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Communications

Organic Superconductors Based on a New Electron Donor, Methyleneedithio-diselenadithiafulvalene (MDT-ST)

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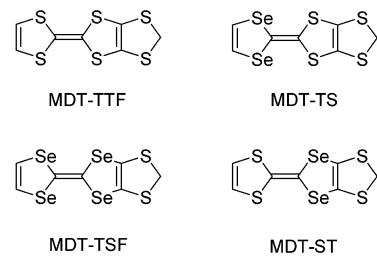
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Recently, we found that a radical cation salt of MDT-TSF (methylenedithio-tetraselenadithiafulvalene) with a linear AuI_2^- anion becomes a superconductor below 4.5 K.¹ This new superconductor is very unique in both conductive and structural characteristics; its conductivity at room temperature (2000 S cm^{-1}) is fairly higher than those of organic superconductors so far reported, and its crystal structure is composed of uniform donor stacks, strikingly different from the conventional organic superconductors comprising β - and κ -type arrangements of donor dimers.² In addition, the lattice of the segregated anion is incommensurate with the donor

lattice, leading to a nonstoichiometric composition, (MDT-TSF)(AuI_2)_{0.436}. A basic question has been raised whether only MDT-TSF can allow the formation of such a unique superconductor or whether the related electron donors also can do so. In this regard, it has already been reported that MDT-TTF (methylenedithio-tetrathiafulvalene), the sulfur counterpart of MDT-TSF, gives a superconducting radical cation salt with an AuI_2 anion ($T_c = 4.1\text{--}4.3 \text{ K}$).³ However, this AuI_2 salt adopts the conventional κ -type structure quite different from that of MDT-TSF. Furthermore, the hybrid MDT-TS (methylenedithio-dithiadiselenadithiafulvalene) has not been reported to form superconducting salts.⁴ To clarify this disharmony, we have developed another related donor, MDT-ST (methylenedithio-diselenadithiafulvalene), which is a structural isomer of MDT-TS in relation to the positions of the incorporated selenium atoms.⁵ We



would now like to report on the synthesis of MDT-ST

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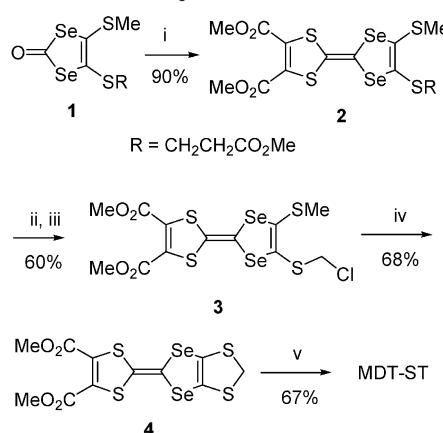
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Scheme 1. Synthesis of MDT-ST^a



^a (i) 4,5-Bis(methoxycarbonyl)-1,3-dithiole-2-thione (5-fold excess), P(OMe)₃, benzene; (ii) CsOH·H₂O, DMF; (iii) BrCH₂Cl; (iv) NaI, 2-butanone; (v) LiBrH₂O.

and the superconducting and structural characteristics of its radical cation salts.

The synthesis of MDT-ST is outlined in Scheme 1. A cross-coupling reaction of 5-methylthio-4-(2-methoxy-carbonyl ethylthio)-1,3-diselenol-2-one (**1**) with excess 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione⁶ in refluxing benzene gave the desired product **2** (90% yield based on **1**). Deprotection of the methoxycarbonyl ethyl part of **2** by an action of CsOH·H₂O in DMF, followed by realkylation of the resulting thiolate intermediate with bromochloromethane produced **3** (60% yield).⁷ After a ring-closing reaction of **3** to **4** promoted by sodium iodide in refluxing 2-butanone (68% yield), **4** was de-esterified by treatment with LiBr·H₂O in hexamethylphosphoric triamide (HMPA) at 160 °C to give MDT-ST in 67% isolated yield.

Electrococrystallization of MDT-ST in chlorobenzene containing three kinds of tetrabutylammonium trihalides ($\text{Bu}_4^{\text{N}}\text{X}$, $\text{X} = \text{I}_3$, I_2Br , $\text{I}_{2.9}\text{Cl}_{0.1}$)⁸ at 15 °C gave the respective radical cation salts 5–7 (Table 1). The room-temperature conductivities of salts 5–7 are in the range of 10^2 – 10^3 S cm^{−1}, which are slightly lower than or almost comparable to that of the AuI_2 salt of MDT-TSF. All the salts show metallic behavior down to 4 K and an abrupt resistivity drop around 3–4 K characteristic of superconducting transition (Figure 1). The magnetic susceptibility measurements with a SQUID magnetometer also support the superconducting transition; all the salts show a diamagnetic shielding signal below 4 K,

(4) Papavassiliou, G. C.; Mousdis, G. A.; Yiannopoulos, S. Y.; Kakoussis, V. C.; Zambounis, J. S. *Synth. Met.* **1988**, *27*, B373.

(5) The IUPAC nomenclature gives *5H*-2-(1,3-dithiol-2-ylidene)-1,3-diselena-4,6-dithiapentalene for MDT-ST and *5H*-2-(1,3-diselenol-2-ylidene)-1,3,4,6-tetra thiapentalene for MDT-TS. Since these lengthy names are apparently impractical, an abbreviated name, methylene-dithio-diselenadithiafulvalene (MDT-STF), can be conveniently used. However, it is not possible to distinguish these two isomers by the common name "MDT-STF", and thus, we adopt the conventional nomenclatures in the field of tetrachalcogenadithiafulvalene chemistry. For example, such nomenclatures for selenium variants of EDT-TTF (ethylenedithiotetrathiafulvalene), see Sato, A.; Ojima, E.; Kobayashi, H.; Kobayashi, A. *J. Mater. Chem.* **1999**, *9*, 2365.

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(8) $Bu^4N_2Cl_{0.1}$ was obtained by recrystallization of an equimolar mixture of Bu^4NCl and iodine from hot ethanol. See Supporting Information.

Table 1. Radical Cation Salts (5–7) of MDT-ST

salt	Bu ⁿ ₄ NX ^a	σ_{rt}^b (S cm ⁻¹)	T_c^c (K)	composition ^d
5	I ₃	600–1200	3.6 (3.8)	(MDT-ST)I _{1.27}
6	I ₂ Br	400 ± 200	3.2 (3.8)	(MDT-ST)I _{1.27–δ} Br _δ ($\delta \approx 0.2$)
7	I _{2.9} Cl _{0.1}	300 ± 100	3.4 (4.0)	(MDT-ST)I _{1.23–δ} Cl _δ ($\delta \approx 0$)

^a Supporting electrolyte used in the electrocrystallization. ^b Measured on a single crystal with a four-probe method. ^c Midpoint of resistivity drop is defined as T_c in the resistivity measurement, and onset of diamagnetic transition in the magnetic susceptibility measurement with SQUID is given in parentheses. ^d Composition is estimated on the basis of population analysis of the anion site in the structural analysis, X-ray oscillation photograph, and EDS (see Supporting Information).

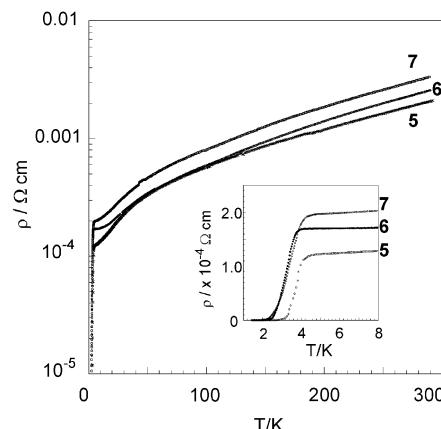


Figure 1. Temperature dependence of resistivity for MDT-ST salts **5–7** ((a)–(c), respectively).

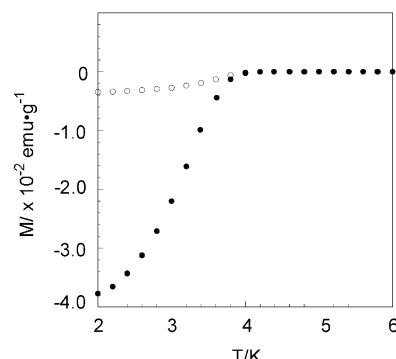


Figure 2. Temperature dependence of ZFC (closed circle) and FC (open circle) dc magnetizations for the salt **5** at an applied field of 5 Oe. Randomly oriented polycrystalline sample of **5** (ca. 1.28 mg) in a gelatin capsule was used.

as shown in Figure 2 for **5** as a representative. The volume fraction of superconductivity at 2 K is ca. 100%, 20%, and 60% of the perfect superconductivity for **5**, **6**, and **7**, respectively, indicating that all these are bulk organic superconductors.

X-ray crystallographic analysis revealed that salts **5–7** are isostructural with one another, and the crystal structures consist of uniform donor stacks and infinite polyhalide chains incommensurate with the donor lattice, reminiscent of superconducting (MDT-TSF)(AuI₂)_{0.436} (Figure 3 for salt **5** as a representative). The positions of the iodine atoms cannot be precisely determined by the usual X-ray structural analysis. To estimate the composition, an X-ray oscillation photograph along the *a*-axis was examined (Figure 4 for salt **5**). In the photograph, together with the strong Bragg spots originating from the donor lattice designated as “Donor = 1, 2, 3”, there are layer lines incommensurate with the

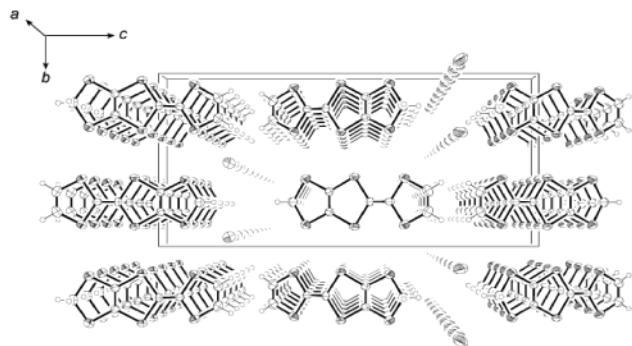


Figure 3. Crystal structure of the salt **5** (*a*-axis projection).

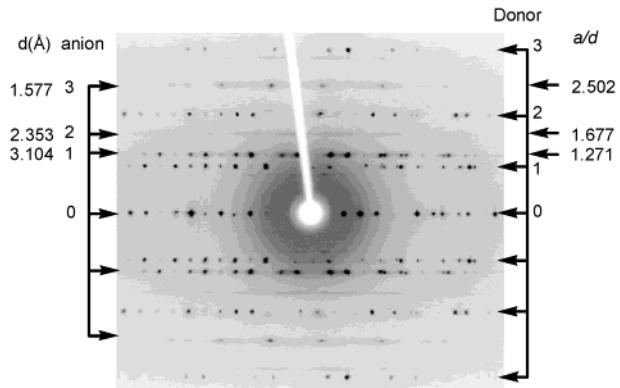


Figure 4. X-ray oscillation photograph of **5**. The vertical direction corresponds to the *a*-axis.

donor lines at $a/d = 1.271$ and 2.502 . Since the first line corresponds to 3.104 \AA in the real space, which is shorter than the I^- (ca. 4.3 \AA), I_3^- (ca. 9.2 – 9.7 \AA), and I_5^- lattices (ca. 15.5 \AA), the existence of infinite polyiodine chains is postulated, where the mean distance between the iodine atoms is 2.8 – 3.2 \AA .⁹ Thus, the chemical composition of **5** can be determined as $(\text{MDT-ST})\text{I}_{1.27}$. The lack of other clear lines assignable to the charged iodine species makes it difficult, on the basis of the X-ray photograph, to determine the actual charged species in the infinite iodine chain and, consequently, the degree of charge transfer of the donor molecule. However, with the aid of the Raman spectroscopy,¹⁰ the

(9) Marks, T. J.; Kalina, D. W. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 1, Chapter 6.

(10) A preliminary result on the Raman spectrum of **5** indicated the existence of I_3^- anions by the observation of a line around 100 cm^{-1} , attributable to the symmetric stretching of the I_3^- anion.

charged species in the chain is determined as I_3^- , which means that **5** has the actual composition of $(\text{MDT-ST})\text{I}_{0.423}$.

The structural aspects of salts **6** and **7** are basically the same as that of **5**, but the situation is complicated owing to the coexistence of different halogen atoms in the anion lattice. Thus, on the basis of the X-ray oscillation photograph and the energy dispersion spectroscopy (EDS), the compositions of **6** and **7** are estimated as summarized in Table 1. Interestingly, the ratio of the halogen atom in these salts is different from that in the supporting electrolyte employed in the electrocrystallization (Table 1).¹¹

In summary, we have found new organic superconductors based on MDT-ST, all of which have nearly the same structural characteristics as the MDT-TSF– AuI_2 superconductor. The common structural features of these superconductors are uniform donor stacks, linear chain structures of the anions incommensurate with the donor lattice, and a nonstoichiometric donor/anion composition. This novel structural type seems to be favored by the radical cation salts derived from the methylenedithio-tetrachalcogenofulvalenes donors containing selenium atoms. Because all the salts possessing this type of structure so far found become superconductors, it is safe to say that the present donor structure is a novel prototype for producing organic superconductors.

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Supporting Information Available: Synthetic procedures and spectroscopic data for MDT-ST and compounds **2**–**4** (PDF) and Crystallographic Information Files (CIFs) for the salts **5**–**7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) The experimental results on structural determination, for example, X-ray diffraction and EDS, indicate that the compositions of salt **5** and **7** are almost identical. There is no significant difference in T_c and absolute conductivity at room temperature, though conductivity of **7** ($300 \pm 50 \text{ S cm}^{-1}$) is slightly lower than that of salt **5** (600 – 1200 S cm^{-1}). Thus, it is very difficult to conclude that these two salts are inherently identical or not.