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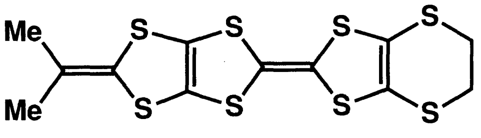
Structure and Electrical Properties of MeDTET Salts

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

Several cation radical salts of MeDTET (2-isopropylidene-1,3-dithiolo[4,5-*d*]ethylenedithiotetrathiafulvalene) showed metallic temperature dependence of conductivity down to 0.6-0.9 K. X-Ray crystal structure of $(MeDTET)_3PF_6TCE_x$ revealed that the donors have "κ-type" arrangement in the conducting sheet. This is the first example of a κ-type salt that has a composition other than 2:1.

Since the discovery of superconducting bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts, multidimensional electrical property has been regarded to be important for preparation of organic metals stable down to low temperatures.$^{1)}$ Recently 1,3-dithiol-2-ylidene group has been noted as a promising substituent for realizing two-dimensional arrangement of donor molecules in the conducting salts, and many TTF derivatives fused with 1,3-dithiol-2-ylidenes have been prepared.$^{2-4)}$ Among them 2-isopropylidene-1,3-dithiolo[4,5-*d*]ethylenedithio-TTF (MeDTET) has yielded ClO_4 and I_3 salts showing metallic conductive behavior down to *ca.* 90 K.$^{2)}$ In this context investigations on electrical properties of these salts at low temperatures and on preparation of other cation radical salts based on MeDTET are of considerable interest. Herein we report electrical properties of several cation radical salts of MeDTET down to low temperatures together with crystal and electronic structures of its PF_6 salt.



MeDTET

Single crystals of MeDTET salts were prepared by electrochemical oxidation with Bu_4NX (X = ClO_4, PF_6, and AuI_2) at a constant current of 0.5-1 μA in 1,1,2-trichloroethane (TCE). The I_3 salt was obtained by the diffusion method with Bu_4NI_3 in TCE. Energy dispersion spectroscopy indicates that electrochemical oxidation of MeDTET with Bu_4NAuI_2 gave alloyed crystals of AuI_2 and I_3. On the other hand the other salts include TCE, though its contents could not be exactly determined. The electrical conductivity was measured by the four-probe technique on single crystals. As summarized in Table 1, all salts obtained so far showed high electrical conductivity of 170-800 S cm^{-1} at room temperature, and metal-like conductive behavior down to 0.6 K (Figs. 1 and 2).$^{5)}$ Among them ClO_4 salt showed minor jumps on cooling process, and a huge hump on heating process around 50 K and 100 K, respectively. When a weak pressure (1.5 kbar) was applied to this sample, resistivity decreased monotonically down to 0.9 K. This result suggests that a metal to metal transition derived from a possible structural modulation occurred around 100 K and that the application of pressure suppressed this

Table 1. Electrical Properties of Cation Radical Salts of MeDTET

Cation radical salt	Form	σ_{rt} / S cm^{-1} [a]	Conductive behavior
$(MeDTET)_3ClO_4TCE_x$[b]	black plate	170	metallic down to 0.6 K
$(MeDTET)_3PF_6TCE_x$[c]	lustrous brown plate	440	metallic down to 0.9 K
$(MeDTET)_4I_3TCE_x$[d]	black plate	440	metallic down to 0.6 K
$(MeDTET)_3(AuI_2)_{0.5}(I_3)_{1.2}$[d]	black plate	800	metallic down to 0.6 K

a) Room temperature conductivity measured by a four-probe technique on a single crystal.

b) Stoichiometry was determined based on elemental analysis. c) Determined by X-ray structure analysis.

d) Determined based on energy dispersion spectroscopy from ratio of S and I (and Au).

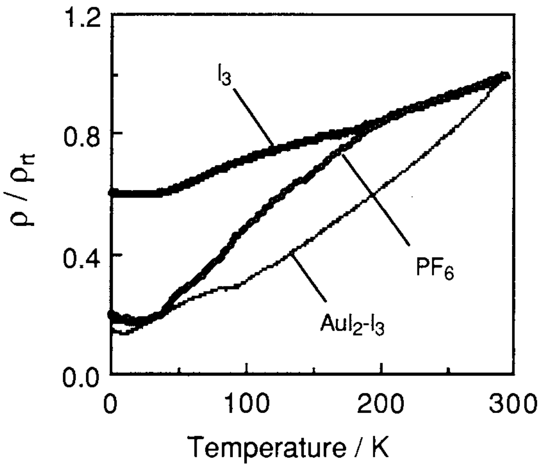


Fig. 1. Electrical resistivity of PF_6, I_3 and AuI_2-I_3 salts of MeDTET (normalized to that at room temperature).

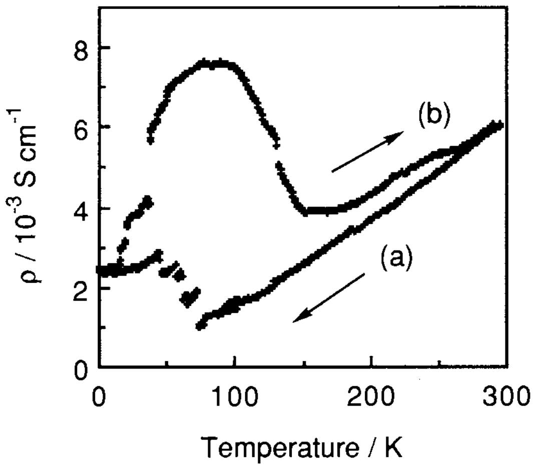


Fig. 2. Electrical resistivity of $(MeDTET)_3ClO_4TCE_x$: (a) cooling process, (b) heating process.

transition. However no superconductivity was observed in all cases. Magnetic susceptibility measurement by means of SQUID also showed no sign of superconductivity at 1.8 K.

Single crystal X-ray structure analysis was carried out for $(MeDTET)_3PF_6TCE_x$.[6] The donors form conducting sheets along the ac-plane (Fig. 3), which are separated from each other by sheets of the anions and the solvents. Along the b-axis, two pieces of sheets are included in a unit cell, and tilt of the donor long axes is opposite in these two sheets. The anion sites are disordered. Population analysis indicates donor : PF_6 ratio to be 3:1. Comparison of the donor bondlengths with those of BEDT-TTF also agrees with the oxidation state of donor being +1/3.[7] The sites of trichloroethane are also so seriously disordered that the exact content of trichloroethane was not able to be determined. One unit cell contains eight donor molecules. The donors have so-called "κ-type" arrangement in the conducting sheet (Fig. 4). There have been known ten "κ-type" salts of BEDT-TTF, most of which show superconductivity.[1] A few salts of other donors, $(MDT\text{-}TTF)_2AuI_2$ and $(DMET)_2AuBr_2$, have also κ-type structure, and these salts show superconductivity. $(BMDT\text{-}TTF)_2Au(CN)_2$, however, does not exhibit superconductivity in spite of its κ-type crystal structure.[8] A structural difference is that this salt has an eclipsed

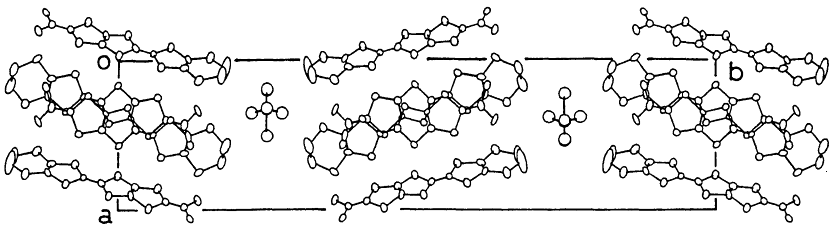


Fig. 3. Crystal structure of $(MeDTET)_3PF_6TCE_x$; projection along the c axis.

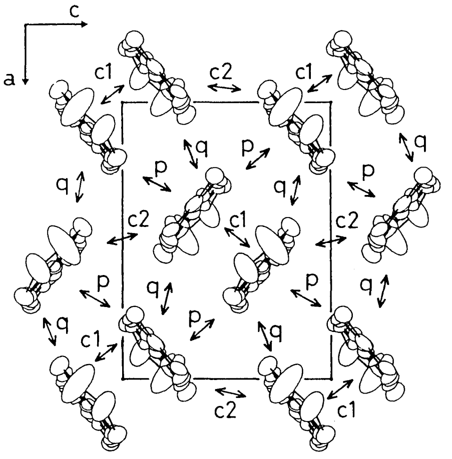


Fig. 4. Donor sheet structure of $(MeDTET)_3PF_6TCE_x$.

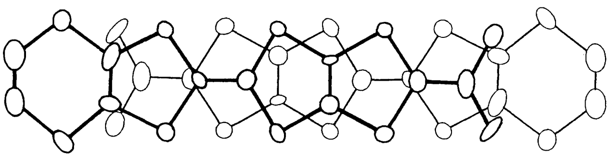


Fig. 5. Overlap mode of a dimer in $(MeDTET)_3PF_6TCE_x$; projection onto the donor molecular plane.

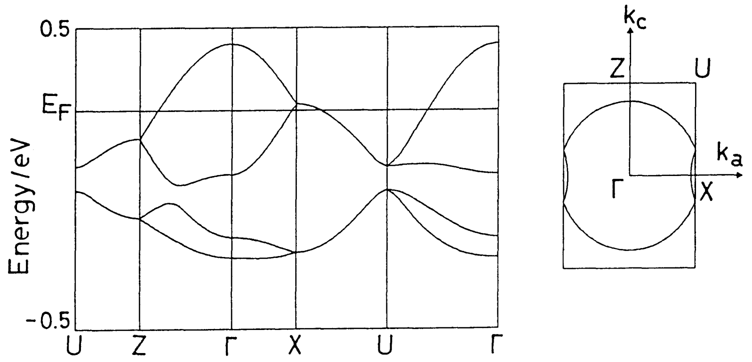


Fig. 6. Energy band structure and Fermi surface of $(MeDTET)_3PF_6TCE_x$. The intermolecular overlap integrals are $c1 = 13.4$, $c2 = 9.5$, $p = 4.6$, $q = 6.3 \times 10^{-3}$.

dimer configuration, but all the former superconducting salts have ring-over-bond type dimer overlap. As shown in Fig. 5, the present salt has the ring-over-bond type overlap within the dimer. There are several short intermolecular S···S contacts less than the sum of the van der Waals radii (3.70 Å) between dimers, but there is no short S···S contact in a dimer.

The band structure is close to that of the reported κ-type salts (Fig. 6),[9] but because the 3:1 composition result in a different band occupancy, the Fermi surface is smaller than those of the other κ-type salts. The present salt is the first example of a κ-type salt that has a composition other than 2:1. Because the space group has an n-glide plane along the a-axis, the energy levels are degenerated on the XU boundary. As a result, the Fermi surface is degenerated on this boundary; this situation is similar to κ-$(BEDT\text{-}TTF)_2I_3$ but different from κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$. The absence of superconductivity, in spite of the κ-type structure with ring-over-bond type dimer overlap, is probably due to (1) the different composition and the band filling, and due to (2) the disorder of the anion sheet.

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5) A few samples of PF_6 salt showed weakly semiconducting behavior even at room temperature, and the resistivity increased typically 6 times down to liquid helium temperature. Even in this case application of a weak pressure (1.5 kbar) recovered a metallic behavior down to low temperatures, but superconductivity was not observed either.
6) Crystal data: Orthorhombic, space group Pnma, a = 11.405(5), b = 43.24(3), c = 8.113(3) Å, V = 4001(4) $Å^3$. Intensities were measured by the ω scan technique on a Rigaku automated four-circle diffractometer AFC-5R with graphite monochromatized Mo Kα radiation ($2\theta < 60°$). Absorption correction was not performed. The structure was solved by the Patterson method and refined by the block-diagonal least squares procedure (R = 0.115) by using 1831 independent reflections ($|F_o| > 3\sigma(F)$). Anisotropic thermal parameters were adopted for all non-hydrogen atoms. Because there is a serious disorder on the anion and trichloroethane sites, the final R factor was considerably large.
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