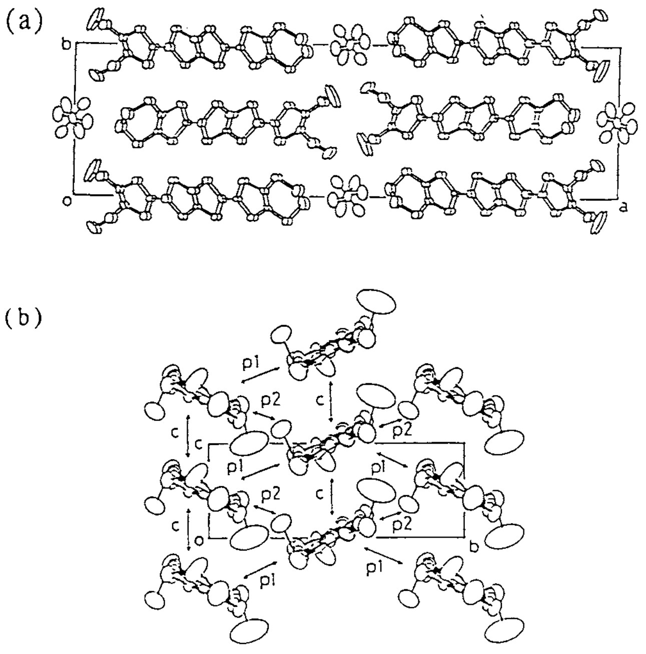


Fig. 3. Crystal structure of (TMET-TTP)$(PF_6)_{0.27}$. (a) ab-projection and (b) projection along the molecular long axis.

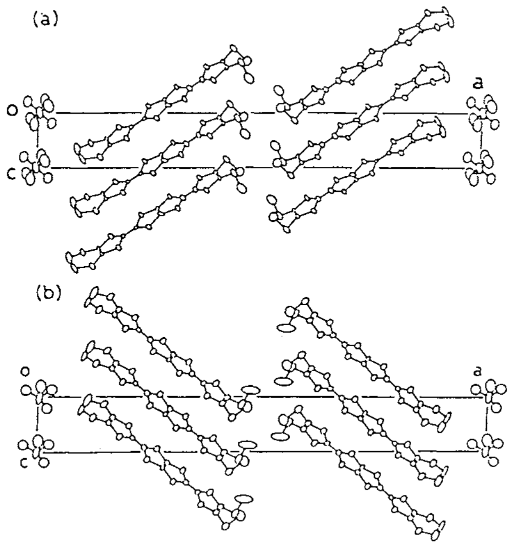


Fig. 4. Crystal structure of (a) (TMET-TTP)$(PF_6)_{0.27}$ and (b) (TMET-TTP)$(ReO_4)_{0.34}$.

appear a strong satellite refections originating from the two-fold structure along the c axis. The $AuBr_2$ and $AuCl_2$ salts have a similar two-fold structure.

Though the lattice constants are quite similar, the salts with various anions are not strictly isostructural. There are (at least) two types of structures: the PF_6 type with space group $P2_1/n$, and the ReO_4 type with $P2_1/a$. In the ac projection depicted in Fig. 4, the donors are packed in

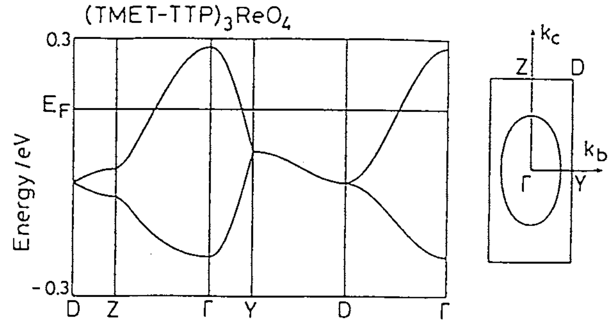


Fig. 5. Band structure and Fermi surface of (TMET-TTP)(ReO$_4$)$_{0.34}$. The calculated overlap integrals are c=-1.8, p1=6.9, and p2=5.3x10^{-3}.

right-up for the PF$_6$ salt, whereas in right-down for the ReO$_4$ salt. The positional relation of donors between the adjacent sheets is also different between these two structures. The donor arrangement in a donor sheet is, however, almost the same. The reflection data of the ClO$_4$ salt show the symmetry of space group P2$_1$, but the Patterson map is a convolution of those of the PF$_6$ and ReO$_4$ salts, indicating its structure is a random mixture of the two types of structures.

The highest occupied molecular orbital (HOMO) has the same symmetry as BEDT-TTF (Fig. 2(c)).[8] The HOMO is, however, extended over the two TTF parts, then the resulting intermolecular overlap integrals tend to be smaller than BEDT-TTF salts. Though the tight-binding band structure and Fermi surface calculated from these overlaps are similar to those of the θ-BEDT-TTF salt (Fig. 5), the bandwidth is about half of the BEDT-TTF salt. In other words, the present donor gives twice larger density of states than the BEDT-TTF salts, which seems to be advantageous in raising superconducting T_c. Because the on-site Coulomb repulsion as well as the transfer integral is smaller, the possibility that the present TTF/TTP system makes a metallic salts is expected to be the same as the BEDT-TTF salts.

References

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6) R = 0.122 for 1464 reflections.

7) R = 0.072 for 1896 reflections.

8) The MO calculation was carried out by the extended Hückel method with using the same parameters as listed in T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **57**, 627 (1984).

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