Bull. Chem. Soc. Jpn., 67, 2685—2689(1994)

Crystal Structure and Physical Properties of (BDT-TTP)$_2$ClO$_4$

Takehiko Mori,* Yohji Misaki,*,[†] Hideki Fujiwara,[†] and Tokio Yamabe[†]
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152
[†] Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-01

(Received June 17, 1994)

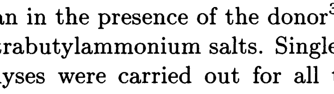
The $\mathrm{ClO_4}$, $\mathrm{BF_4}$, and $\mathrm{ReO_4}$ salts of BDT-TTP, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene, are isostructural, having uniform columns of the donor molecules. These salts are essentially metallic down to low temperatures, though the resistivity increases to some extent below 200 K. The thermoelectric power and ESR show simple metal-like behavior down to low temperatures.

Newly designed organic electron donors, bis-fused tetrathiafulvalenes (TTF) have given many highly conducting radial-cation salts which maintain metallic conductivity down to liquid helium temperatures.[1] In particular most radical-cation salts of unsubstituted BDT-TTP, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (Scheme 1), exhibit metallic conductivity down to liquid helium temperatures regardless of the counter anions.[2,3] In this paper we present the detailed investigation of the BDT-TTP salts with tetrahedral anions, $\mathrm{ClO_4}$, $\mathrm{BF_4}$, and $\mathrm{ReO_4}$, including the results of their single-crystal structure analyses, energy-band calculation, electrical conductivity, thermoelectric power, and ESR measurements.

Experimental

Black plate-like crystals were electrochemically grown in tetrahydrofuran in the presence of the donor[3] and the corresponding tetrabutylammonium salts. Single crystal X-ray structure analyses were carried out for all three kinds of salts; the crystallographic data are listed in Table 1. Because the data of the $\mathrm{BF_4}$ and the $\mathrm{ReO_4}$ salts were, however, rather poor, here we mainly report the results of the $\mathrm{ClO_4}$ salts. Intensity data were measured at 298 K for a single crystal with approximate dimensions $0.4\times0.25\times0.02$ mm^3 by the ω–2θ scan technique on a Rigaku automated four-circle diffractometer AFC-5R with graphite monochromatized Mo $K\alpha$ ($\lambda=0.71073$ Å) radiation ($2\theta<60°$). Absorption correction was not carried out. The structure was solved by the direct method[4] and was refined by the block-diagonal least-squares procedure (UNICS III).[5] The atomic scattering factors were taken from the "International Tables for X-ray Crystallography."[6] Anisotropic thermal parameters were adopted for all non-hydrogen atoms, and the hydrogen atoms were refined isotropically. The final $R=0.077$ and $R_\mathrm{w}=0.075$ (weighting scheme $1/w=\sigma^2+(0.015F_\mathrm{o})^2$ for independent 1370 reflections ($|F_\mathrm{o}|>3\sigma(F_\mathrm{o})$).[7]

The details of the electrical conductivity, thermoelectric power, and ESR measurements are the same as the previously published methods.[8]



BDT-TTP

Scheme 1.

Results and Discussion

The atomic coordinates and equivalent thermal parameters are listed in Table 2. Atomic numbering scheme of the donor is shown in Fig. 1(a). The BDT-TTP molecule is located on a general position, and one unit is crystallographically independent, whereas $\mathrm{ClO_4}$ lies on a two-fold axis. Therefore the composition is (BDT-TTP)$_2$ClO$_4$. The chemical analysis by means of the energy dispersion spectroscopy (EDS) shows, from the ratio of S and Cl, BDT-TTP : $\mathrm{ClO_4}$ to be 1 : 0.43.[2] Though this EDS result suggests the presence of a small amount of anion defect, the R-value of the X-ray analysis never decreased when the population of the anion is reduced. Because the accuracy of EDS is considered to be limited for the atoms which appear succeedingly in the periodic table, namely S and Cl, we will regard the composition as approximately 2 : 1.

The structure analysis of the $\mathrm{ReO_4}$ salt indicates that BDT-TTP : $\mathrm{ReO_4}$ is 1 : 0.36, in consistent with the EDS result, BDT-TTP : $\mathrm{ReO_4}$=1 : 0.37. The structure analysis of the $\mathrm{BF_4}$ salt dose not show any evidence of the anion defect, but the X-ray structure analysis is not sensitive to the population of such light atoms as B and F. To these light elements, EDS is not applicable either. Therefore the composition of the $\mathrm{BF_4}$ salt is not very clear from these measurements.

The BDT-TTP molecule is basically planar; the deviations from the optimal plane are within 0.1 Å. This contrasts with the neutral molecule, where BDT-TTP has a chair conformation.[3] The intramolecular bond lengths are compared with those of neutral BDT-TTP and (BDT-TTP)$_2$SbF$_6$ in Table 3, where the listed bond lengths are averaged by assuming hypothetical *mmm* symmetry, because each bond length is not accurate enough to discuss the changes derived from the charge transfer. Since nodes of the HOMO exist on all S–C bonds, all S–C bonds are expected to become shorter in the charged molecule, and all C=C bonds become longer. This basically holds in Table 3, though the changes of the S–C bonds are not very large. The changes of C(5)=C(6) and C(3)=C(4) seem to be reasonably large (0.01—0.03 Å) to be used to estimate the degree of charge transfer.

The donor sheet is composed of face-to-face stack-

Table 1. Crystallographic Data

	$(BDT\text{-}TTP)_2ClO_4$	$(BDT\text{-}TTP)_2BF_4$	$(BDT\text{-}TTP)_2(ReO_4)_{0.72}$
Chemical formula	$C_{20}H_8S_{16}ClO_4$	$C_{20}H_8S_{16}BF_4$	$C_{20}H_8S_{16}(ReO_4)_{0.72}$
Formula weight	860.789	848.144	941.487
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$
a/Å	35.067(6)	35.566(9)	34.71(5)
b/Å	6.934(3)	6.936(2)	6.99(3)
c/Å	12.504(3)	12.514(4)	12.50(1)
β/°	102.43(2)	102.09(2)	102.44(7)
V/Å^3	2969(1)	3018(1)	2962(12)
Z	4	4	4
D_c/g cm^{-1}	1.925	1.867	2.111
μ (Mo $K\alpha$)/cm^{-1}	12.42	11.43	41.17
σ/S cm^{-1}	140	400	160

Table 2. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Thermal Parameters of $(BDT\text{-}TTP)_2ClO_4$

Atom	x	y	z	B_{eq}/Å^2
Cl	0	601 (11)	7500	6.7
O(1)	116 (5)	1446 (45)	8418 (23)	36.8
O(2)	−316 (4)	−381 (26)	7537 (12)	12.0
S(1)	1499 (1)	924 (6)	−70 (2)	2.6
S(2)	1261 (1)	926 (6)	2035 (2)	2.7
S(3)	2403 (1)	916 (5)	1130 (2)	2.1
S(4)	2179 (1)	895 (5)	3305 (2)	2.3
S(5)	3266 (1)	870 (6)	2276 (2)	2.4
S(6)	3043 (1)	865 (5)	4454 (2)	2.3
S(7)	4170 (1)	1058 (6)	3457 (2)	2.9
S(8)	3967 (1)	945 (6)	5627 (2)	3.0
C(1)	1008 (3)	970 (21)	−114 (9)	3.1
C(2)	886 (3)	887 (19)	841 (9)	2.7
C(3)	1648 (3)	934 (18)	1348 (8)	1.9
C(4)	2026 (3)	888 (18)	1864 (7)	1.6
C(5)	2774 (3)	855 (19)	2312 (8)	2.0
C(6)	2669 (3)	878 (18)	3288 (7)	1.8
C(7)	3416 (3)	865 (18)	3698 (8)	2.3
C(8)	3808 (3)	899 (19)	4203 (8)	2.3
C(9)	4551 (3)	1312 (20)	4603 (11)	3.6
C(10)	4460 (3)	1153 (24)	5591 (10)	4.3

$B_{eq}=4/3(\sum\sum B_{ij}\,a_i\cdot a_j)$.

ing of the donor molecules extending along the b axis (Fig. 2). Table 4 lists the intermolecular overlap integrals S of the HOMO of the adjacent molecules,[9] the angle of the intermolecular vector from the molecular plane ϕ, and the slip distance along the molecular long axis D. Owing to the crystal symmetry there is only one intrachain interaction, which is designated as "b" in Fig. 2. Then the stacking is completely uniform. As shown in Fig. 1(b) the overlap mode is so-called ring-over-bond type, where the adjacent molecule slips by a half unit ($D=1.6$ Å) of the dithiole ring along the molecular long axis. The interplanar distance is 3.464 Å. The intrastack overlap integral $S=-25.2\times10^{-3}$ gives a comparatively large bandwidth $4t=1.0$ eV.

The interstack interactions are about one third of the intrastack interaction (Table 4). Therefore the interchain interaction is reasonably strong. The tight-binding energy band structure and Fermi surface are calculated from these interactions as shown in Fig. 3. Owing to the existence of the c glide plane, the energy band on the ZM zone boundary is degenerated. Then, though Fig. 3 is depicted in the folded zone, in the unfolded zone one can imagine a set of open Fermi surface. The detail around the Γ point is, however, somewhat tricky; a small change may result in a closed Fermi surface. Actually the Fermi surface calculated from the crystal structure of the ReO_4 salt gives closed Fermi surface (partly due to the smaller amount of the charge transfer in the ReO_4 salt).

The conductivity is in the order of 140—400 S cm^{-1} and metal-like at room temperature. In the cooling run the conductivity is metal-like down to about 100 K, but it undergoes a few jumps, becoming more than one order larger than the room-temperature value. However, it is not semiconductive even at liquid helium temperatures. In the heating run, which is shown in Fig. 4, the conductivity behaves like a metal at He temperatures, but in the region of 100—200 K, it gradually goes back to the original room-temperature value. This anomalous behavior has been observed reproducibly, though the ratio of the minimum and maximum has not been completely the same. Such a behavior may come either from cracks formed in the cooling run or from some structural change at around 100—200 K. Because this behavior is common to the salts of the tetrahedral anions, but not observed in other salts,[2] we temporarily assume that it may be related to some kind of intrinsic structural change.

The thermoelectric power (Seebeck coefficient) is shown in Fig. 5. The thermoelectric power is positive and T-linear in the whole temperature range, agreeable with a simple donor conductor. Two-dimensional conductors such as BEDT-TTF salts tend to show complicated temperature dependence, but ordinary one-dimensional conductors show simple T-linear behavior.[10] Therefore the observed T-linear depen-

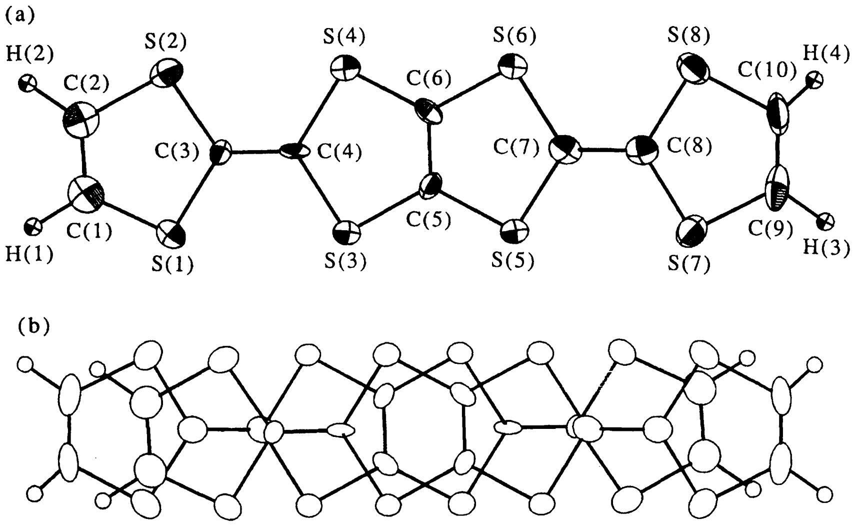


Fig. 1. (a) Atomic numbering scheme of BDT-TTP, and (b) intrastack overlap mode.

Table 3. Intramolecular Bond Lengths (Å) of BDT-TTP Averaged by Assuming *mmm* Symmetry

Compound	C(1)–C(2) C(9)–C(10)	S(1)–C(1) S(2)–C(2) S(7)–C(9) S(8)–C(10)	S(1)–C(3) S(2)–C(3) S(7)–C(8) S(8)–C(8)	C(3)–C(4) C(7)–C(8)	S(3)–C(4) S(4)–C(4) S(5)–C(7) S(6)–C(7)	S(3)–C(5) S(4)–C(6) S(5)–C(5) S(6)–C(6)	C(5)–C(6)
BDT-TTP[3)]	1.332(6)	1.734(4)	1.759(4)	1.336(5)	1.769(4)	1.750(4)	1.327(5)
$(BDT\text{-}TTP)_2SbF_6$[2)]	1.29(2)	1.74(2)	1.75(2)	1.36(2)	1.76(2)	1.74(2)	1.34(2)
$(BDT\text{-}TTP)_2ClO_4$	1.35(2)	1.74(2)	1.74(1)	1.36(2)	1.76(1)	1.74(1)	1.35(2)

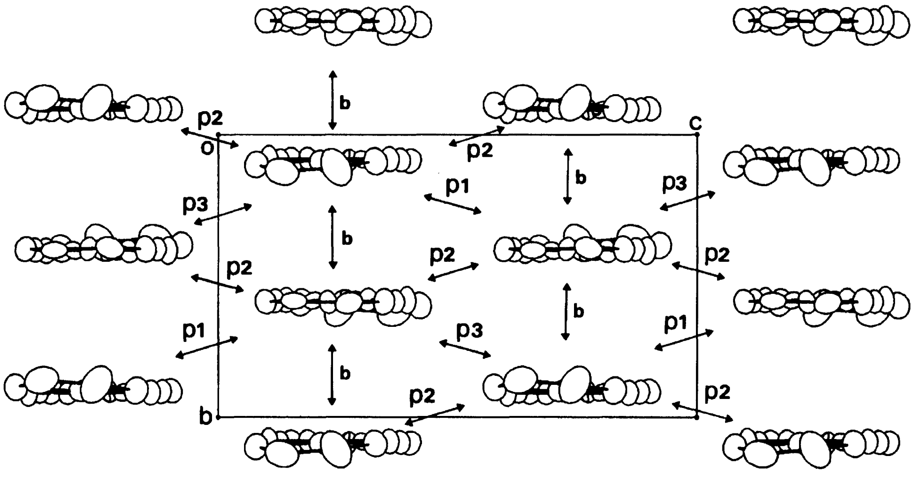


Fig. 2. Donor arrangement of $(BDT\text{-}TTP)_2ClO_4$, viewed along the donor long axis.

dence of the present salts may be related to the basically one-dimensional energy band. If a tight-binding one-dimensional band is assumed, the thermoelectric power is given as:

$$S=\frac{\pi^2 k_B^2 T}{6et}\frac{\cos(1/2\pi\rho)}{1-\cos^2(1/2\pi\rho)}.$$

From this relation, the gradient of the observed thermoelectric power gives the bandwidths $4t=1.3$ eV for the ClO_4 salt, $4t=1.1$ eV for the BF_4 salts, and $4t=2.2$ eV for the ReO_4 salts. The values of the ClO_4 and the BF_4 salts are basically consistent with the calculated bandwidth, $4t=1.0$ eV. These bandwidths are a little larger than those of usual organic metals, probably due to the good face-to-face overlap of the donors along the stacking direction.

The anomalously large estimated bandwidth of the ReO_4 salt comes from the cosine factor of the above equation, i.e. the difference of the charge transfer ρ. It is, however, not evident whether the analysis on the basis of the one-dimensional tight-binding band is valid or not, because the calculated Fermi surface is closed in this case.

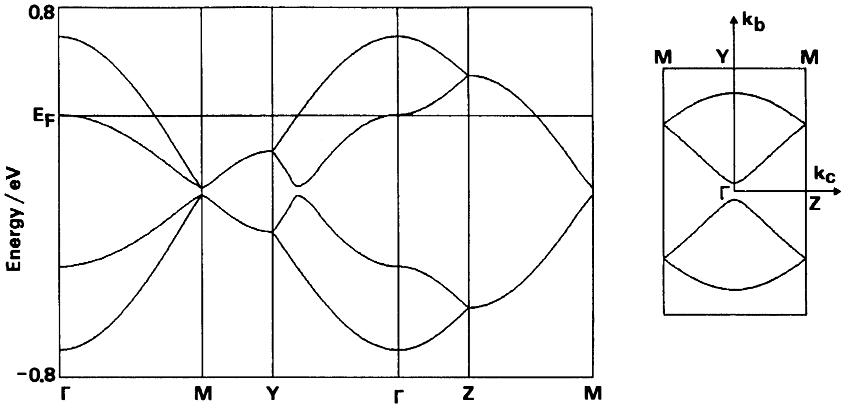


Fig. 3. Tight-binding energy band structure and Fermi surface of $(BDT-TTP)_2ClO_4$.

Table 4. Intermolecular Overlap Integrals of the HOMO, S, and the Parameters ϕ and D Which Define the Orientation of Neighboring Molecules (See Text) in $(BDT-TTP)_2ClO_4$

	$S/\times10^{-3}$	$\phi/°$	D/Å
c	−25.4	90	1.6
p1	9.4	20	0.0
p2	−0.2	11	1.6
p3	8.1	20	3.2

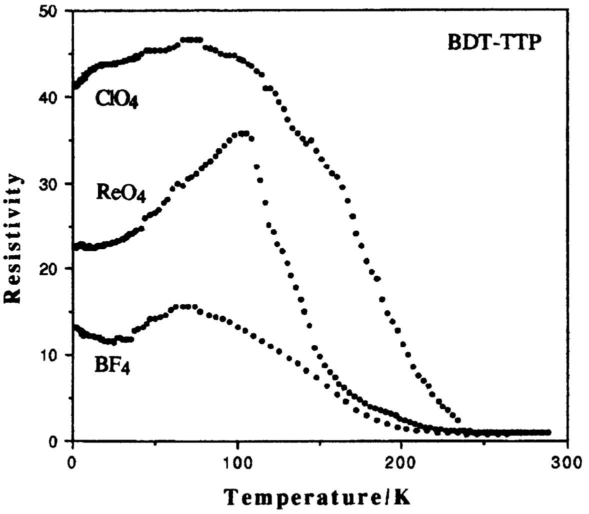


Fig. 4. Electrical resistivity of $(BDT-TTP)_2X$ along the stacking direction (//b), normalized to the room-temperature values.

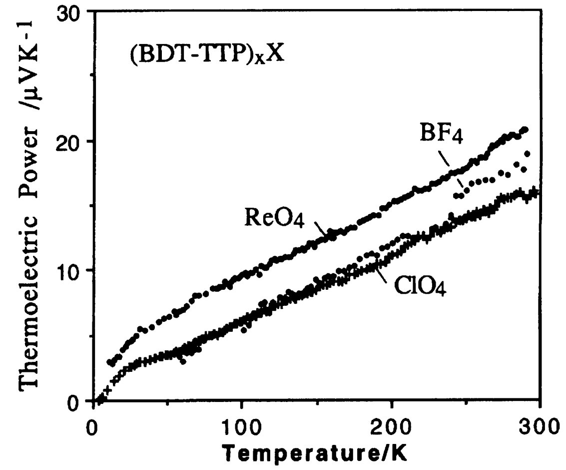


Fig. 5. Thermoelectric power of $(BDT-TTP)_2X$ (//b).

The ESR peak-to-peak linewidth and intensity are shown in Fig. 6. The g-values are 2.007—2.012 along H//c and 2.013 along H//a, and do not depend on the temperature. The room-temperature linewidths are 12—14 G along H//c and 18—19 G along H//a. These linewidths are rather narrow in comparison with BEDT-TTF salts (BEDT-TTF: bis(ethylenedithio)-tetrathiafulvelene),[11] suggesting comparatively one-dimensional Fermi surface of the present salt. The approximately T-linear dependence of the linewidth is consistent with the metallic conduction. Above 100 K the ESR intensity slightly decreases with lowering the temperature; this might be attributable to some gradual change of the electronic structure. Below 100 K, the intensity is almost T-independent.

The crystal structure of the present salts resembles that of β-$(BEDT-TTF)_2I_3$.[12] However, β-$(BEDT-TTF)_2I_3$ have a strong dimerization along the stacking direction. On the contrary, the present salts are perfectly uniform along the stacking direction. As a result the Fermi surface is between one-dimensional and two-dimensional. The possible structure change around 100 K, to which the resistance increase is attributable, may be associated with some sort of one-dimensional instability. The low-temperature phase is, however, not semiconductive but seemingly semimetal-like. Moreover, this "transition," if any, does not give any influence to the thermoelectric power and ESR. Therefore we consider that the present salts are rather one-dimensional, but the one-dimensional instability is nearly suppressed.

In this context, we should point out the similarity of the present salts to $(TMEO-TTP)_2Au(CN)_2$ (TMEO-TTP: 2-(4,5-bis(thiometyl)-1,3-dithiol-2-ylidene)-5-(4,5-ethylenedioxy-1,3-dithiol-2-ylidene)-1,3,4,6-tetra-

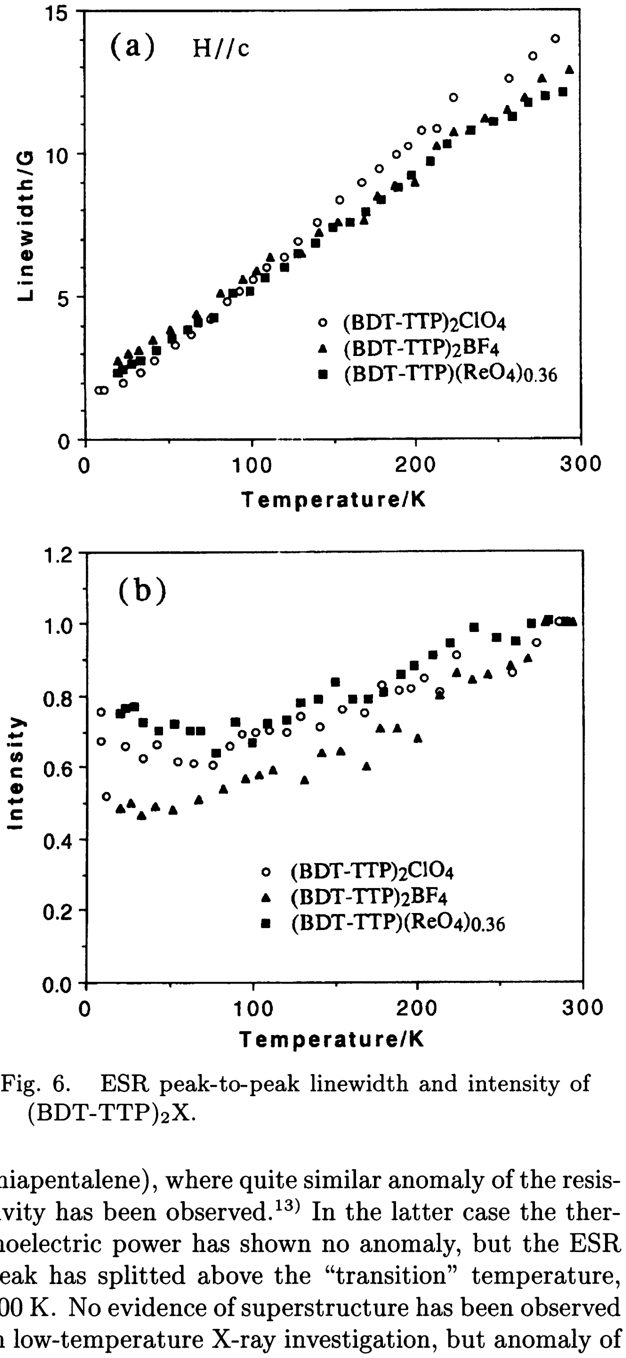


Fig. 6. ESR peak-to-peak linewidth and intensity of $(BDT\text{-}TTP)_2X$.

thiapentalene), where quite similar anomaly of the resistivity has been observed.[13] In the latter case the thermoelectric power has shown no anomaly, but the ESR peak has splitted above the "transition" temperature, 200 K. No evidence of superstructure has been observed in low-temperature X-ray investigation, but anomaly of the temperature dependence of the lattice constants has been found around 200 K,[14] indicating the occurrence of some structural change at this temperature. In the present BDT-TTP salts also careful low-temperature X-ray investigation is expected to elucidate the nature of the anomalous behavior.

The present salts have close structural resemblance to $(EP\text{-}TTP)_2Au(CN)_2$ (EP-TTP: 2-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-5-(4,5-trimethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene),[15] where the stacking is not completely uniform but the dimerization is very weak. $(EP\text{-}TTP)_2Au(CN)_2$ has open Fermi surface and shows simple "metal-like" behavior down to 0.7 K. $(BDT\text{-}TTP)_2SbF_6$, another salt of the same donor whose crystal structure has been known,[2] has also nearly uniform stack and shows metal-like conductivity down to liquid helium temperatures. Its calculated Fermi surface is closed, but is very close to be open. In contrast to these bis-fused donors, simple TTF in general forms highly one-dimensional salts which undergo the typical Peierls transitions at comparatively high temperatures.[16] It seems to be characteristic of the bis-fused TTF's that one-dimensional instabilities are basically suppressed due to their sufficient interstack interaction, even if their Fermi surface is still open. Therefore the extension of the molecular skeleton in the bis-fused TTF series is considered to give an important tool for stabilizing the metallic state against the one-dimensional instabilities.

References

1) Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori, H. Inokuchi, H. Mori, and S. Tanaka, *Chem. Lett.*, **1993**, 729, 733, 2073, and 2085; *Bull. Chem. Soc. Jpn.*, **67**, 661 (1994).

2) Y. Misaki, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, and S. Tanaka, *Chem. Lett.*, in press.

3) Y. Misaki, T. Matsui, K. Kawakami, H. Nishikawa, T. Yamabe, and M. Shiro, *Chem. Lett.*, **1993**, 1337.

4) G. M. Sheldrick, "Crystallographic Computing 3," Oxford University Press, Oxford II (1985), pp. 175—189.

5) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55**, 69 (1979).

6) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

7) The structure factor table and the list of anisotropic thermal parameters are deposited as Document No. 67064 at the Office of the Editor of Bull. Chem. Soc. Jpn.

8) T. Mori, H. Inokuchi, A. Kobayashi, R. Kato, and H. Kobayashi, *Phys. Rev. B*, **38**, 5913 (1988).

9) T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **57**, 627 (1984).

10) T. Mori and H. Inokuchi, *J. Phys. Soc. Jpn.*, **57**, 3674 (1988).

11) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M.-H. Whangbo, "Organic Superconductors," Prentice Hall, New Jersey (1992), p. 189.

12) T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Chem. Lett.*, **1984**, 957.

13) T. Mori, H. Inokuchi, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori, and S. Tanaka, *Chem. Lett.*, **1993**, 2085.

14) T. Mori, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori, and S. Tanaka, "Proceedings of International Conference of Synthetic Metals," Seoul, 1994.

15) T. Mori, H. Misaki, and T. Yamabe, to be published.

16) R. J. Warmack, T. A. Callcott, and C. R. Watson, *Phys. Rev. B*, **12**, 3336 (1975).