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Synthesis of Bis[1,2-bis(methylseleno)vinylenedithio]-tetrathiafulvalene (TMSVT)

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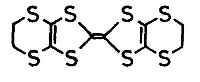
Synopsis. The title molecule was synthesized as an effective donor molecule for highly conductive organic complexes. It is a TTF dirivative possessing four selenium atoms and eight sulfur atoms. Its oxidation potential ($E_{1/2}$) is 0.86 V vs. SCE in THF,which is slightly higher than that of VT and TMTVT.

TTF derivatives possessing multi-chalcogen atoms have recently been found to give materials of interesting solid-state electrical properties. For example, the ion radical salt (BEDT-TTF)$_2$Cu(SCN)$_2$ gave organic superconductors of high T_c (10.4 K)[1] without applying pressure. The superconductivity of various BEDT-TTF salts is a subject of extensive study.[2] Other aspects of the multi-chalcogen TTF derivatives are a molecular fastener effect[3] of a series of TTC$_n$-TTF and high mobility of TTeC$_1$-TTF.[4] One of the important factors governing the electrical properties of these materials is the existence of a chalcogen-chalcogen network in the solid. The syntheses of various TTF derivatives were reviewed by Krief.[5] We have synthesized bis[1,2-bis(methylthio)vinylenedithio]-tetrathiafulvalene (TMTVT)[6] which has twelve sulfur atoms. This molecule has the largest number of chalcogen atoms in TTF derivatives known at present. This paper reports the synthesis of bis[1,2-bis(methylseleno)vinylenedithio]tetrathiafulvalene (TMSVT) which also has twelve chalcogen atoms in the molecule.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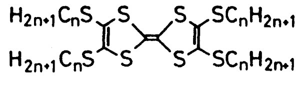
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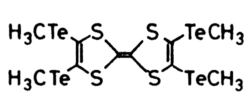
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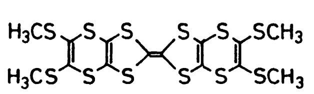
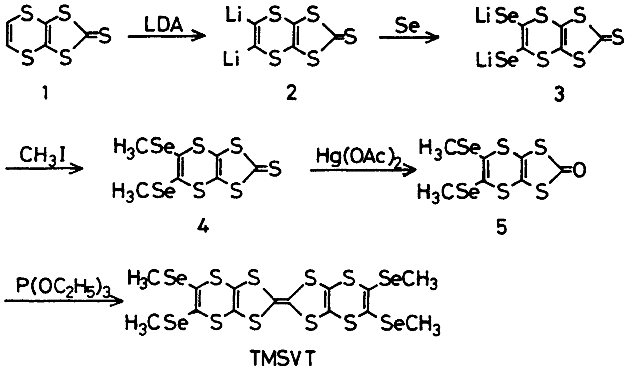

TMTVT

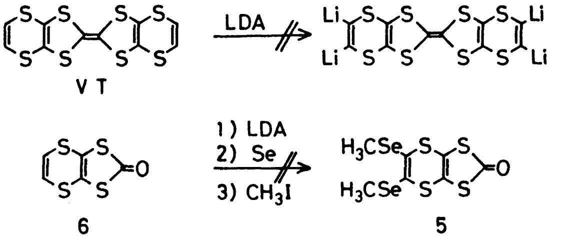
Results and Discussion

Synthesis of TMSVT. The synthetic route of TMSVT is shown in Scheme 1. 4,5-(Vinylenedithio)-1,3-dithiole-2-thione (**1**) was synthesized from 4,5-(ethoxyethylenedithio)-1,3-dithiole-2-thione as reported previously[7,8] with slight modifications.[9] It was lithiated by lithium diisopropylamide (LDA), followed by the selenium insertion reaction under supersonic wave irradiation for 2.5 h. Without supersonic wave irradiation, it took 4—5 h for the completion of the insertion reaction. The selenolate **3** was then reacted with methyl iodide to give 4,5-[1,2-bis(methylseleno)vinylenedithio]-1,3-dithiole-2-thione (**4**). The conversion of the thiocarbonyl group of **4** to a carbonyl group was made by mercury(II) acetate[10] to give 4,5-[1,2-bis-(methylseleno)vinylenedithio]-1,3-dithiol-2-one (**5**). The coupling reaction of **5** was made by heating it in neat triethyl phosphite to give TMSVT.



Scheme 1.

Two other synthetic routes of TMSVT are conceivable. One is a reaction starting with the lithiation of bis(vinylenedithio)tetrathiafulvalene (VT). However, the poor solubility of VT in THF hampered this route. The other is the reaction starting from the lithiation of 4,5-(vinylenedithio)-1,3-dithiol-2-one (**6**) followed by the selenium insertion reaction and the subsequent reaction with methyl iodide. However, the carbonyl group of **6** was found to be decomposed after the reaction.



Cyclic voltammetry of TMSVT in THF gave a single and electrochemically irreversible wave. The separation of the redox peak positions was about 0.2 V, which is much larger than that of the reversible wave (0.059 V). In spite of this, if we define the oxidation potential as the mid-point of the redox peaks, $E_{1/2}$ was 0.86 V vs. SCE. This value was higher than those of TMTVT (0.83 V vs. SCE),[6] VT (0.83 V vs. SCE),[7] bis(methylvinylenedithio)tetrathiafulvalene (0.80 V vs. SCE),[7] bis(dimethylvinylenedithio)tetrathiafulvalene (0.80 V vs. SCE),[11] and BEDT-TTF ($E_{1/2}(1)=0.69$ V, $E_{1/2}(2)=0.82$ V vs. SCE). The order of the oxidation potential, TMSVT>TMTVT≈VT, seems to conflict with that reported for methylthio- and methylseleno-derivatives of TTF or TSeF.[12] However, strict comparison can not be made, because VT, TMTVT, and TMSVT are electrochemically irreversible materials, and only one redox wave is observed for them unlike the cases of TTF, TTC_1-TTF, $TSeC_1$-TTF, TSeF, TTC_1-TSeF, and $TSeC_1$-TSeF;[12] all of the latter compounds gave two redox waves $E_{1/2}(1)$ and $E_{1/2}(2)$.

Experimental

All of the following reactions except the one from **4** to **5** were carried out in a nitrogen atmosphere. The mass spectra of the molecular ion peaks of the following products agreed with those calculated by computer simulation.

4,5-[1,2-Bis(methylseleno)vinylenedithio]-1,3-dithiole-2-thione (4). To the THF solution (150 ml) of diisopropylamine (0.94 g, 9.3 mmol) was added a hexane solution of butyllithium (9 mmol) at −78 °C, and the solution was stirred for 40 min at −78 °C. To this stirred solution was added **1** (1.00 g, 4.5 mmol) in one portion at −78 °C. The solution became dark red. The temperature of the solution was elevated gradually to 0 °C, and it was stirred for another 2 h at 0 °C to obtain the solution of **2**. It was then cooled to −78 °C, and well-ground selenium powder (0.711 g, 9.0 mmol) was added in one portion. The temperature of the stirred solution was elevated gradually to 0 °C under supersonic wave irradiation using a Bransonic 220 (Yamato Kagaku Co. Ltd). The solution was stirred for another 2.5 h at 0 °C to obtain a black solution. No selenium powder could be seen at this stage. The solution was then cooled to −78 °C, and methyl iodide (1.4 g, 9.9 mmol) was added with stirring. The temperature of the solution was then allowed to rise to room temperature, and the solution was stirred for another 1 h at this temperature to obtain a black solution. After evaporating the solvent, the residue was extracted with benzene, washed with water, and the benzene layer dried over Na_2SO_4. The crude product was chromatographed on silica gel using the mixed solvent of chloroform and hexane (1 : 4) as an eluent. The first pale yellow portion was discarded, and the second orange portion gave a yellow powder of **4** (0.338 g, 18.4%). It was recrystallized from the mixed solvent of THF and ethyl alcohol to obtain yellow needles. Mp: 126—127 °C. ^{1}H NMR δ=2.37 (s). MS *m/z* 410 (strongest M^+). Found: C, 21.03; H, 1.63%. Calcd for $C_7H_6S_5Se_2$: C, 20.59; H, 1.48%.

4,5-[1,2-Bis(methylseleno)vinylenedithio]-1,3-dithiol-2-one (5). The molecule **4** (0.2 g, 0.49 mmol) was dissolved in a mixed solvent of chloroform (40 ml) and acetic acid (40 ml), and mercury (II) acetate (0.312 g, 0.98 mmol) was added in one portion with stirring. The solution was stirred for 30 min at room temperature, and the pale yellow powder filtered off. The filtrate was washed with water, and the organic layer was dried over Na_2SO_4. After evaporating the solvent, the residue was chromatographed on silica gel using a mixed solvent of chloroform and hexane (1 : 1) as eluent, and the first pale yellow portion gave **5** (0.144 g, 75%). It was recrystallized from hexane or ethyl alcohol to obtain pale yellow needles. Mp: 96.5—97.5 °C. ^{1}H NMR δ=2.36 (s). MS *m/z* 394 (strongest M^+). Found C, 21.64; H, 1.72%. Calcd for $C_7H_6OS_4Se_2$: C, 21.44; H, 1.54%.

Bis[1,2-bis(methylseleno)vinylenedithio]tetrathiafulvalene (TMSVT). The reaction vessel containing **5** (0.204 g, 0.52 mmol) was purged with nitrogen gas, and triethyl phosphite (2.5 ml), which was distilled just before the reaction, was then added. The solution was stirred for a while to obtain a homogeneous solution. It was then heated with stirring, and red powder began to precipitate at around 100 °C. It was stirred at 110 °C for 2 h. After cooling to room temperature, the red powder was collected, washed with methyl alcohol, and dried in vacuum (0.155 g, 75.1%). The product was recrystallized from carbon tetrachloride to obtain red needles. Mp: 185 °C (decomp). ^{1}H NMR δ=2.31 (s). MS *m/z* 754 (strongest M^+). UV (THF): 338 nm (log ε 4.30) and 306 nm (log ε 4.37). Found: C, 22.24; H, 1.83%. Calcd for $C_{14}H_{12}S_8Se_4$: C, 22.35; H, 1.61%.

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