3250 *Chem. Mater.* **2003,** *15,* 3250−3255

Articles

New Organic Superconductors with an Incommensurate Anion Lattice Consisting of Polyhalide Chains (MDT-TSF)X_y (MDT-TSF = Methylenedithiotetraselenafulvalene; X = Halogen; y = 1.27−1.29)

Kazuo Takimiya,*,† Mie Kodani,† Yoshiro Kataoka,† Yoshio Aso,† Tetsuo Otsubo,†
Tadashi Kawamoto,‡ and Takehiko Mori‡

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-8527, Japan, and Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8552, Japan

Received April 2, 2003. Revised Manuscript Received June 9, 2003

The title radical cation salts of MDT-TSF (methylenedithiotetraselenafulvalene) with polyhalide anions prepared by electrocrystallization in the presence of various tetrabutylammonium trihalides show high conductivity at room temperature ($>10^3$ S cm^{-1}) and become superconductors at below 4.0−5.5 K under ambient pressure. Their crystal structures elucidated by X-ray structural analysis are characterized by quasi two-dimensional conducting sheets consisting of uniform donor stacks. Their X-ray oscillation photographs reveal the existence of an incommensurate anion lattice originating from the infinite polyhalide chains. The chemical composition of these salts, as determined on the basis of the X-ray photographs together with the combustion elemental analyses, is (MDT-TSF)$X_{1.27-1.29}$ (X = halogen). Considering that the most probable charged unit in the polyhalide chain is the trihalide (X_3^-), the charge-transfer degree on each donor molecule is estimated to be nonstoichiometric, 0.42−0.43.

Introduction

The synthesis and characterization of new organic superconductors has been an important topic in solid-state science since the discovery of the first organic superconductor (TMTSF)$_2$PF$_6$ (TMTSF: tetramethyltetraselenafulvalene) in 1979.[1] Continuous endeavors to develop advanced materials have created more than one hundred molecular-based superconductors,[2,3] the majority of which are (Donor)$_2X$-type radical cation salts, where Donor is a TTF-type electron donor such as BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene],[2a] BO [bis(ethylenedioxy)tetrathiafulvalene],[4] BETS [bis(ethylenedithio)tetraselenafulvalene],[5] or MDT-TTF (methylenedithiotetrathiafulvalene),[6] and X is a monovalent inorganic anion. Among them, the most representative are (BEDT-TTF)$_2X$ superconductors, and an organic superconductor with the highest T_c, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, was found from this family.[7]

Most of these organic superconductors, regardless of the electron donors or the donor arrangements in the conducting layers (usually distinguished by the Greek phase names such as β, κ, λ[8]) are structurally characterized by quasi two-dimensional conducting donor layers, the basic unit of which is a dimer consisting of two donor molecules stacked on top of each other. Since the formal charge on each donor molecule is +0.5 owing to the 2:1 donor-to-anion ratio, such dimerization makes the donor HOMO band "effective half-filled", which is regarded as

---

* Corresponding author. Tel: +81-824-24-7734. Fax: +81-824-24-5494. E-mail: ktakimi@hiroshima-u.ac.jp.

† Hiroshima University.

‡ Tokyo Institute of Technology.

(1) Jerome, D.; Mazaud, A. Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, *41*, L95−L98.

(2) For comprehensive reviews on organic superconductors: (a) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992. (b) Ishiguro, T.; Yamaji, K.; Saito, G. *Organic Superconductors,* 2nd ed.; Springer-Verlag: Berlin, 1998.

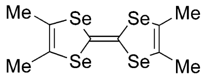
(3) Recently, new superconductors based on newly developed electron donors have been reported; see (a) Yamada, J.; Watanabe, M.; Akutsu, H.; Nakatsuji, S.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 4174−4180. (b) Imakubo, T.; Tajima, N.; Tamura, M.; Kato, R.; Nishio, Y.; Kajita, K. *J. Mater. Chem.* **2002**, *12*, 159−161. (c) Nishikawa, H.; Morimoto, T.; Kodama, T.; Ikemoto, I.; Kikuchi, K.; Yamada, J.; Yoshino, H.; Murata, K. *J. Am. Chem. Soc.* **2002**, *124*, 730−731. (d) Kodani, M.; Takamori, A.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Solid State Chem.* **2002**, *168*, 582−589. (4) Nishikawa, H.; Mochida, A.; Morimoto, T.; Kikuchi, K.; Kodama, T.; Ikemoto, I.; Yamada, J.; Yoshino, H.; Murata, K. *Chem. Commun.* **2003**, 494−495.

(4) (a) Beno, M. A.; Wang, H. H.; Kini, A. M.; Carlson, K. D.; Geiser, U.; Kwok, W. K.; Thompson, J. E.; Williams, J. M.; Ren, J.; Wangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 1599−1601. (b) Kahlich, S.; Schweitzer, D.; Heinen, I.; Lan, S. E.; Nuber, B.; Keller, H. J.; Winzer, K.; Helberg, H. W. *Solid State Commun.* **1991**, *80*, 191−195.

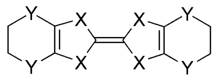
10.1021/cm034222i CCC: $25.00

one of the crucial conditions for the emergence of the superconducting ground state.[9]

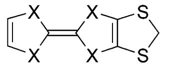
Recently, we have found a new organic superconductor, (MDT-TSF)(AuI$_2$)$_{0.436}$ with $T_c = 4.5$ K,[10a–c] where MDT-TSF is methylenedithiotetraselenafulvalene.[11] This organic superconductor is significantly different from the conventional ones in terms of structural and electronic characteristics; its conducting layer consists of uniform donor stacks without dimerization, and the ratio of the donor to anion is not expressed as integers, reflecting the fact that the AuI$_2$ lattice is incommensurate with the donor lattice. Such nonstoichiometric ratio brings the charge-transfer degree of the donor to be $+0.436$. Although there have been several reports on organic superconductors with uniform donor stacks[3b,12] or with an incommensurate anion lattice,[13] their superconducting behaviors are strongly sample-dependent or require high pressure. Thus, for the development of such unique organic superconductors, it is very important to know whether the structural features of (MDT-TSF)(AuI$_2$)$_{0.436}$ are limited to just this particular salt. From this standpoint, we have tried to synthesize novel MDT-TSF salts with linear trihalide anions such as I_3^- and I_2Br^- and found that the four new radical salts of MDT-TSF isostructural with the AuI$_2$ salt become superconductors.[14] In this article, we describe the synthesis, physical properties, and structural features of these MDT-TSF superconductors.



TMTSF



X = Y = S BEDT-TTF
X = S, Y = O BO
X = Se, Y = S BETS



X = S MDT-TTF
X = Se MDT-TSF

Experimental Section

Synthesis. The synthesis of MDT-TSF was described in previous papers.[10a,d] Tetrabutylammonium salts [(n-Bu$_4$N)X, $X = I_3$,[15] I$_2$Br,[16] IBr$_2$[17]] were prepared according to the reported methods. Tetrabutylammonium iodochloride [(n-Bu$_4$N)I$_{2.9}$Cl$_{0.1}$] was obtained using a procedure similar to that for (n-Bu$_4$N)I$_2$Br as follows.[18] An equimolar mixture of tetrabutylammonium chloride [(n-Bu$_4$N)Cl, 2.77 g, 10 mmol] and iodine (2.54 g, 10 mmol) in a hot ethanol solution (50 mL) was slowly cooled and allowed to stand overnight at room temperature. The purple rods precipitated were collected, washed with cold ethanol, and dried. Mp 66 °C. Anal. Calcd for $C_{16}H_{36}NCl_{0.1}I_{2.9}$: C, 31.30; H, 5.91; N, 2.28; Cl, 0.58; I, 59.93. Found: C, 30.53; H, 6.03; N, 2.29; Cl, 0.54; I, 58.86.

Radical cation salts of MDT-TSF (**1**–**4**) were prepared by electrochemical crystallization in the presence of tetrabutylammonium salt [(n-Bu$_4$N)X, $X = I_3$, I$_2$Br, IBr$_2$, I$_{2.9}$Cl$_{0.1}$,

---

(5) (a) Kobayashi, H.; Udagawa, T.; Tomita, H.; Bun, K.; Naito, T.; Kobayashi, A. *Chem. Lett.* **1993**, 1559–1562. (b) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368–377. (c) Tanaka, H.; Kobayashi, A.; Sato, A.; Akutsu, H.; Kobayashi, H. *J. Am. Chem. Soc.* **1999**, *121*, 760–768. (d) Otsuka, T.; Kobayashi, A.; Miyamoto, Y.; Kiuchi, J.; Wada, N.; Ojima, E.; Fujiwara, H.; Kobayashi, H. *Chem. Lett.* **2000**, 732–733. (e) Kobayashi, H.; Kobayashi, A.; Cassoux, P. *Chem. Soc. Rev.* **2000**, *29*, 325–333. (f) Gritsenko, V.; Tanaka, H.; Kobayashi, H.; Kobayashi, A. *J. Mater. Chem.* **2001**, *11*, 2410–2411. (g) Fujiwara, H.; Fujiwara, E.; Nakazawa, Y.; Narymbetov, B. Z.; Kato, K.; Kobayashi, H.; Kobayashi, A.; Tokumoto, M.; Cassoux, P. *J. Am. Chem. Soc.* **2001**, *123*, 306–314. (h) Uji, S.; Shinagawa, H.; Terashima, T.; Yakabe, T.; Terai, Y.; Tokumoto, M.; Tanaka, H.; Kobayashi, H. *Nature* **2001**, *410*, 908–910. (i) Balicas, L.; Brooks, J. S.; Storr, K.; Uji, S.; Tokumoto, M.; Tanaka, H.; Kobayashi, H.; Kobayashi, A.; Barzykin, V.; Gor'kov, L. P. *Phys. Rev. Lett.* **2001**, *87*, 067002. (j) Fujiwara, H.; Kobayashi, H.; Fujiwara, E.; Kobayashi, A. *J. Am. Chem. Soc.* **2002**, *124*, 6816–6817. (k) Zhang, B.; Tanaka, H.; Fujiwara, H.; Kobayashi, H.; Fujiwara, E.; Kobayashi, A. *J. Am. Chem. Soc.* **2002**, *124*, 9982–9983. (l) Fujiwara, E.; Fujiwara, H.; Kobayashi, H.; Otsuka, T.; Kobayashi, A. *Adv. Mater.* **2002**, *14*, 1376–1379.

(6) (a) Papavassiliou, G. C.; Mousdis, G. A.; Zambounis, J. S.; Terzis, A.; Hountas, A.; Hilti, B.; Mayer, C. W.; Pfeiffer, J. *Synth. Met.* **1988**, *27*, B379–B383. (b) Kini, A. M.; Beno, M. A.; Son, D.; Wang, H. H.; Carlson, K. D.; Porter, L. C.; Welp, U.; Vogt, B. A.; Williams, J. M.; Jung, D.; Evain, M.; Whangbo, M.-H.; Overmyer, D. L.; Schirber, J. E. *Solid State Commun.* **1989**, *69*, 503–507.

(7) Williams, J. M.; Kini, A. M.; Wang, H. H.; Carlson, K. D.; Geiser, U.; Montgomery, L. K.; Pyrka, G. J.; Watkins; D. M.; Kommers, J. M.; Boryschuk, S. J.; Crouch, A. V. S.; Kwok, W. K.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 3272–3274. Very recently, the highest record of T_c in the organic superconductors has been renewed: β'-(BEDT-TTF)$_2$ICl$_2$ shows a superconductivity transition at 14.2 K under high pressure (8.2 GPa). Taniguchi, H.; Miyashita, M.; Uchiyama, K.; Satoh, K.; Môri, N.; Okamoto, H.; Miyagawa, K.; Kanoda, K.; Hedo, M.; Uwatoko, Y. *J. Phys. Soc. Jpn.* **2003**, *72*, 468–471.

(8) Mori, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2509–2526.

(9) (a) McKenzie, R. H. *Science* **1997**, *278*, 820–821. (b) Kanoda, K. *Hyperfine Interact.* **1997**, *104*, 225–249. (c) Kawamoto, A.; Miyagawa, K.; Kanoda, K. *Phys. Rev. B* **1997**, *55*, 14140–14143. (d) Kondo, H.; Moriya, T. *J. Phys. Soc. Jpn.* **2001**, *70*, 2800–2801.

(10) (a) Takimiya, K.; Kataoka, Y.; Aso, Y.; Otsubo, T.; Fukuoka, H.; Yamanaka, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1122–1125. (b) Kawamoto, T.; Mori, T.; Takimiya, K.; Kataoka, Y.; Aso, Y.; Otsubo, T. *Phys. Rev. B* **2002**, *65*, 140508. (c) Kawamoto, T.; Mori, T.; Terakura, C.; Terashima, T.; Uji, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Phys. Rev. B* **2003**, *67*, 020508. (d) Takimiya, K.; Kataoka, Y.; Niihara, N.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **2003**, *68*, 5217–5224.

(11) The all-sulfur analogue of MDT-TSF, namely MDT-TTF, coincidentally gives a superconductor with the AuI$_2$ anion, *k*-(MDT-TTF)$_2$AuI$_2$. This superconductor shows slightly lower T_c (3.5–4.5 K, onset) and much lower conductivity of 36 S cm^{-1} at room temperature than those of MDT-TSF. To our knowledge, this is the only superconducting salt derived from MDT-TTF, and the I$_3$ salt of MDT-TTF with a crystal structure different from that of the AuI$_2$ salt showed no superconducting transition. Terzis, A.; Hountas, A.; Underhill, A. E.; Clark, A.; Kaye, B.; Hilti, B.; Mayer, C.; Pfeiffer, J.; Yiannopoulos, S. Y.; Mousdis, G.; Papavassiliou, G. C. *Synth. Met.* **1988**, *27*, B97–B102.

(12) (a) Kato, R.; Kobayashi, H.; Kobayashi, A.; Nishio, Y.; Kajita, K.; Sakaki, W. *Chem. Lett.* **1986**, 957–960. (b) Misaki, Y.; Higuchi, N.; Fujiwara, H.; Yamabe, T.; Mori, T.; Mori, H.; Tanaka, S. *Angew. Chem., Int. Ed.* **1995**, *34*, 1222–1225. (c) Kondo, R.; Hasegawa, T.; Mochida, T.; Kagoshima, S.; Iwasa, Y. *Chem. Lett.* **1999**, 333–334. (d) Kondo, R.; Hasegawa, T.; Mochida, T.; Kagoshima, S.; Iwasa, Y.; Hiraki, K.; Takahashi, T. *J. Phys. Soc. Jpn.* **2001**, *70*, 3023–3030.

(13) (a) Lyubovskaya, R. N.; Lyubovskii, R. B.; Shibaeva, R. P.; Aldoshina, M. Z.; Gol'denberg, L. M.; Rozenberg, L. P.; Khidekel', M. L.; Shul'pyakov, Y. F. *Pis'ma Zh. Eksp. Teor. Fiz.* **1985**, *42*, 380–383. [*Sov. Phys. JETP Lett.* **1985**, *42*, 468–472]. (b) Lyubovskaya, R. N.; Zhilyaeva, E. I.; Pesotskii, S. I.; Lyubovskii, R. B.; Atovmyan, L. O.; D'yachenko, O. A.; Takhirov, T. G. *Pis'ma Zh. Eksp. Teor. Fiz.* **1987**, *46*, 149–152. [*Sov. Phys. JETP Lett.* **1987**, *46*, 188–191]. (c) Shibaeva, R. P.; Rozenberg, L. P. *Kristallografiya* **1988**, *33*, 1402–1407 [*Sov. Phys. Crystallogr.* **1988**, *33*, 834–837].

(14) A series of new organic superconductors isostructural with (MDT-TSF)(AuI$_2$)$_{0.436}$ have recently been developed based on a related selenium-containing electron donor, methylenedithio-diselenadithiafulvalene (MDT-ST). Takimiya, K.; Takamori, A.; Aso, Y.; Otsubo, T.; Kawamoto, T.; Mori, T. *Chem. Mater.* **2003**, *15*, 1225–1227.

(15) Williams, J. M.; Emge, T. J.; Wang, H. H.; Beno, M. A.; Copps, P. T.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 2558–2560.

(16) Emge, T. J.; Wang, H. H.; Beno, M. A.; Leung, P. C. W.; Firestone, M. A.; Jenkins, H. C.; Cook, J. D.; Carlson, K. D.; Williams, J. M.; Venturini, E. L.; Azevedo, L. J.; Schirber, J. E. *Inorg. Chem.* **1985**, *24*, 1738–1740.

(17) Williams, J. M.; Wang, H. H.; Beno, M. A.; Emge, T. J.; Sowa, L. M.; Copps, P. T.; Behroozi, F.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 3839–3841.

(18) Although, to our knowledge, tetrabutylammonium diiodochloride [(n-Bu$_4$N)I$_2$Cl] is unknown, the syntheses of related tetramethylammonium- and tetraethylammonium-diiodochloride have been described. (a) Probert, A. I.; Swensen, R. F. *J. Am. Chem. Soc.* **1955**, *77*, 3724–3726. (b) Chattaway, F. D.; Hoyle, G. *J. Chem. Soc.* **1923**, *127*, 654–662.

Table 1. Conductive Properties and Chemical Composition of Salts 1−4

salt	$(n\text{-Bu}_4\text{N})X$ [a]	σ_{rt}/S cm^{-1} [b]	T_c [c]/K	chemical composition[d]	degree of CT [e]
1	I_3	1.5×10^3	4.6 (4.4)	$(\text{MDT-TSF})I_{1.27}$	0.42
2	I_2Br	1.5×10^3	5.0 (4.8)	$(\text{MDT-TSF})I_{1.19}Br_{0.08}$	0.42
3	IBr_2	1.3×10^3	4.0 (4.4)	$(\text{MDT-TSF})I_{0.77}Br_{0.52}$	0.43
4	$I_{2.9}Cl_{0.1}$	1.5×10^3	5.5 (5.0)	$(\text{MDT-TSF})I_{1.27-\delta}Cl_\delta$ ($\delta \approx 0$)	0.42

[a] Supporting electrolyte used in the electrocrystallization. [b] Measured on a single crystal with a four-probe method. [c] The midpoint of resistivity drop is defined as T_c in the resistivity measurement, and the onset of diamagnetic transition in magnetic susceptibility measurement with SQUID is in parentheses. [d] The chemical composition was determined on the basis of the X-ray oscillation photograph and the elemental analysis as described in the text. [e] The degree of charge-transfer (CT) was estimated based on the assumption that the trihalide anion is the charged species.

Table 2. Crystal Data for 1−4

	1	**2**	**3**	**4**
formula	$C_7H_4S_2Se_4I_{1.27}$	$C_7H_4S_2Se_4I_{1.19}Br_{0.08}$	$C_7H_4S_2Se_4I_{0.52}Br_{0.77}$	$C_7H_4S_2Se_4I_{1.27}$
formula weight	629.24	625.48	607.34	629.24
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
color of crystal	golden-olive	golden-olive	bronze	golden-olive
a/Å	4.013(4)	4.010(2)	4.026(8)	4.012(6)
b/Å	12.539(2)	12.543(2)	12.515(2)	12.546(3)
c/Å	25.620(2)	25.584(2)	25.315(3)	25.635(5)
V/Å^3	1289(1)	1286.7(5)	1275(1)	1290(2)
temperature/K	296	296	296	296
Z	4	4	4	4
R; Rw	0.053; 0.051	0.027; 0.024	0.031; 0.045	0.048; 0.061
GOF	1.37	1.66	1.17	1.28

respectively]. MDT-TSF (3−7 mg) was placed in the anode compartment of a 20-mL H-shaped glass cell with a fine frit dividing the anode and cathode compartments, and 10−20 mg of the appropriate $(n\text{-Bu}_4\text{N})X$ was placed in the cathode compartment. Chlorobenzene containing 10% of ethanol (ca. 18 mL) was added, and the resulting solution was degassed by a dry nitrogen stream. Electrodes made of 1-mm platinum wires were set in the cell, and a constant current of 0.1−0.5 μA was applied. Within two weeks, bronze or golden-olive thin needles of the radical cation salts of MDT-TSF grew on the anode and the glass frit. The crystals were collected by filtration, washed with dichloromethane, and dried.

Physical Properties. The electrical resistivities of the crystals were measured along the needle direction (parallel to the crystallographic a-axis) by the conventional four-probe method in the range from room temperature to 1.5 K for **3** or 4.2 K for other salts, using gold wires with a diameter of 15 or 20 μm attached to the crystals with a gold conducting paste. The magnetic susceptibility measurements were performed on a SQUID magnetometer (Quantum Design MPMS-5) using 0.3−2.5 mg of randomly oriented crystals. The physical properties of salts **1**−**4** are summarized in Table 1.

Determination of Compositions. The X-ray oscillation photographs were taken on a Rigaku Raxis CS area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at room temperature. Elemental analyses of **1**−**4** were carried out for C, H, N, S, Cl, Br, and I atoms in the microanalytical laboratory at the Tokyo Institute of Technology. Energy dispersion spectroscopy (EDS) was recorded on an EDAX PV-9900 with an accelerated voltage of 16 kV at The Center for Advanced Materials Analysis in Tokyo Institute of Technology. The relative ratio of selenium and iodine was estimated using *K*α line of selenium (11.22 keV) and *L*α line of iodine (3.94 keV). The chemical composition was determined on the basis of the elemental analysis together with information from the X-ray photograph, and was in good agreement with the ratio of the donor to iodine atom estimated from EDS. Elemental analysis. (**1**) Calcd for $C_7H_4S_2Se_4I_{1.27}$: C, 13.36; H, 0.64; S, 10.19; I, 25.61. Found: C, 13.37; H, 0.63; S, 10.47; I, 25.43. (**2**) Calcd for $C_7H_4S_2Se_4I_{1.19}Br_{0.08}$: C, 13.44; H, 0.64; S, 10.25; Br, 1.02; I, 24.14. Found: C, 13.43; H, 0.70; S, 10.17; Br, 0.91; I, 24.04. (**3**) Calcd for $C_7H_4S_2Se_4I_{0.77}Br_{0.52}$: C, 13.84; H, 0.66; S, 10.56; Br, 6.84; I, 15.89. Found: C, 14.04; H, 0.70; S, 10.76; Br, 6.72; I, 15.81. (**4**) Calcd for $C_7H_4S_2Se_4I_{1.27}$: C, 13.36; H, 0.64; S, 10.19; I, 25.61. Found: C, 13.43; H, 0.70; S, 10.19; I, 25.55.

X-ray Structural Analysis. The X-ray crystal structure analyses were made on a Rigaku AFC7R four-circle diffractmeter (Mo Kα radiation, $\lambda = 0.7107$ Å, graphite monochromator, $T = 296$ K, ω scan, $2\theta_{\max} = 55.0°$). The structures were solved with the direct method (SHELX 86)[19] and refined by full-matrix least-squares on $|F|$. The structural solutions were obtained by applying a model in which the anion was monoatomic iodine, and the occupancy of the anion site was refined. For salts **2** and **3** containing both the iodine and bromine atoms, approximation that the contribution of each atom to the occupancy of the anion site is proportional to the atomic number (I 53 and Br 35) affords a reasonable weight of the site that qualitatively agrees with the composition determined based on the X-ray photograph and the elemental analysis. All calculations were performed on the crystallographic software package teXsan.[20] The crystal data are listed in Table 2.

Results and Discussion

Synthesis of Radical Cation Salts. Electrocrystallization of MDT-TSF in the presence of $(n\text{-Bu}_4\text{N})I_3$, $(n\text{-Bu}_4\text{N})I_2Br$, and $(n\text{-Bu}_4\text{N})IBr_2$ as electrolyte afforded the respective salts **1**−**3** as bronze or golden-olive needles with metallic luster possessing sufficient quality for conductivity measurements and X-ray crystallographic analyses. In contrast, $(n\text{-Bu}_4\text{N})ICl_2$ and $(n\text{-Bu}_4\text{N})Br_3$ having higher oxidation abilities, reacted immediately with the donor in the solution, and no single crystal formed. To examine another tetrabutylammonium trihalide salt with lower oxidation ability, we focused on "$(n\text{-Bu}_4\text{N})I_2Cl$" and attempted its synthesis in a manner similar to the preparation of $(n\text{-Bu}_4\text{N})I_2Br$. A reaction of $(n\text{-Bu}_4\text{N})Cl$ with an equimolar iodine in a hot ethanol solution gave black crystals upon cooling. Elemental analysis of the crystals, however, did not support the expected composition of $(n\text{-Bu}_4\text{N})I_2Cl$, but a largely modified composition of $(n\text{-Bu}_4\text{N})I_{2.9}Cl_{0.1}$.[18] Electro-

---

(19) Sheldrick, G. M. SHELXS86. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford; pp 175−189.

(20) *teXsan: Single-Crystal Structure Analysis Software, Version 1.11*; Molecular Structure Corporation, Rigaku Corporation, 2000.

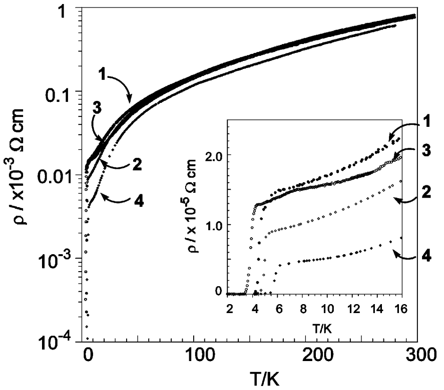


Figure 1. Temperature dependence of resistivities for **1**−**4**.

crystallization of MDT-TSF in the presence of this tetrabutylammonium salt afforded the radical cation salts **4** as golden-olive needles.

Physical Properties. As summarized in Table 1, all the salts were highly conductive at room temperature ($\sigma_{rt} > 10^3$ S cm^{-1}) and metallic down to low temperature (Figure 1). Similarly to the conducting behavior of (MDT-TSF)$(AuI_2)_{0.436}$,[10] an abrupt drop of resistivity around 4.0−5.5 K characteristic of a superconducting transition was observed for all the salts as shown in Figure 1 (inset).

To confirm the resistivity drop as a superconducting transition, the magnetic susceptibility of the salts was measured with a SQUID magnetometer. Figure 2 shows the temperature dependence of zero-field-cooled (ZFC) as well as field-cooled (FC) dc magnetization of randomly oriented polycrystalline samples recorded under an applied magnetic field of 5 Oe. All the salts show large diamagnetic shielding, clearly showing that they are superconductors. Judging from the diamagnetic shielding at 2.0 K, the superconducting volume fractions are ca. 90% for **1**, 40% for **3**, and roughly 100% for **2** and **4** of the estimated values for the perfect superconductivity, indicating that all the salts are bulk superconductors. The T_c determined with SQUID is slightly lower than those found in the resistivity measurements except for **3**, and the orders of T_c are the same in both measurements (Table 1).

Crystal Structures. X-ray crystallographic analyses have revealed that all the salts belong to the orthorhombic *Pnma* space group and are isostructural with (MDT-TSF)$(AuI_2)_{0.436}$ as summarized in Table 2.[10a] Figure 3 shows the crystal structure of salt **1** as a representative. Half of the donor molecule is crystallographically independent, and a mirror symmetry operation along the molecular long axis gives the complete donor molecule. The donor molecules are almost flat and overlap in the so-called ring-over-bond[8] and head-to-head manner as shown in Figure 3(a). With this overlapping manner, the donor molecules form a uniform stacking column along the *a*-axis. The donor stacks are arranged in 2-fold periodicity along the transverse direction (*b*-axis) with short Se−Se and Se−S contacts to form a corrugated sheetlike donor layer as shown in Figure 3(b). Between the donor layers, there are anion channels surrounded by six donor stacks, and the anions exist as infinite polyiodide chains running parallel to the donor stacks (*a*-axis direction).

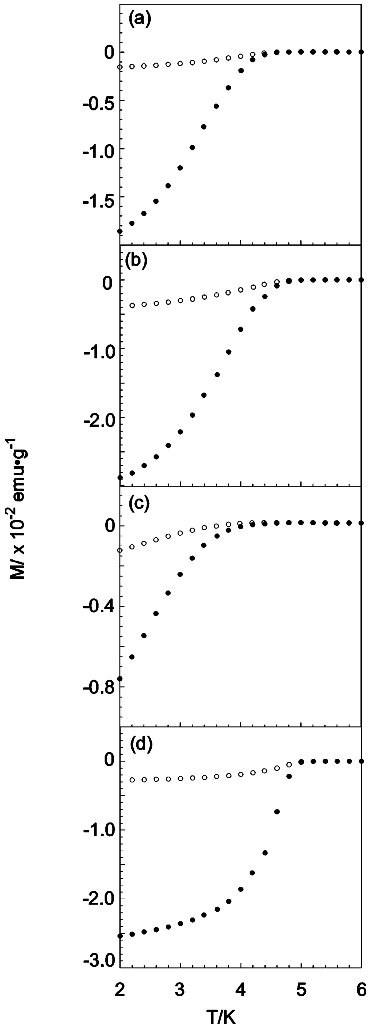


Figure 2. Temperature dependence of ZFC (closed circle) and FC (open circle) dc magnetizations for **1**−**4** [(a)−(d), respectively] at an applied field of 5 Oe.

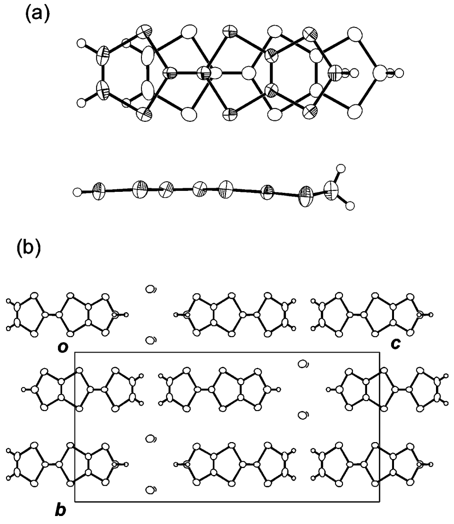


Figure 3. Crystal structure of **1**: molecular structure and overlap manner (a) and *a*-axis projection (b).

In the present structural analysis, the anisotropic displacement parameter of the iodine atom for the *a*-axis direction (U_{11}) is very large, and furthermore, the length of the *a*-axis (ca. 4 Å) is markedly shorter than the expected length of the I_3^- lattice (>9 Å). These facts

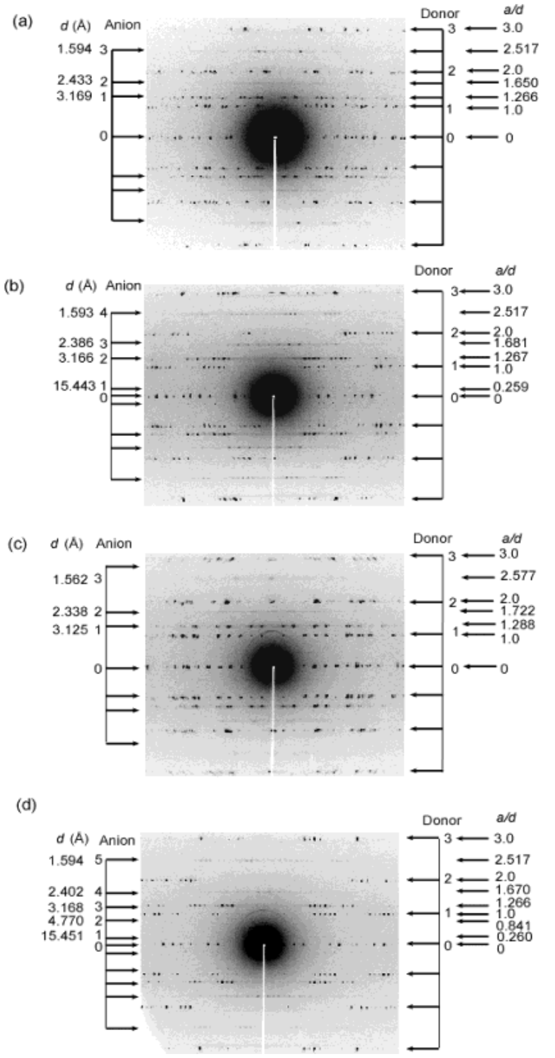


Figure 4. X-ray oscillation photographs of **1**−**4** [(a)−(d), respectively].

indicate that the position of the iodine atom cannot be precisely determined by the present analysis, suggesting that the anion lattice is incommensurate with the donor subcell. This is also supported by the optimized occupancy of the iodine atom being ca. 20% smaller than the value expected from the usual 2:1 composition, (MDT-TSF)$_2$I$_3$. The situation is the same for other salts (**2**−**4**) prepared from the mixed trihalide anions. Thus, it is not possible to determine the ratio of the donor to the anion and the ratio of halogen atoms in the anion, i.e., I/Br ratio or I/Cl ratio, in salts **2**−**4** by the present X-ray analyses.

Composition and Degree of Charge-Transfer. To decide the chemical composition of the salts, their X-ray oscillation photographs were investigated together with elemental analysis and EDS. Figure 4(a) shows an X-ray photograph of **1**, in which the ordinate is parallel to the donor stacking axis (*a*-axis). In the photograph, together with the strong Bragg spots originating from the donor lattice (designated by "Donor 1, 2, 3"), there are clear lines at $a/d = 1.266$ and 2.517 in the reciprocal space. The first layer line located at $a/d = 1.266$ corresponds to the length of 3.169 Å in the real space, which is shorter than the reported length for I$^-$ lattice (ca. 4.3 Å), I$_3^-$ lattice (9.2−9.7 Å), and I$_5^-$ lattice (ca. 15.5 Å).[21] On the other hand, the mean distance of the I−I bond in the polyiodide linear chain is reported to be 2.8−3.2 Å,[21] and thus, it is reasonable to assign the lines at $a/d = 1.266$ and 2.517 to the infinite polyiodide lattice. The ratio of the donor to iodine is accordingly determined to be 1:1.266, which is in excellent agreement with (MDT-TSF)I$_{1.27}$ calculated from the combustion elemental analysis of **1** (see Experimental Section).

Because it has been reported that charged iodine species in the solid can exist as I$^-$, I$_3^-$, or I$_5^-$,[21] the actual charged unit in the polyiodide chains is any one of these anionic species. Taking the isostructural organic superconductor (MDT-TSF)(AuI$_2$)$_{0.436}$ into consideration, it is rational to speculate that the charged iodine unit is I$_3^-$, leading to (MDT-TSF)(I$_3$)$_{0.42}$ possessing a similar charge-transfer degree as that in the AuI$_2$ salt. The Raman spectrum of **1** also supports the existence of the I$_3^-$ anion by the observation of a specific line around 100 cm^{-1}, attributable to a symmetric stretching of the I$_3^-$ anion.

The X-ray photograph of **2** [Figure 4(b)] contains clear layer lines at $a/d = 1.267$ and 2.517 together with weak lines at $a/d = 0.259$ and 0.1681. Because no line corresponding to the I$_2$Br$^-$ lattice is detected, the existence of an infinite polyhalide chain with the mean distance between halogen atoms of 3.166 Å can be postulated. Thus, the ratio of the donor to the halogen atom (iodine or bromine) in **2** is 1:1.267. The result of EDS suggests that the ratio of donor to iodine atom is 1:1.19, which leads to the chemical composition of (MDT-TSF)I$_{1.19}$Br$_{0.08}$. The elemental analysis is in excellent agreement with this estimation. In the same manner, the composition of **3** is determined to be (MDT-TSF)I$_{0.77}$Br$_{0.52}$.

Similarly, the ratio of the donor to halogen atom in salt **4** is determined to be 1:1.266 based on the first line in the X-ray photograph assignable to the polymeric halogen lattice [Figure 4(d)]. However, the EDS and elemental analysis failed to detect a chlorine atom, and thus the composition of **4** may be expressed as (MDT-TSF)I$_{1.27-\delta}$Cl$_\delta$ ($\delta \approx 0$). The elemental analysis of **4** agrees with this composition, which is seemingly identical to that of **1** prepared in the presence of the ordinary (*n*-Bu$_4$N)I$_3$.

Regardless of the salts, the ratio of the donor to halogen atom is nearly 1:1.27. As discussed for salt **1**, it is reasonable to assume that the trihalide anion is the charged species in the polyhalide chain, which corresponds to the degree of charge-transfer, 0.42−0.43. As shown in Table 1, the contents of iodine in **2**−**4** are greater than that in the supporting electrolytes. Although the reason for the spontaneous anion reconstruction during electrocrystallization is not clear, it is likely that the system prefers to include the infinite polyiodide chains as a basic structure.

Electronic Band Structure Calculation. Using the crystal structures and the degree of charge-transfer determined as above, the band structures and Fermi surfaces were calculated with the extended Hückel

---

(21) (a) Cowie, M.; Gleizes, A.; Grynkewich, G. W.; Kalina, D. W.; McClure, M. S.; Scaringe, R. P.; Teitelbaum, R. C.; Ruby, S. L.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2921−2936. (b) Marks, T. J.; Kalina, D. W. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. I, Chapter 6.

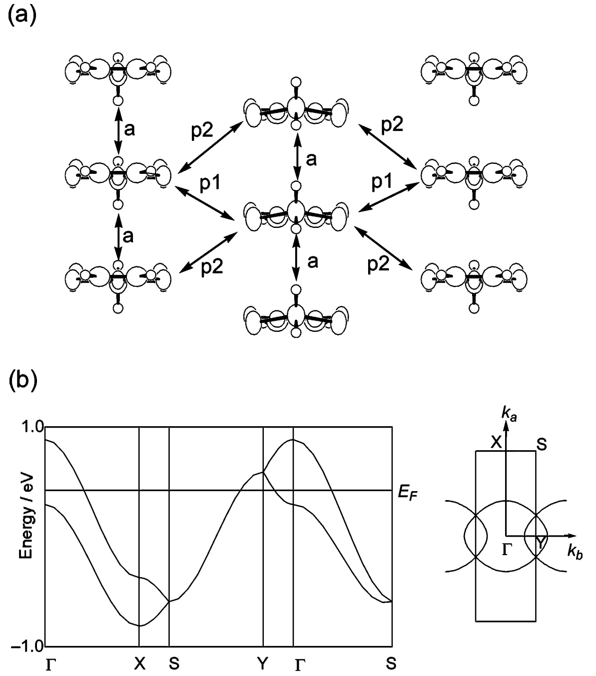


Figure 5. Calculated overlap integrals (a) and band structure and Fermi surface of **1** (b).

Table 3. Calculated Overlap Integrals of 1−4 ($\times$ 10^{-3})

	1	2	3	4
a	−29.5	−26.6	−23.8	−25.6
p1	1.88	2.76	3.38	3.12
p2	12.9	12.2	12.0	12.2

method and a tight-binding approximation[22] using the Hückel parameters recently developed for the selenium-containing BETS salts.[23,24] The calculated overlap integrals are summarized in Table 3. The band structure and Fermi surface of **1** depicted in Figure 5 are quite similar to those of the AuI_2 salt.[10b] The calculated overlap integrals and the band structures for **2−4** are essentially the same as those of **1**, indicating the invariable electronic structures of the present salts.

Anion Dependence of T_c. The influence of anions on the crystal structures and the superconducting property in a series of β-(BEDT-TTF)$_2X$ ($X = I_3$,[13] IBr_2,[15] AuI_2[26]) is well-documented;[2a] a longer anion brings a larger unit cell (cell volume of the I_3 salt = 855.9 Å^3, the AuI_2 salt = 845.2 Å^3, and the IBr_2 salt = 828.7 Å^3), which is correlated with the T_c (the I_3 salt = ca. 8 K, the AuI_2 salt = 4.98 K, and the IBr_2 salt = 2.8 K). On the other hand, the unit cell volumes of the present salts **1**, **2**, and **4** are almost equal to one another, and that of **3**, which has the lowest T_c is smaller by only ca. 1% than that of the other salts (Table 2). This can be attributed to the fact that the present unit cells of the salts are exclusively determined on the basis of the donor subcells.

Instead of the unit cell size, we speculate that the internal structure of the polymeric halogen chain reflected by the X-ray oscillation photographs may play an important role in determining T_c. In the X-ray photographs (Figure 4), together with the lines originating from the donor lattice (a/d = 1, 2, 3) and polyhalide infinite chains (a/d = 1.26−1.29, 2.51−2.57), extra lines around a/d = 0.26, 0.85, and 1.7 exist. The latter lines are much pronounced in salts **2** and **4**, which have higher T_c. Particularly, the noticeable difference in T_c between **1** (4.6 K) and **4** (5.5 K), which are almost identical in terms of their crystal structures and chemical composition, can be related to the absence (salt **1**) or presence (salt **4**) of the extra lines in the X-ray photographs [Figure 4(a) and (d) for **1** and **4**, respectively]. Because the origin of these extra lines is not clear at this moment, further investigations to clarify this point in relation with the actual factor for determining T_c are in progress.

Conclusion

Electrocrystallization of MDT-TSF in the presence of tetrabutylammonium trihalide gave a series of new superconducting salts. The conductivities of these salts at room temperature are very high (>10^3 S cm^{-1}), and their T_c range from 4.0 to 5.5 K under ambient pressure. X-ray studies elucidated the existence of uniform donor stacks and an incommensurate anion lattice consisting of linear polyhalide chains. Furthermore, the MDT-TSF molecules in the present salts have a nonstoichiometric charge-transfer degree. All these structural and electronic characteristics of the MDT-TSF superconductors are quite different from those of conventional organic superconductors such as β- and κ-(BEDT-TTF)$_2X$ salts (X = monovalent anion). Thus, it can be concluded that the present MDT-TSF salts constitute a novel class of organic superconductors. In addition, taking into consideration the present data showing varying T_c with subtle change of the anion structure, it might be possible to change, hopefully increase, T_c by introducing different polyhalogen anions, e.g. I_5^-, I_7^- etc. A study to this end is now under way.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (13740399) from the Ministry of Education, Culture, Sports, Science and Technology of Japan and Industrial Technology Research Grant Program in 2002 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan. We thank Izumi Science and Technology Foundation for financial support and the Cryogenic Center at Hiroshima University for a supply of liquid helium.

Supporting Information Available: Crystallographic information files (CIFs) for **1−4**. This material is available free of charge via the Internet at http://pubs.acs.org.

CM034222I

---

(22) Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 627−633.

(23) Mori, T.; Katsuhara, M. *J. Phys. Soc. Jpn.* **2002**, *71*, 826−844.

(24) Although in the first paper on the AuI_2 salt of MDT-TSF (ref 10a) a quasi one-dimensional band structure was proposed by the calculations with the Hückel parameters reported by Tanaka et al. in ref 25, recent observation of the Shubnikov−de Haas (SdH) oscillation strongly suggests that the salt has a closed two-dimensional Fermi surface rather than the one-dimensional open Fermi surface (see ref 10c). Recalculation of the band structure with the Hückel parameters in ref 23 predicts that the Fermi surface consists of overlapping cylinders, which is in good agreement with the result from SdH oscillation. See also ref 10b and 10c.

(25) Tanaka, H.; Kobayashi, A.; Sato, A.; Akutsu, H.; Kobayashi, H. *J. Am. Chem. Soc.* **1999**, *121*, 760−768.

(26) Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Nunes, L.; Crabtree, G. W.; Carlson, K. D.; Williams, J. M.; Azevedo, L. J.; Kwak, J. F.; Schirber, J. E. *Inorg. Chem.* **1985**, *24*, 2466−2468.