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Structure and Conducting Properties of BDT-TTP Salts

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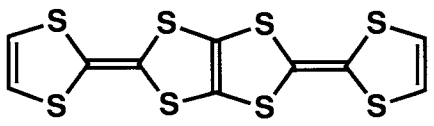
Many cation radical salts of BDT-TTP (2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) showed metallic conducting behavior down to 0.6-1.2 K. X-Ray crystal structure analysis of (BDT-TTP)$_2$SbF$_6$ revealed that this salt has a two-dimensional "β-type" arrangement of donor molecules in the conducting sheet.

Realization of two-dimensional electrical property has been regarded as the most important strategy for preparation of organic metals showing metallic conducting behavior down to low temperature.[1] A bis-fused tetrathiafulvalene (TTF), 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP), is of considerable interest as a promising skeleton that gives charge-transfer salts possessing two-dimensional electronic structure, whereas the parent TTF generally affords one-dimensional metals. Recently, we have synthesized many derivatives of BDT-TTP,[2-4] several of which have yielded metallic cation radical salts down to low temperature (≤4.2 K).[3,5] However, the investigation on structure and electrical properties of cation radical salts based on the parent BDT-TTP is desirable in order to prove ability of BDT-TTP to form two dimensional conducting sheets. We report herein the preparation and conducting properties of cation radical salts of BDT-TTP together with crystal and electronic structures of the SbF_6 salt.



BDT-TTP

Single crystals of BDT-TTP salts were prepared by electrochemical oxidation in the presence of the corresponding tetrabutylammonium salts at a constant current of 0.3-1 μA/cm^2 in THF, 1,1,2-trichloroethane or 1,2-dichloroethane. The I_3 salt was obtained using the diffusion technique with Bu_4NI_3 in THF. Most of salts showed high electrical conductivity of 10^2-10^3 S cm^{-1} at room temperature as summarized in Table 1. It is noted that all of salts except for IO_4 salt exhibited metal-like conductive behavior down to 0.6-1.2 K (Fig. 1), although the resistivity of several salts increase a little at low temperature. This

Table 1. Composition and Electrical Conductivity of BDT-TTP Salts (BDT-TTP·A_x)

Anion	Solvent	Form[a]	x[b]	σ_{rt} / Scm^{-1}	
ClO_4	THF	P	0.43(Cl), 0.5(X)	140	Metallic[c]
BF_4	THF	P	0.5(X)	400	Metallic[c]
IO_4	THF	P	0.41(I)	1.0	E_a = 0.043 eV
ReO_4	THF	P	0.37(Re), 0.36(X)	160	Metallic[c]
$GaCl_4$	THF	P	0.76(Ga), 0.52(Cl)	210	Metallic down to 1.2 K
PF_6	THF	N	0.49(P)	500	Metallic[c]
AsF_6	THF	P	0.50(As)	880	Metallic down to 0.6 K
SbF_6	THF, DCE[d]	P	0.5(X)	48	Metallic down to 0.6 K
I_3	THF	N	0.40(I)	1000	Metallic down to 0.6 K
AuI_2	THF	N	0.38(Au), 0.53(I)	520	Metallic down to 0.6 K
$AuBr_2$	THF	N	0.40(Au), 0.29(Br)	130	Metallic down to 1.2 K
$Au(CN)_2$	THF, TCE[e]	N	0.46(Au)	200	Metallic down to 0.6 K
Br	THF	Poly	0.51(Br)	13	Metallic[c]

a) P = plate, N = needle, Poly = polycrystal. b) Determined by the energy dispersion spectroscopy from the ratio of sulfur and the elements designated in the parentheses. X designates the value determined from the single crystal X-ray structure analysis.[8] c) The resistivity increases a little at low temperatures, but is essentially metallic down to 1.2 K. d) DCE = 1,2-dichloroethane. e) TCE = 1,1,2-trichloroethane.

result indicates that the parent BDT-TTP has a strong tendency to afford charge-transfer salts which retain metallic states down to low temperature. However, no superconductivity was observed in all cases.

Single crystal X-ray structure analysis was performed for (BDT-TTP)$_2$SbF$_6$.[6] The donor molecule is almost planar (Fig. 2), while the neutral BDT-TTP has a chair conformation tilted at the sulfur atoms in the central tetrathiapentalene moiety.[4] The deviations from the optimal plane are within 0.14(2) Å. The exocyclic C=C bonds of (BDT-TTP)$_2$SbF$_6$ (1.36(2) and 1.35(2) Å for C3-C4 and C7-C8, respectively) become a little longer by 0.02-0.03 Å compared with those of the neutral BDT-TTP (1.332(5) and 1.336(6) Å) because of contribution of the single bond character due to partial ionization. However, there is no systematic change for other bonds because the HOMO of BDT-TTP spreads more than that of TTF. The donors form conducting sheets along the ac-plane, which are separated from each other by sheets of the centrosymmetric SbF_6 anions (Fig. 3(a)). As shown in Fig. 3(b), the arrangement of the donors is close to β-(BEDT-TTF)$_2$I$_3$, where BEDT-TTF is bis(ethylenedithio)-TTF.[7,8] Thus, the donors are stacking in a face-to-face manner, and the overlap mode of donor molecules is so called ring-over-bond type. The slip distance along the molecular axis in the stack is 1.6 Å. The donors form almost uniform stacks with the interplanar distances of 3.46 and 3.47 Å, respectively, while they are dimerized in β-(BEDT-TTF)$_2$I$_3$ with the interplanar distances of 3.75 and 3.86 Å, respectively. There are several "side-by-side" intermolecular S···S contacts

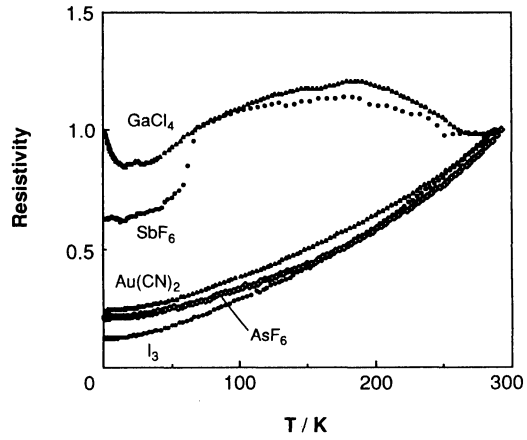


Fig. 1. Electrical resistivity of BDT-TTP salts.

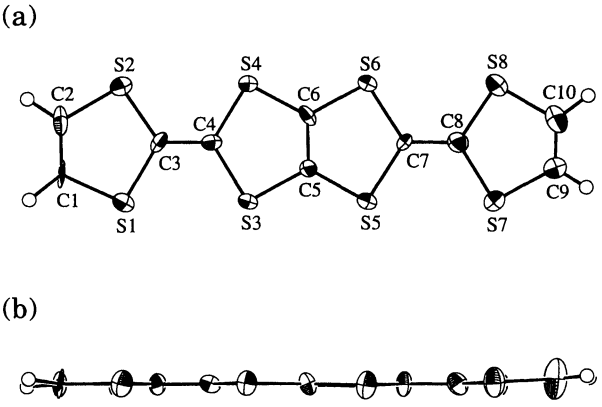


Fig. 2. (a) The donor structure of $(BDT\text{-}TTP)_2SbF_6$, and (b) the side view.

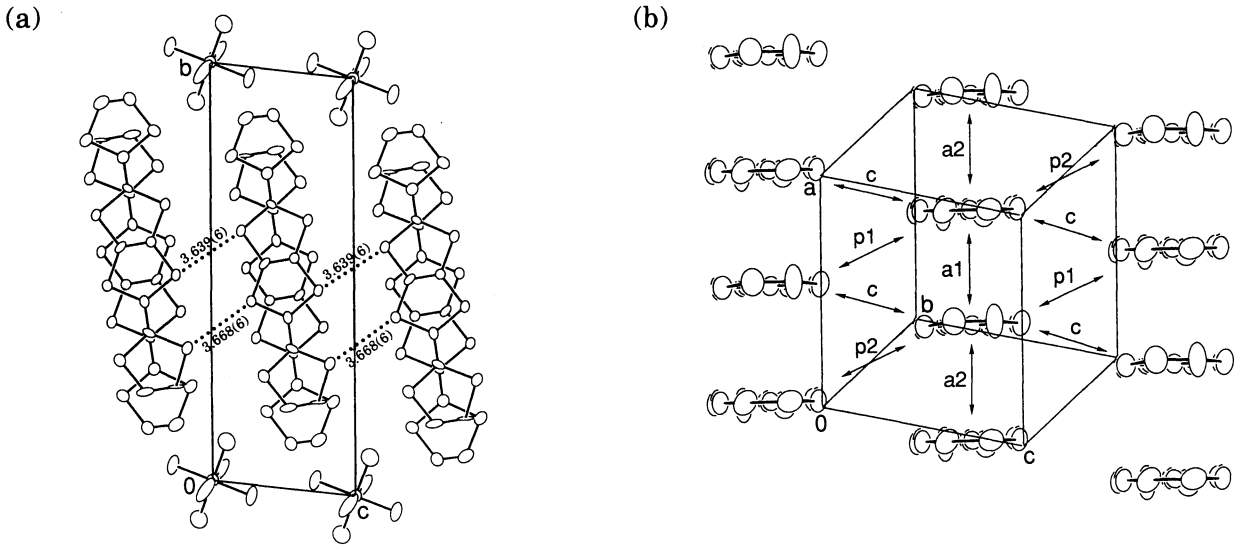
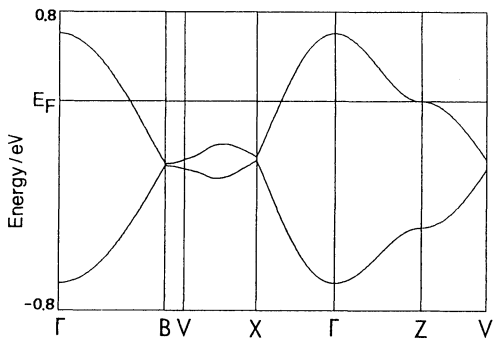


Fig. 3. Crystal structure of $(BDT\text{-}TTP)_2SbF_6$; (a) projection onto bc plane, and (b) arrangement of donor molecules viewed along the molecular long axis.



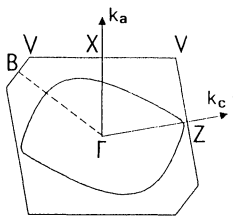


Fig. 4. Energy band and Fermi surface of $(BDT\text{-}TTP)_2SbF_6$. The intermolecular overlap integrals ($\times 10^{-3}$) are a1 = 25.1, a2 = 25.3, c = 0.8, p1 = 7.9, p2 = 8.6.

less than the sum of the van der Waals radii (3.70 Å) along the transverse direction. Whereas such short S···S distances are not observed in a stack, the shortest one being 3.749(7) Å.

The band structure of (BDT-TTP)$_2$SbF$_6$ calculated by the tight binding method is shown in Fig. 4.[9] Because both the intrastack interactions (a1 and a2) are comparatively strong, the bandwidth (1.36 eV) is more than twice as large as that of β-(BEDT-TTF)$_2$I$_3$.[8] On the other hand, the overlap integrals along the transverse direction (p1 and p2) are about one third compared to those along the stacking one. Such somewhat strong interstack interactions give a closed Fermi surface, although it is not a typical ellipse as is observed in β-(BEDT-TTF)$_2$I$_3$.[8] The details of structure and physical property of the present salts with tetrahedral anions will be reported elsewhere.[10]

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References

1) 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).
2) Y. Misaki, H. Nishikawa, K. Kawakami, S. Koyanagi, T. Yamabe, and M. Shiro, *Chem. Lett.*, **1992**, 2321.
3) Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori, H. Inokuchi, H. Mori, and S. Tanaka, *Chem. Lett.*, **1993**, 729; Y. Misaki, H. Nishikawa, K. Kawakami, T. Yamabe, T. Mori, H. Inokuchi, H. Mori, and S. Tanaka, *ibid.*, **1993**, 2073; Y. Misaki, K. Kawakami, T. Matsui, T. Yamabe, and M. Shiro, *J. Chem. Soc., Chem. Commun.*, **1994**, 459.
4) Y. Misaki, T. Matsui, K. Kawakami, H. Nishikawa, T. Yamabe, and M. Shiro, *Chem. Lett.*, **1993**, 1337.
5) T. Mori, H. Inokuchi, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori, and S. Tanaka, *Chem. Lett.*, **1993**, 2085.
6) Crystal data: Triclinic, space group $P\bar{1}$, a = 6.935(4), b = 18.167(9), c = 6.405(2) Å, α = 98.34(4), β = 101.11(4), γ = 81.50(5)°, V = 777.4(7) Å^3. Intensities were measured by the ω-2θ scan technique on a Rigaku automated four-circle diffractometer AFC-7R with graphite monochromatized Mo $K\alpha$ radiation ($2\theta < 60°$). After absorption correction was performed, the structure was solved by the direct method and refined by the full-matrix least squares procedure (R = 0.077) by using 1517 independent reflections ($|I_0| > 3\sigma(I)$). Anisotropic thermal parameters were adopted for all non-hydrogen atoms.
7) V. F. Kaminskii, T. G. Prokhoroea, R. P. Shibaeva, and E. B. Yagubskii, *Pis'ma Eksp. Teor. Fiz.*, **39**, 15 (1984).
8) T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Chem. Lett.*, **1984**, 957.
9) T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc., Jpn.*, **57**, 627 (1984).
10) T. Mori, Y. Misaki, and T. Yamabe, to be published.

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