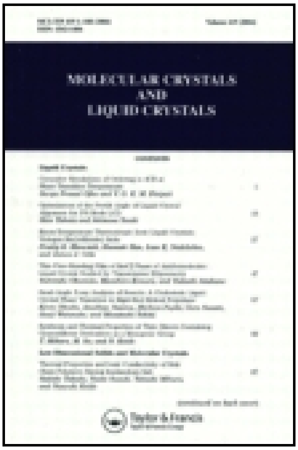

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Syntheses, Structures, and Physical Properties of the Charge-Transfer Salts of Dimethyltrimethylene-Tetraselenafulvalene

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SYNTHESES, STRUCTURES, AND PHYSICAL PROPERTIES OF THE CHARGE-TRANSFER SALTS OF DIMETHYLTRIMETHYLENE-TETRASELENAFULVALENE

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Abstract Dimethyltrimethylenetetraselenafulvalene (DMtTSF) of high purity was obtained by use of GPC, and the electrical and optical properties of its charge-transfer salts were studied. The crystal structures of $(DMtTSF)_2X$ ($X=BF_4$, ReO_4) were also investigated.

INTRODUCTION

Recently, Fabre et al. have investigated the charge-transfer salts of asymmetrical donors,$^{1)}$ and reported that the salts of dimethyltrimethylenetetraselenafulvalene $(DMtTSF)_2X$ remained to be metallic down to 0.1 K,$^{2)}$ but the purification of DMtTSF was rather hard so that their synthesized salts may contain a small amount of TMTSF etc. as impurities.

In the present study, we succeeded to obtain DMtTSF of high purity, and measured the electrical and optical properties of its charge-transfer salts. The crystal structures of $(DMtTSF)_2X$ ($X=BF_4$, ReO_4) were also investigated.

Syntheses

The synthesis of DMtTSF was carried out by the method reported by Fabre et al.[2)] The selene coupling yielded a mixture of TMTSF, DMtTSF, and HMTSF. A repetition of the recrystallization of the products, gave a mixture mainly composed of DMtTSF, which was further purified by recycling high-speed preparative liquid chromatograph by use of the GPC column JAIGEL 1H, 2H. The peaks due to DMtTSF and TMTSF were well separated after 10 cycles in GPC, so that we were able to collect a high purity sample of DMtTSF. The sample (mp. > 220°C) was checked by an analytical HPLC, no signal due to TMTSF being detected. (H-NMR($CDCl_3$) 2.00 (6H, s), 2.34 (m), and 2.52 (m)).

The charge-transfer salts $(DMtTSF)_2X$ ($X=PF_6$, AsF_6, SbF_6, BF_4, ClO_4 and ReO_4) were prepared by the electrochemical method using a constant current (1-2 μA) by use of 1,1,2-trichloroethane as the solvent. The black high-conductive form of DMtTSF-TCNQ was prepared electrochemically from the solution containing DMtTSF and NMQ-TCNQ while the red low-conductive form of DMtTSF-TCNQ was prepared by slowly cooling a hot dichloromethane solution containing DMtTSF and TCNQ. The stoichiometries of these salts were confirmed by XPS.

Electrical Properties

Electrical conductivity was measured by standard four-probe, low-frequency AC technique, with contacts applied by silver paint. The values of room-temperature conductivity are given in Table 1. In the cases of $(DMtTSF)_2X$, the conductivity values were found to be almost the same order as those of $(TMTSF)_2X$ salts. As shown in Fig. 1, these salts have two regions judging from the temperature dependence of electrical conductivity. Above 180 K, these salts show metallic behaviors with $\sigma \propto T^{-\alpha}$ (α is slightly less than 2). Below 180 K, the temperature dependence of conductivity shows a curve with a much gentle slope. A sudden jump of conductivity, which may be due to the formation of a crack, occured in this region. This kind of behavior was also reported by P. Delhaes on $(DMtTSF)_2X$ ($X=ClO_4$, AsF_6, etc.).$^{3)}$

Table 1. Room Temperature conductivities of DMtTSF salts

	σ / $\Omega^{-1}cm^{-1}$
$(DMtTSF)_2X$	
$X=ClO_4$	770, 900
ReO_4	670, 990
BF_4	130, 380
PF_6	480
AsF_6	770
SbF_6	370
DMtTSF-TCNQ	
(black)	650
(red)	$< 10^{-6}$

Figure 2 shows the

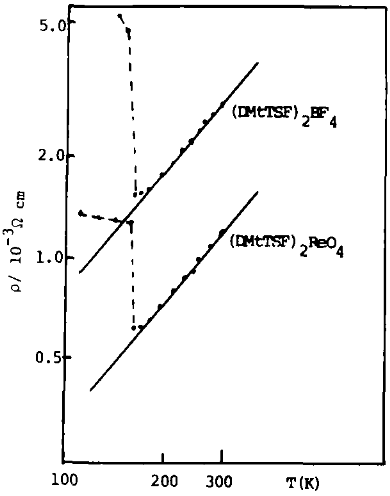

Fig.1. The resistivities of $(DMtTSF)_2X$

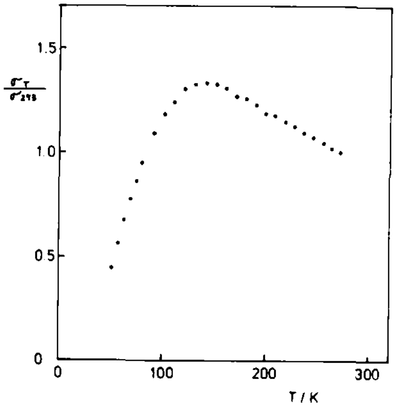

Fig.2. The conductivity of DMtTSF-TCNQ

temperature dependence of the conductivity of the black form of DMtTSF-TCNQ. This salt exhibits a metal-insulator transition around 130 K with a very broad temperature region of transition. This behavior is similar to the one observed in DEDMTSF-TCNQ.[4)] In both these salts, donors have an assymetrical molecure structure, which may give a disorder in respect to the orientation of donor molecule in the crystal. Possibly, the conductivity behaviors found in these salts are related in some respect with the presence of this kind of disorder.

Optical Properties

The polarized reflectance spectra in the region of 5000-25000 cm^{-1} were measured on the single crystals of DMtTSF salts at room temperature by means of the microspectrophotometric method.[5)] As shown in Figs. 3 and 4, every salt shows metallic high reflectance in the infrared region with a Drude-like plasma edge near 7 × $10^3 cm^{-1}$ when the light is

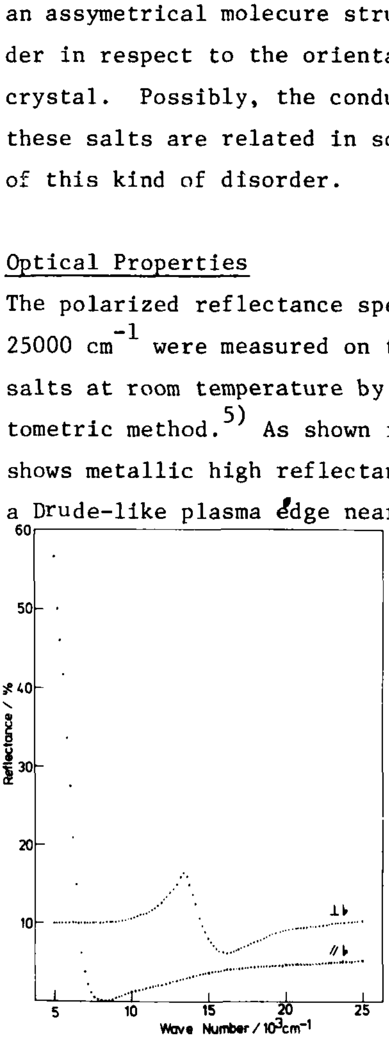

Fig.3 The reflectance spectra of $(DMtTSF)_2ReO_4$

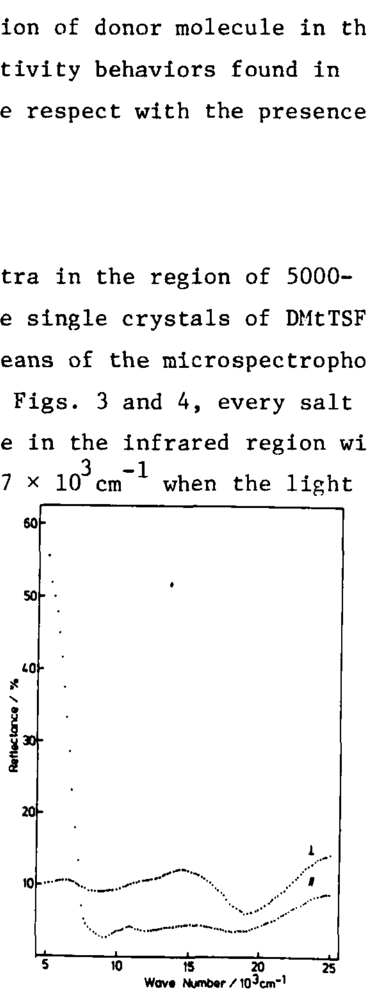

Fig.4 The reflectace spectra of DMtTSF-TCNQ

polarized parallel to the growing crystal axis, which is likely to correspond to the direction of DMtTSF stack (this axis was confirmed to be *b* axis in the case of $(DMtTSF)_2ReO_4$ by X-ray), whereas no such metal-like dispersion can be found when the light is polarized perpendicular to it. From the // *b* reflectance spectrum of $(DMtTSF)_2ReO_4$, we obtained by Drude model that the frequency independent dielectric constant ε_∞ is 2.36, the plasma frequency ω_p is 1.20 eV, the electronic relaxation time τ is 3.31×10^{-15} s. The band width, $4t$. in $(DMtTSF)_2ReO_4$ is concluded to be 0.93 eV, which is almost the same with that of $(TMTSF)_2ClO_4$. 6) The $\perp$ *b* spectrum shows a dispersion at 13.6×10^3 cm^{-1}. This must be due to the intramolecular excitation of $DMtTSF^+$. A dispersion at 10.8×10^3 cm^{-1} observed in the spectrum of DMtTSF-TCNQ for the light polarization perpendicular to the growing axis is attributable to the intramolecular excitation of $TCNQ^-$.

Crystal Structures

The crystal structures of $(DMtTSF)_2X$ ($X=BF_4$, ReO_4) were investigated at room temperature. The crystal data are as follows:

$(DMtTSF)_2BF_4$; M_γ=1008.82, triclinic, $P\bar{1}$, a=8.497 (2), b=13.352 (2), c=7.293 (2), Å, α=92.12 (2), β=122.60 (2), γ=96.11 (1)°, V=688.7A^3, Z=1, (R=0.045, R_ω=0.046 for 2158 observed reflections.)

$(DMtTSF)_2ReO_4$$^{8)}$; M_γ=1170.32, monoclinic, C2/c, a=28.518 (2), b=7.327 (1), c=14.364 (1)Å, β=109.84 (1)°, V=2823Å^3, Z=4, (R=0.056, R_ω=0.067 for 2279 observed reflections.)

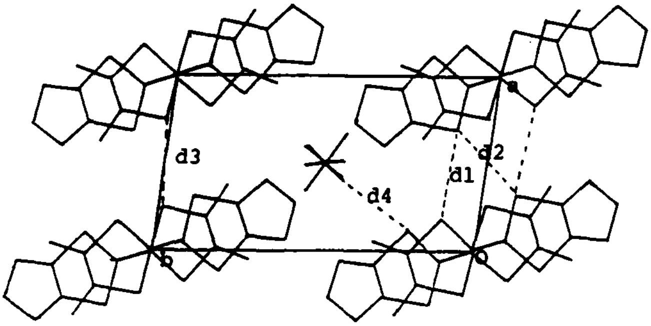

Fig. 5 The view of the crystal structure of $(DMtTSF)_2BF_4$ along the *c* axis. The short interstack distances (Se-Se and Se-O); d1= 3.760(1), d2= 3.740(1), d3= 3.664(1), d4= 3.19(2)Å.

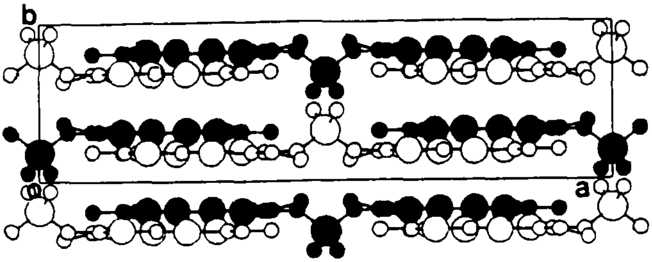

Fig. 6 The view of the crystal structure of $(DMtTSF)_2ReO_4$ along the *c* axis. The front molecules are drawn by open circles.

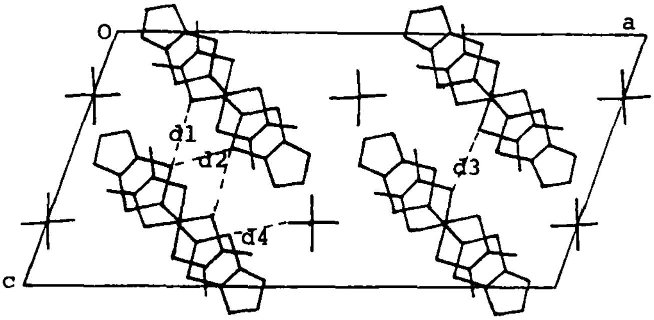

Fig. 7 The view of the crystal structure of $(DMtTSF)_2ReO_4$ along the *b* axis. The short interstack distances (Se-Se and Se-O); d1= 3.784(1), d2= 3.655(2), d3= 3.705(2), d4= 2.98(1)Å.

The Crystal structure of $(DMtTSF)_2BF_4$ is very similar to that of the corresponding TMTSF salt,[7a] as shown in Fig. 5. DMtTSF molecules form ordered centrosymmetric dimers with a zig-zag stacking mode. BF_4 anions occupy randomly the two different but symmetrically related positions like the anions in $(TMTSF)_2BF_4$.

In the crystal of $(DMtTSF)_2ReO_4$, DMtTSF molecules are also stacked along *b* axis to form a zig-zag column, as shown in Fig. 6. However in constrast with BF_4 salt, the neighboring DMtTSF molecules within a stack are muntually related by the screw axis. The molecular plane of DMtTSF is almost perpendicular to the stacking axis and the interplanar distance is exactly equal to *b*/2. So there is no dimerization of molecules within a stack. ReO_4 anions are ordered at room temperature unlike the corresponding TMTSF salts. However the pattern of interchain coupling in $(DMtTSF)_2ReO_4$ is very similar to that in BF_4 salt, as shown in Fig. 7.

The intermolecular separations in the donor stack and some intermolecular Se-Se distances in these $(DMtTSF)_2X$ salts are given in Table 2 together with those of $(TMTSF)_2X$ salts. The data shown in this table tells us

Table 2. Intermolecular distances

Distances (Å) **Compound**	**intrastack**		**interstack**	**anion-cation**	
	spacing distance	**Se-Se***	**Se-Se***	**Se-O or F***	
$(TMTSF)_2$-ReO_4	3.64, 3.64	3.87	3.83	3.16	ref 7b
-ClO_4	3.63, 3.64	3.87	3.78	3.34	ref 7b
-BF_4	3.61, 3.64	3.86	3.74	--	ref 7a
$(DMtTSF)_2$-ReO_4	3.66	3.90	3.66	2.98	this work
-ClO_4	3.66, 3.68	3.90	3.70	3.18	ref 3
-BF_4	3.63, 3.66	3.88	3.66	3.19	this work

(* These distances are the shortest ones) some common features of the crystal structures of $(DMtTSF)_2X$ salts when compared with those of the corresponding TMTSF salts, which are as follows.

(1) The intrastack Se-Se contacts are almost equal to those of the corresponding TMTSF salts.

(2) The interstack Se-Se contacts are considerably shorter in the DMtTSF salts than in the corresponding TMTSF salts.

(3) The Se-anion contacts are shorter in the DMtTSF salts than in the corresponding TMTSF salts.

The feature (2) suggests that $(DMtTSF)_2X$ salts have a stronger two-dimensional character than $(TMTSF)_2X$. As we mentioned, ReO_4 anions are ordered at room temperature in $(DMtTSF)_2ReO_4$ and Se-O distance is 2.98 Å, which is very short and nearly the same as that in $(TMTSF)_2ReO_4$ at 120 K,⁹⁾ where the ReO_4 anions are ordered.

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