Pressure-Induced Superconductivity in $(MDT\text{-}TS)(AuI_2)_{0.441}$ [MDT- TS = 5*H*-2-(1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalene]: A New Organic Superconductor Possessing an Incommensurate Anion Lattice

Kazuo Takimiya,*,† Mie Kodani,† Naoto Niihara,† Yoshio Aso,‡ Tetsuo Otsubo,† Yoshimasa Bando,§ Tadashi Kawamoto,§ and Takehiko Mori§

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-8527, Japan, The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-8479, 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

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A selenium-containing TTF-type electron donor, MDT-TS [5*H*-2-(1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalene] was effectively synthesized by a two-step reaction and utilized for electrocrystallization with an AuI_2^- anion. The resulting salt, $(MDT\text{-}TS)(AuI_2)_{0.441}$, has a unique crystal packing, in which the donor subcell and the anion lattice are incommensurate. Although the salt has relatively high conductivity at room temperature (600 S cm^{-1}), it showed a metal−insulator (MI) transition at $T_{MI} = 50$ K. Application of hydrostatic pressure suppressed the MI transition, and at 11.4 kbar $(MDT\text{-}TS)(AuI_2)_{0.441}$ showed a superconducting transition at $T_c = 4.7$ K.

Introduction

Most organic superconductors are radical cation salts of electron donors with inorganic anions expressed as D_2X (D, electron donors; X, monovalent inorganic anions), a representative of this class being κ-(BEDT-TTF)$_2X$ [BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene].[1] Their conducting bands arise from the highest occupied molecular orbitals (HOMOs) of the donor molecules being effectively “half-filled”, owing to the strong dimerization of the donor molecules. Such an electronic structure is recognized as one prerequisite for superconductivity.[2] On the other hand, a recently developed organic superconductor, $(MDT\text{-}TSF)(AuI_2)_{0.436}$ (MDT-TSF = methylenedithiotetraselenafulvalene) with $T_c = 4.5$ K at ambient pressure, is not classified as a conventional organic superconductor;[3] this salt has uniform columnar stacks of the donor molecules and the AuI_2^- anions form their own lattice incommensurate with that of the donor, resulting in a nonintegral donor/anion ratio, 1:0.436.[4] Furthermore, detailed physical studies revealed that the material is an anisotropic three-dimensional superconductor[4] and the incommensurate anion lattice strongly affects the Fermi surface.[5] Such unique “AuI_2-type” structure was also observed for the trihalide salts of MDT-TSF, all of which become superconductors at relatively high T_c ranging from 4.0 to 5.5 K at ambient pressure.[6] The related donor, MDT-ST [5*H*-2-(1,3-dithiol-2-ylidene)-1,3-diselena-4,6-dithiapentalene] gave similar superconducting trihalide salts,[7] whereas MDT-TTF (methylenedithiotetrathiafulvalene)[8] and MDSe-TSF (methylenediselenotetraselenafulvalene)[9] gave superconducting radical cation salts with an AuI_2^- and a Br^- anion, respectively, both of which, however, have a conventional κ-type of crystal structure with a donor/anion ratio of 2:1.

To further explore the potential of the methylenedichalcogenotetrachalcogenafulvalene family as electron donors capable of producing such intriguing supercon-

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* To whom correspondence should be addressed. Tel: +81-824-24-7734. Fax: +81-824-24-5494. E-mail: ktakimi@hiroshima-u.ac.jp.
† Hiroshima University.
‡ Osaka University.
§ Tokyo Institute of Technology.

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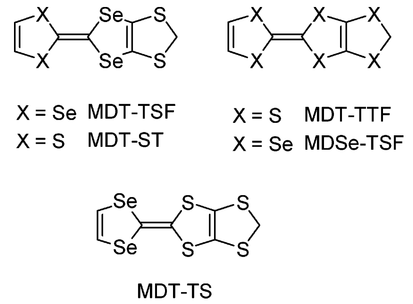


Figure 1. Methylenedichalcogenotetrachalcogenafulvalene donors.

ducting salts, we focused our attention on MDT-TS [5*H*-2-(1,3-diselenol-2-ylidene)-1,3,4,6-tetrathiapentalene], a structural isomer of MDT-ST (Figure 1). In this article, we report the synthesis, structural characteristics, metal−insulator transition, and pressure-induced superconductivity of the AuI_2 salt of MDT-TS.

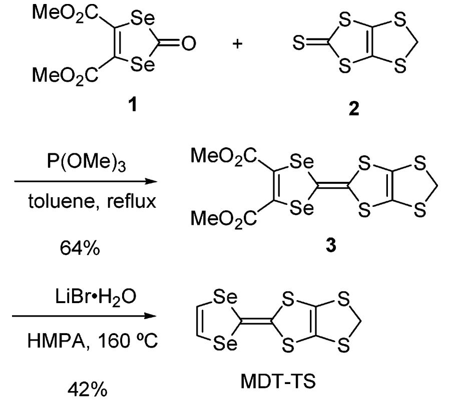
Experimental Section

Synthesis. All chemicals and solvents were of reagent grade and used without further purification. All reactions were carried out in a nitrogen atmosphere. Melting points are uncorrected. Microanalyses were carried out by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University. NMR spectra were obtained in deuterated chloroform with a JEOL Lambda 400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C using tetramethylsilane as internal reference; chemical shifts (δ) are reported in parts per million. IR spectra were taken on a Shimadzu FTIR 8100 spectrophotometer with a KBr disk method. MS spectra were measured at 70 eV on a Shimadzu GCMS-QP 2000 spectrometer using a direct injection technique. The molecular ion peaks of the selenium-containing compounds showed a typical isotopic pattern, and all the mass peaks are reported for ^{80}Se. Cyclic voltammogram (CV) was measured in benzonitrile containing 0.1 M tetrabutylammonium perchlorate at room temperature using a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

Bis(methoxycarbony)methylenedithiodiselenadithiafulvalene (3). To a mixture of 4,5-bis(methoxycarbonyl)-1,3-diselenol-2-one[10] (**1**, 0.43, 1.3 mmol) and 4,5-methylenedithio-1,3-dithiole-2-thione[11] (**2**, 0.55 g, 2.6 mmol) in refluxing toluene (15 mL) was added trimethyl phosphite (10 mL), and the resulting mixture was refluxed for 3 h. After the mixture cooled, the solvent and the excess trimethyl phosphite were evaporated off, and the resulting oily residue was purified by column chromatography on silica gel eluted with dichloromethane to give **3** (R_f 0.5, 0.41 g, 64%). Recrystallization of crude **3** from dichloromethane gave analytically pure **3** as purple crystals. Mp 116−118 °C. ^{1}H NMR δ 3.77 (s, 6H, CH_3), 4.94 (s, 2H,CH_2). ^{13}C NMR δ 45.03, 53.00, 101.49, 117.86, 124.29, 135.22, 161.46. IR 1720, 1699 cm^{-1} (C=O). MS (EI) *m/z* 492 (M^+). Anal. Calcd for $C_{11}H_8O_4S_4Se_2$: C, 26.94; H, 1.64%. Found: C, 26.96; H, 1.68%.

Methylenedithiodiselenadithiafulvalene (MDT-TS). A mixture of **3** (200 mg, 0.41 mmol) and lithium bromide monohydrate (200 mg, 2.0 mmol) in hexamethylenephosphoric triamide (HMPA, 20 mL) was degassed carefully and heated 15 min in an oil bath (160 °C). The reaction mixture was poured onto crushed ice (ca. 50 g), and the aqueous mixture was saturated with ammonium chloride to effect precipitation of the crude product, which was collected by filtration. The precipitate was first purified with column chromatography on silica gel eluted with carbon disulfide (R_f 0.6) and then recrystallized from carbon disulfide/hexane (1:1 v/v) to give red rods (63 mg, 42%). Mp 187−189 °C (melt with decomposition). ^{1}H NMR δ 4.91 (s, 2H, CH_2), 7.19 (s, 2H, CH). MS (EI) *m/z* 376 (M^+). Anal. Calcd for $C_7H_4S_4Se_2$: C, 22.46; H, 1.08%. Found: C, 22.56; H, 1.06%. CV $E^{ox}_{1/2}(1) = +0.48$ V, $E^{ox}_{1/2}(2) = +0.76$ V.

Scheme 1. Synthesis of MDT-TS



Preparation of (MDT-TS)$(AuI_2)_{0.441}$. Crystals of (MDT-TS)$(AuI_2)_{0.441}$ were prepared by an electrochemical crystallization method using a two-compartment H-shaped glass cell equipped with platinum wire as the electrodes. MDT-TS (3 mg) and tetrabutylammonium diiodoaurate[12] [(n-Bu_4N)AuI_2, 20 mg] were placed in the anode and the cathode compartment, respectively. Chlorobenzene containing ca. 10% of ethanol (ca. 18 mL) was added, and the resulting solution was degassed with a dry nitrogen stream. A constant current of 0.1−0.2 μA was applied at 25 °C. Within two weeks, black needles of the salts grew on the anode. The crystals were collected by filtration, washed with dichloromethane, and dried.

X-ray Experiments. The X-ray crystal structure analysis was made on a Rigaku AFC7R four-circle diffractometer (Mo Kα radiation, $\lambda = 0.71069$ Å, graphite monochromator, $T = 296$ K, ω scan, $2\theta_{max} = 55.0°$). The structure was solved with direct method (SHELX 86)[13] and refined by full-matrix least-squares on $|F|$. The structural solutions were obtained based on a model in which the anion is monatomic gold, and the occupancy of the gold site was included in the refinement. All calculations were performed using the crystallographic software package teXsan.[14] Crystal data for (MDT-TS)$(AuI_2)_{0.441}$: $C_7H_4S_4Se_2Au_{0.441}I_{0.882}$, $M = 573.06$, orthorhombic, $a = 3.993(5)$ Å, $b = 12.448(4)$ Å, $c = 25.119(5)$ Å, $V = 1248(1)$ Å^3, space group *Pnma* (no. 62), $Z = 4$, $D_{calc} = 3.049$ gcm^{-3}, $R = 0.031$, $R_w = 0.038$ for 854 observed reflections ($I > 3\sigma(I)$) from 1499 unique data points. The X-ray oscillation photographs were taken on a Rigaku Raxis II area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at room temperature.

Electrical Resistivity Measurement. The electrical resistivities were measured along the thin needle direction of crystals (parallel to the crystallographic *a*-axis) by the conventional four-probe method using gold wires (15 or 20 μm diameter) attached to the crystal with gold conducting paste. Temperature dependence of the electrical resistivity was measured in the temperature range of room temperature to 1.5 K. The high-pressure resistivity measurements were carried out by the conventional clamped cell technique. Because the pressure is released by ca. 1.5 kbar between room temperature and 4 K, this value has been subtracted from the room-temperature value.

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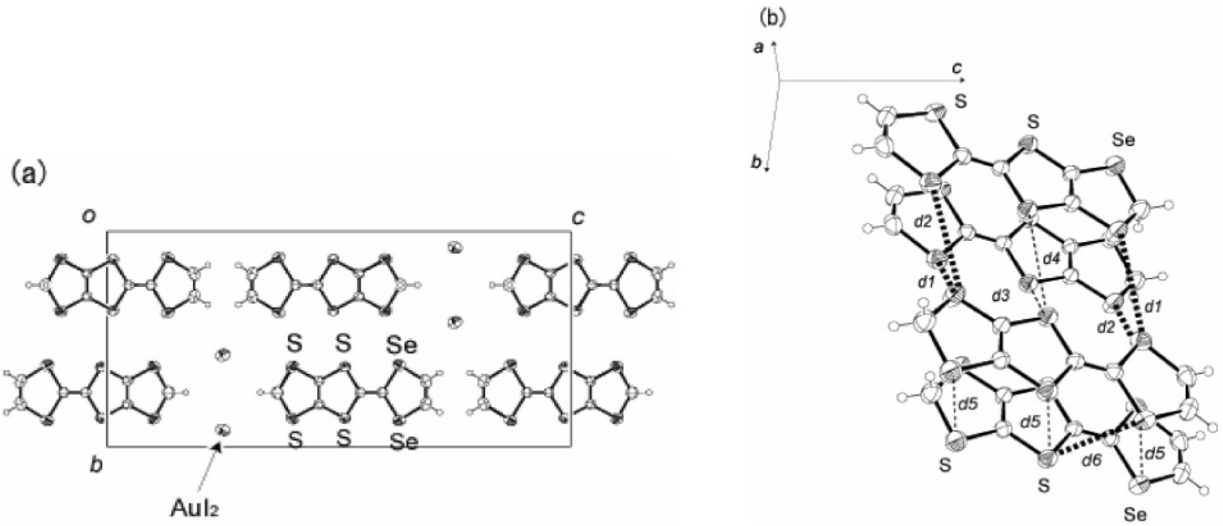

Figure 2. (a) Projection of the crystal packing perpendicular to the *bc* plane of (MDT-TS)$(AuI_2)_{0.441}$. (b) Intermolecular S−S, Se−Se (dotted line), and Se−S (bold dotted line) contacts in the donor conducting layer: *d1* = 3.782(3) Å, *d2* = 3.790(3) Å, *d3* = 4.042(4) Å, *d4* = 3.703(4) Å, *d5* = 3.993(5) Å, *d6* = 3.874(3) Å.

Results and Discussion

Synthesis. The synthesis of MDT-TS was carried out as shown in Scheme 1.[15] A phosphite-promoted cross-coupling reaction between 4,5-bis(methoxycarbony)-1,3-diselenol-2-one[10] (**1**) and 4,5-methylenedithio-1,3-dithiole-2-thione[11] (**2**) gave the diselenadithiafulvalene derivative **3** in 64% isolated yield. A deesterification reaction of **3** with lithium bromide hydrate gave MDT-TS in 42% isolated yield as orange rodlike crystals. Electrocrystallizaion of MDT-TS in chlorobenzene containing *n*-Bu_4NAuI_2[12] gave the corresponding AuI_2 salt as black needles.

Determination of Structure and Composition. Single-crystal X-ray diffraction revealed that the AuI_2 salt of MDT-TS is isostructural with the superconducting (MDT-TSF)$(AuI_2)_{0.436}$.[3] Figure 2(a) shows its crystal packing projected along the crystallographic *a*-axis, in which uniform donor stacks along the *a*-axis direction and anion lattice incommensurate with the donor lattice exist. The donor stacks reside with 2-fold periodicity in the *b*-axis direction to form the conducting donor layers. Compared with the MDT-TSF salts, intermolecular interactions in the conducting layer of the MDT-TS salt, in particular, the side-by-side direction, are fairly reduced; although relatively short intermolecular Se−S contacts (*d1* and *d2*) are observed, there exists almost no contact through the sulfur atoms in the central 1,3-dithiole ring (*d3* and *d4*), at which the charge density of the atomic π orbitals is the highest in the HOMO (Figure 2b). This is in sharp contrast to the MDT-TSF salt, in which strong side-by-side interactions through Se atoms (Se−Se distance: 3.570 and 3.865 Å) in the central 1,3-diselenole rings exist.[3] The reduced intermolecular interaction may result in the different solid-state properties of the present salt from those of the MDT-TSF salt (vide infra).

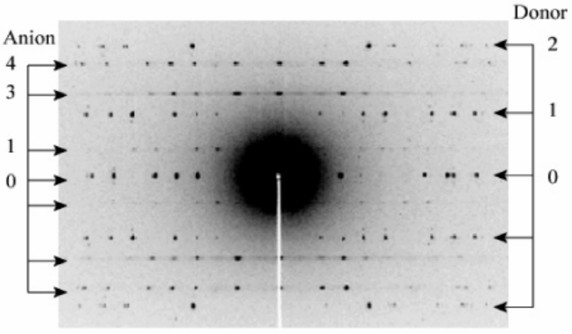

Figure 3. X-ray oscillation photograph of (MDT-TS)$(AuI_2)_{0.441}$, in which the vertical direction is the *a*-axis.

As in the case of related radical cation salts with the "AuI_2-type" structure, owing to different periodicity of the donor stacks and the anion lattice, the donor/anion ratio of the MDT-TS salt was determined on the basis of the X-ray oscillation photograph along the crystallographic *a*-axis (Figure 3).[4] Together with the donor layer lines, distinct incommensurate layer lines originating from the anion lattice are observed. Using these lines, the *a*-axis of the donor lattice is determined to be a = 3.992(3) Å, whereas the anion lattice a' = 9.045(6) Å, which corresponds well to the length of the discrete AuI_2^- anion. From the ratio of the lattice constants, a/a' = 0.4413(3), the composition of the salt is determined to be (MDT-TS)$(AuI_2)_{0.441}$. This value is almost the same as that of the MDT-TSF salt,[4] indicating that the band filling of these salts is essentially the same.

Conducting Properties. Reflecting the reduced intermolecular interaction in the conducting donor layer, the room-temperature conductivity of (MDT-TS)-$(AuI_2)_{0.441}$ is approximately one-third (600 S cm^{-1}) of that of (MDT-TSF)$(AuI_2)_{0.436}$ (2000 S cm^{-1}). Furthermore, the conducting behavior of these AuI_2 salts is strikingly different: the former salt shows a resistivity minimum at around T_ρ = 85 K and shows a metal−insulator transition around T_{MI} = 50 K (Figure 4),[16] whereas the latter salt remains metallic down to low temperature and becomes superconducting at T_c = 4.5

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[15] Although Papavassiliou et al. showed a synthetic route to MDT-TS starting from 4,5-bis(methoxycarbony)-1,3-diselenole-2-selone and **2** in a conference proceedings, the combination of these compounds gave only a trace amount of **3** in our hands. Papavassiliou, G. C.; Mousdis, G. A.; Yiannopoulos, S. Y.; Zambounis, J. S. *Synth. Met.* **1988**, *27*, B373−B378.

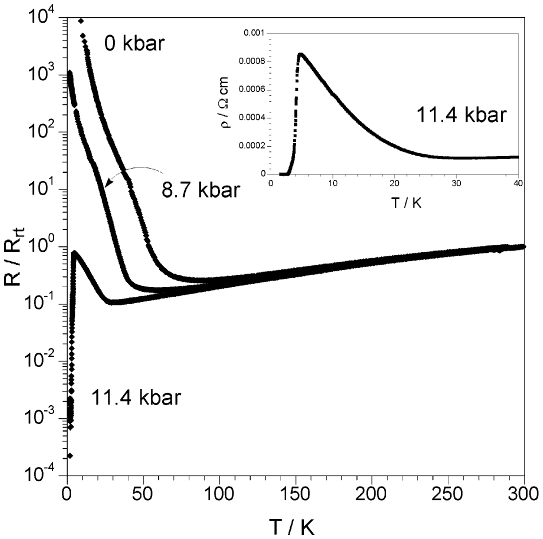

Figure 4. Temperature dependence of resistivity of (MDT-TS)(AuI$_2$)$_{0.441}$. The inset shows the resistivity in low-temperature region at 11.4 kbar.

K. This implies that the intermolecular overlaps in (MDT-TS)(AuI$_2$)$_{0.441}$ are too small to sustain the metallic state at low temperature. Considering that the structural isomer MDT-ST forms radical cation salts that retain the metallic state to low temperature and become superconducting at $T_c = 3.0-4.0$ K, it may be noted that the introduction of the selenium atoms into the central 1,3-dichalcogenole ring is very important for stabilizing the metallic state.

The insulating behavior of (MDT-TS)(AuI$_2$)$_{0.441}$ was suppressed by the application of hydrostatic pressure. With increasing applied pressure, T_ρ and T_{MI} of (MDT-TS)(AuI$_2$)$_{0.441}$ shift to lower temperatures, and at 11.4 kbar, following the hump below T_ρ, an abrupt drop in the resistivity to zero was observed at $T_c = 4.7$ K (onset) (Figure 4).[17] This resistivity drop was suppressed by application of magnetic field (Figure 5), confirming that (MDT-TS)(AuI$_2$)$_{0.441}$ is a new organic superconductor. The T_c of the present salt is almost the same as that of the AuI$_2$ salt of MDT-TSF, implying the difference between the MDT-TS and MDT-TSF salts can be regarded as a "chemical pressure effect"[1b] owing to the different chalcogen atoms in the molecular framework.

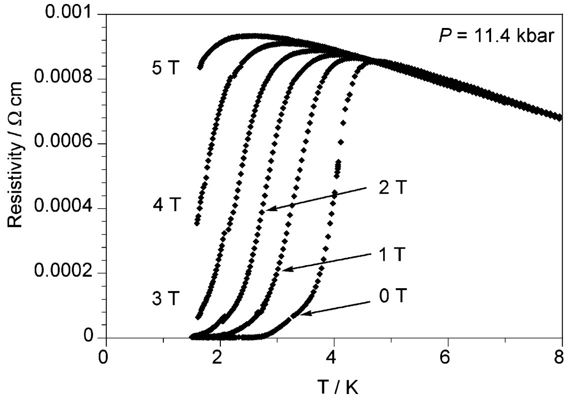

Figure 5. Conducting behavior of (MDT-TS)(AuI$_2$)$_{0.441}$ at 11.4 kbar under magnetic field.

The present (MDT-TS)(AuI$_2$)$_{0.441}$ is the first of the family of "AuI$_2$-type" radical salts having both an insulating and superconducting ground state, depending on the applied pressure. Such organic superconductors with different ground states as a function of temperature and pressure are important for elucidating superconducting mechanisms.[18] Further studies on the physical properties of (MDT-TS)(AuI$_2$)$_{0.441}$ and the exploration of related salts are now under way.[19]

Acknowledgment. We are grateful for financial support from Grants-in-Aid for Scientific Research on Priority Areas of Molecular Conductors (15073211 and 15073218) and Scientific Research (14740377) from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Crystallographic Information File (CIF) for (MDT-TS)(AuI$_2$)$_{0.441}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The midpoint T_c, determined from 50% recovery of the expected low-temperature resistance was 4.0 K.

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(19) Preliminary experiments on electrocrystallization of MDT-TS in the presence of tetrabutylammonium triiodide gave the corresponding I$_3$ salt as bronze needles. The conductivity of the salt at room temperature was 400 S cm^{-1}, and the salt retained metallic down to ca. 100 K. The detailed study on the I$_3$ salt, including determination of its crystal structure and composition, as well as the conducting properties under high pressure, is in progress.