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Syntheses and Physical Properties of Tetrakis(methylthio)tetraselenafulvalene (TTC_1-TSeF) and Tetrakis(methylseleno)tetraselenafulvalene ($TSeC_1$-TSeF)

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The synthesis of tetrakis(methylthio)tetraselenafulvalene (TTC_1-TSeF) by a convenient one-pot reaction using dimethyldisulfide is reported for the first time as well as that of tetrakis(methylseleno)tetraselenafulvalene ($TSeC_1$-TSeF). The physical properties and lattice constants of these compounds are compared with those of TYC_1-TTF (Y = sulfur, selenium, and tellurium). TTC_1-TSeF is considered to have the smallest on-site Coulomb repulsive energy among these five compounds.

Multiple chalcogen systems, $C_6X_4Y_4$ (X,Y = sulfur, selenium, and tellurium; Fig. 1), are currently investigated in our group and the syntheses, physical properties, and crystal structures of TYC_n-TTF (X = sulfur and Y = sulfur, selenium, and tellurium; n = 1-18) have been reported.$^{1-4)}$ This series showed many attractive features concerning about the molecular packing and stacking in the crystal. When n is large enough, they show low resistivities due to fastener effect. $TTeC_1$-TTF showed high mobility (20-30 $cm^2/V\ s$) and low resistivity ($8.1 \times 10^4\ \Omega\ cm$) due to quasi-covalent Te••Te••Te chains in the crystal.$^{4)}$ In order to investigate the effects of the inner and the outer chalcogen atoms of a $C_6X_4Y_4$ group to the on-site Coulomb repulsive energy, molecular overlapping, and dimensionality, we try to replace the inner sulfur atoms of TYC_n-TTF by selenium atoms to obtain TYC_n-TSeF. Among this series only $TSeC_1$-TSeF is already known.$^{5)}$ But the yield is low and the synthetic procedure of this compound includes the tedious step such as the electrochemical reduction of carbon diselenide. Here we report a simple and easy synthetic route to make TTC_n- and $TSeC_n$-TSeF (n = 1) from TSeF, their physical properties, and structural data.

At first we tried to introduce the outer chalcogenoalkyl group to tetralithiated TSeF by the two step method which was adopted for the syntheses of $TSeC_n$-TTF and $TTeC_n$-TTF.$^{2,3)}$ TSeF was lithiated by LDA and then sulfur or selenium was inserted followed by the addition of methyliodide (Scheme 1). The mass spectra of the crude products revealed that they contained the desired material, TTC_1-TSeF or $TSeC_1$-TSeF (M/z = 578 and 766, respec-

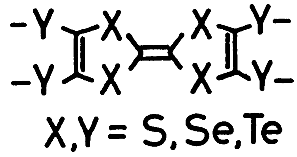
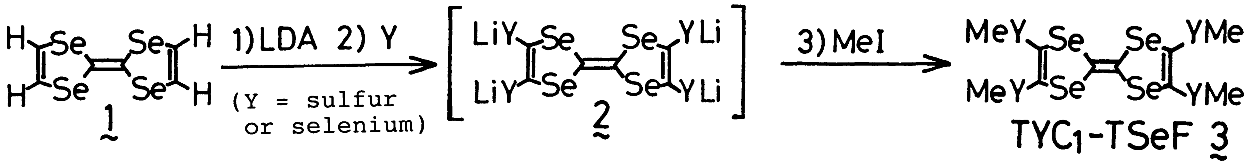


Fig. 1. $C_6X_4Y_4$.

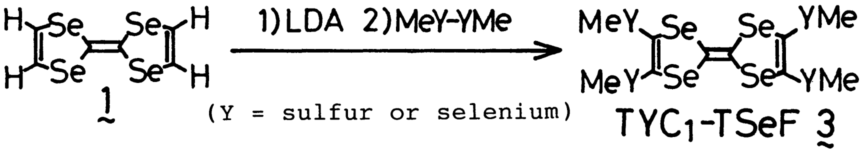


Scheme 1. Synthetic scheme using the two step method.

tively). But the separation of the target material was disturbed by many by-products. The formation of these undesired products was attributed to the complicated reaction where chalcogen atoms were inserted to the tetralithiated TSeF. So it is necessary to introduce chalcogenoalkyl groups directly without passing through the intermediate 2. Dimethyl dichalcogenide was chosen for the reagent to introduce chalcogenomethyl group. The synthetic procedures using this direct method for TTC_1-TSeF and $TSeC_1$-TSeF are as follows (Scheme 2).

The reaction was carried out under an inert atmosphere. To the 16 ml THF solution of diisopropylamine (570 mg, 5.63 mmol) was added 1.45 mol dm^{-3} hexane solution of n-BuLi (2.90 ml, 4.20 mmol) at -78 °C and stirred for 30 minutes. To this solution TSeF (400 mg, 1.02 mmol) was added at -78 °C and stirred for 1 h at the same temperature. Then the reaction temperature was gradually raised to 0 °C and stirred for another 2 h at 0 °C. After the solution was cooled to -78 °C, the 4 ml THF solution of dimethyldisulfide (394 mg, 4.18 mmol) was added to the obtained orange suspension at -78 °C and stirred for 1 h. Then the reaction solution was gradually warmed to room temperature and stirred for another 1 h. Water was added to the reaction solution and the crude product was extracted with benzene. The organic layer was washed with water four times and then two times with brine. This extract was dried with anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by the silica gel column chromatography (benzene-hexane) and recrystallized from benzene-hexane. The orange needle-like single crystals (388 mg) were obtained. The yield was 66% from TSeF. The elemental analysis (C:20.92, H:2.15, N:0%) was consistent with the calculated value of $C_{10}H_{12}S_4Se_4$ (C:20.84, H:2.10, N:0%). The parent peak (M/z = 578) and its isotope pattern of this product were agreeable to those of the calculated ones of TTC_1-TSeF. Mp: 119.0-119.7 °C ; IR: 2976(w), 2910(w), 1420(s), 1411(s), 1306(s), 964(s), and 817(s) cm^{-1} (in KBr); UV: 492, 360, and 305 nm (CH_3CN); and ^1H NMR: 2.45 ppm (δ, $CDCl_3$).

By the same reaction procedures, $TSeC_1$-TSeF was synthesized. The isolation procedure of $TSeC_1$-TSeF was somewhat different from that of TTC_1-TSeF. After the end of the reaction, water was added to the reaction mixture with stirring. The orange precipitates were filtered and washed with water and then hexane. After purification reddish orange needle-like single crystals were obtained. The yield



Scheme 2. Synthetic scheme using the direct method.

was 43% from TSeF (mp: 115.2-116.2 °C, lit. 112-113 °C[5]). The elemental analysis (C:15.88, H:1.55, N:0%) and the mass spectra of this product were consistent with the calculated value of $C_{10}H_{12}Se_8$ (C:15.72, H:1.58, N:0%; M/z = 766). ^{1}H NMR: δ, 2.37 ppm in CCl_4 (lit. 2.35 ppm[5]).

Table 1. Redox Potentials (V)[a]

	$E^1_{1/2}$	$E^2_{1/2}$	ΔE
TTF	0.35	0.72	0.37
TTC_1-TTF	0.52	0.75	0.23
$TSeC_1$-TTF	0.47	0.74	0.27
TSeF	0.48	0.76	0.28
TTC_1-TSeF	0.64	0.84	0.20
$TSeC_1$-TSeF	0.62	0.86	0.24

a) 0.1 M Bu_4NBF_4/CH_3CN, vs. SCE.

The redox potentials of TTC_1-TSeF and $TSeC_1$-TSeF were measured by the cyclic voltammetry (0.1 M Bu_4NBF_4/CH_3CN, vs. SCE) (Table 1). The introduction of four chalcogenoalkyl groups outside the TSeF skeleton makes $E^1_{1/2}$ of TTC_1-TSeF and $TSeC_1$-TSeF (0.64 and 0.62 V vs. SCE, respectively) larger than that of TSeF (0.48 V), in accordance with the electronwithdrawing ability of the substituents, MeS- > MeSe- > H-. The donor abilities of these donors are almost comparable to that of DBTTF (0.62 V). The difference between $E^1_{1/2}$ and $E^2_{1/2}$ (ΔE) is considered to be a measure of the on-site Coulomb repulsive energy. To design a molecule of small on-site Coulomb repulsive energy is essential to obtain a metallic compound as well as to increase the critical temperature of a superconductor. By introducing four chalcogenomethyl groups to TSeF, ΔE values of TTC_1-TSeF and $TSeC_1$-TSeF (0.20 and 0.24 V, respectively) become smaller than that of TSeF (0.28 V). It is noticeable that ΔE of TTC_1-TSeF is the smallest among the TYC_n-TXF series already synthesized. Table 1 compares the effect of chalcogen atoms to the redox properties of these TYC_1-TXF compounds. When the "outer" chalcogen Y changes from sulfur to selenium, $E^1_{1/2}$ decreases and ΔE increases. On the contrary when the "inner" chalcogen X changes from sulfur to selenium, $E^1_{1/2}$ increases and ΔE decreases.

The X-ray crystallography was carried out using four-circle diffractometer. The lattice constants of TTC_1-TSeF and $TSeC_1$-TSeF are summarized in Table 2. There are two phases for TTC_1-TTF. The central part $C_6S_4S_4$ of TTC_1-TTF takes a bent form in Phase 1,[6] and a flat form in Phase 2.[7] After the refinement (R = 6.8%), the crystal structure of TTC_1-TSeF revealed to be isomorphous with Phase 1 of TTC_1-TTF. The central $C_6Se_4S_4$ part of TTC_1-TSeF takes the bent form just like the $C_6S_4S_4$ segment of TTC_1-TTF (Phase 1). The replacement of the

Table 2. Crystal data of TYC_1-TXF compounds

	TTC_1-TTF[6] (Phase 1)	TTC_1-TTF[7] (Phase 2)	TTC_1-TSeF	$TSeC_1$-TSeF
	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	15.668(1)	5.141(2)	15.841(3)	16.462(4)
b/Å	7.804(1)	7.565(3)	7.957(1)	8.010(1)
c/Å	14.010(2)	10.950(2)	14.386(3)	14.436(2)
α/°		72.46(2)		
β/°	106.16(1)	79.03(2)	106.90(1)	106.80(1)
γ/°		84.87(3)		
V/Å^3	1645.5(4)	398.4	1735.0(5)	1822.2(6)
Z	4	1	4	4

Table 3. Semiconductive paramaters of TYC_1-TXF compounds

Compound	$\rho_{r.t.}$/Ω cm	Ea[a)]/eV
TTC_1-TTF (Phase 1)	2.9×10^{10}	0.38[4c)]
$TSeC_1$-TTF (High mp phase)	2.7×10^{8}	0.58[8)]
$TSeC_1$-TTF (Low mp phase)	1.0×10^{6}	0.26[8)]
TTC_1-TSeF	1.3×10^{9}	0.60[b)]
$TSeC_1$-TSeF	3.3×10^{9}	0.68[b)]

a) Ea: activation energy. b) This work.

inner chalcogen atoms from sulfur to selenium in this case does not give an effective change to the molecular structure and packing in the crystal. The refinement of the crystal structure of $TSeC_1$-TSeF is in progress.

For the single crystals of TTC_1-TSeF and $TSeC_1$-TSeF the electrical resistivities were measured by the 2-probe method using Au paste as contacts under a vacuum of 4×10^{-6} Torr to avoid the oxidation effect (Table 3). The resistivities of them are in the order of 10^9 Ω cm and comparable to those of TTC_1-TTF (Phase 1)[4c)] and $TSeC_1$-TTF (High melting point phase), but by three orders of magnitude higher than that of $TSeC_1$-TTF (Low melting point phase).[8)] The bent form of the molecule of TTC_1-TSeF makes the molecular packing loose and prevents the formation of suitable chalcogen chains, and consequently may be the reason for the poor conductivity of the compound.

A triiodide complex of TTC_1-TSeF was obtained in the donor and anion ratio of about 2 : 0.8 and showed a metallic character ($\rho_{r.t.} = 3.0 \times 10^2$ Ω^{-1} cm^{-1}) as a preliminary result. Details will be reported soon.

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