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Synthesis, Conductivity, and Structure of a Novel Organic Conductor $(TMET\text{-}STF)_2ClO_4$. Coexistence of One- and Two-dimensional Donor Columns

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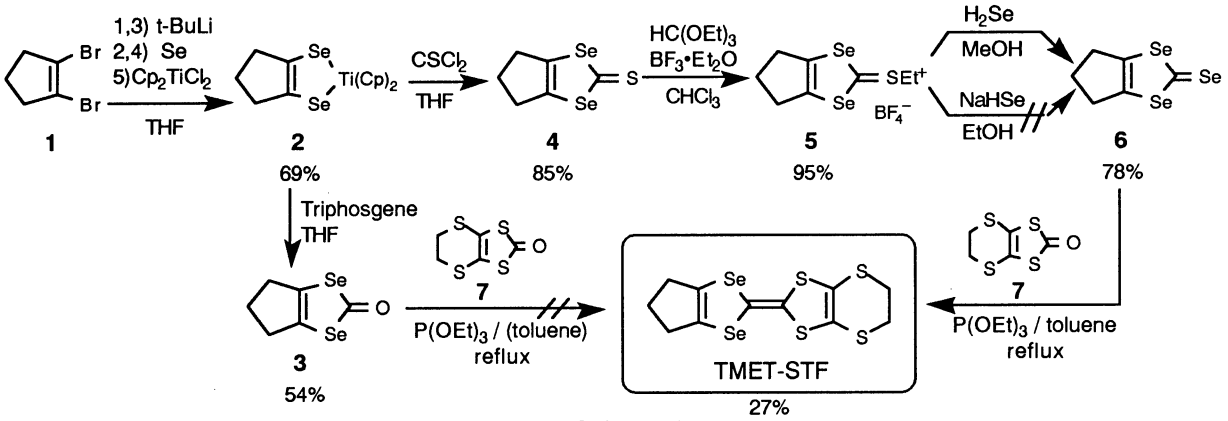
An organic π-donor TMET-STF (trimethylene(ethylenedithio)diselenadithiafulvalene) was synthesized using a method via a titanocene complex. The cation radical salt $(TMET\text{-}STF)_2ClO_4$ is metallic down to 22 K and shows an upturn of resistivity. Crystal structure analysis and band calculation indicate that this system contains two types of donor columns; the one is one-dimensional and the other is two-dimensional.

For the development of organic conductors, control of the dimensionality of electronic structure is a key point. Recent successful cases (for example, the BEDT-TTF system) indicate that two-dimensional Fermi surface resists the Peierls instability. In the case of TTF-like donor molecules, replacement of S atoms in the TTF skeleton to Se atoms is one of the choices for the increase in the dimensionality. The larger van der Waals radius of Se atom is effective for enhancement of side-by-side intermolecular interactions. In the conventional synthesis of TSeF derivatives, however, the use of highly toxic reagents such as CSe_2 or H_2Se is indispensable. In order to avoid this problem, we have investigated the synthetic method of the TSeF precursor units with the external heteroring via titanocene complexes, which uses elemental Se instead of the toxic reagents.[1] In this work, our method was applied to an improved synthesis of a unit with an external hydrocarbon ring, cyclopenta-1,3-diselenole-2-selone (**6**).[2]



Scheme 1.

TMET-STF was synthesized following the procedure described in Scheme 1. Dibromocyclopentene (**1**) in THF was reacted with 2 equiv. of t-BuLi at −78 °C. After being stirred for 2.5 h, the reaction mixture was warmed up to −20 °C, and 1 equiv. of gray Se powder was added. Within 0.5 h the Se powder disappeared. The solution turned from clear yellow to red. This process was repeated again, except that the Se powder was added at room temperature. To the resultant solution, 1 equiv. of titanocene dichloride was added at −78 °C. The brown solution turned green in a few minutes. The reaction mixture was gradually warmed to room temperature and stirred overnight. The product was separated by a column chromatography (SiO_2 / CH_2Cl_2) and dark green titanocene complex **2** was obtained. In this type of reaction, the yield of titanocene complexes depends on the substrates. In this case, the yield is satisfactorily high (69%). The reaction of **2** with 1 equiv. of triphosgene gave the ketone **3**. Neither a cross nor a homo coupling reaction of **3** by the use of triethylphosphite has failed with nor without a solvent (toluene). Since some cross coupling reactions of the selone **6** have been reported, the synthetic route via the selone was adopted.[3,4] We did not use the thione **4** for the cross coupling reaction to avoid the scrambling reaction.[5] The reaction of the titanocene complex **2** with thiophosgene gave the thione **4**,[6] which was reacted with $CH(OEt)_3$ and BF_3•Et_2O to afford the dithiolium salt **5**.[7] Failure of the reaction of **5** with NaHSe led us to the reluctant use of H_2Se. This synthetic route via the titanocene complex gives a moderate and reproducible yield and reduces the use of the toxic reagents.

The cross coupling reaction of the selone **6** and the ketone **7** afforded TMET-STF.[8] This donor molecule was first synthesized in 1986 by Kikuchi *et al.*[3] They reported preparations of a few cation radical salts without detailed physical properties and crystal structures. So, we have examined crystal structures and physical properties of some cation radical salts of this donor. Among them, $(TMET\text{-}STF)_2ClO_4$ was found out to have a unique crystal structure.

There are at least two types of ClO_4 salts. The one is $(TMET\text{-}STF)_2ClO_4$ (hereafter called 2:1 salt) and the other is $(TMET\text{-}STF)_2(ClO_4)_2$•$C_6H_5Cl$ (hereafter called 1:1 salt). Black thin plates of the 2:1 salt were prepared by electrochemical oxidation of TMET-STF in the presence of $(n\text{-}Bu)_4NClO_4$ in THF using a constant current (1 μA) under argon at 20 °C. Black plates of the 1:1 salt were prepared under almost the same conditions except for the solvent (chlorobenzene with 5% ethanol).[9]

Crystal data of $(TMET\text{-}STF)_2ClO_4$ are: $C_{22}H_{20}Se_4S_8ClO_4$, FW=956.17, triclinic, space group $P\bar{1}$, a=8.021 (2), b=29.730 (7), c=6.556 (1) Å, α=92.72 (2), β=105.20 (2), γ=93.80 (2)°, V= 1501.7 (6) $Å^3$, Z=2, D_{calc}=2.12 g/cm^3. Intensities were measured on a Mac Science four-circle diffractometer with Mo-Kα radiation. The structure was solved by the direct method and refined by the full matrix least-squares method using independent 3143 reflections ($2\theta \leq 60°$, $|Fo| \geq 4\sigma(|Fo|)$). The final R-value is 0.073.

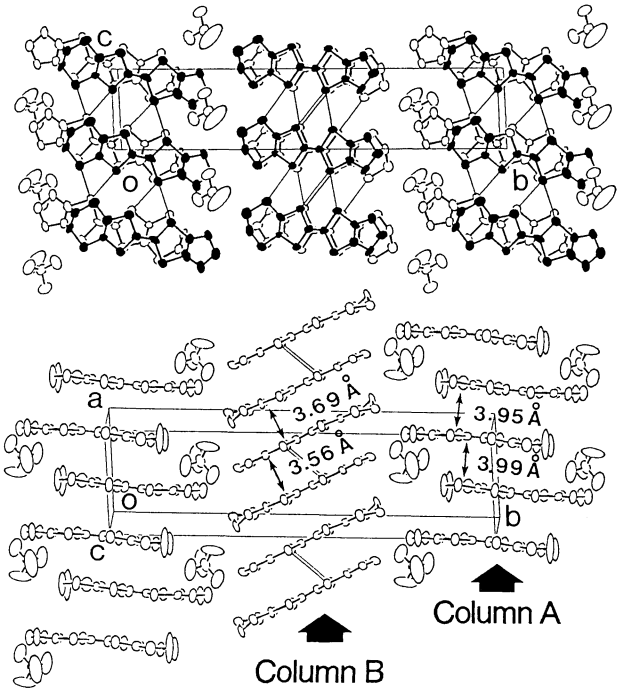


Fig. 1. Crystal structure of $(TMET\text{-}STF)_2ClO_4$.

In the crystal, there are two crystallographically

independent donor molecules (A, B), each of which constructs independent column (Column A and Column B, in Fig. 1). It is well known that the bond lengths in TTF derivatives can be correlated to the formal charge.[10] Comparison of the bond lengths in these two donor molecules indicates that there is not distinct difference in the formal charge. Columns A and B are separated by anion layers and form independent layers.

In Column A, the donor molecules stack alternately with the external cyclopentene rings sticking out from the column. Interplanar distances are 3.95 and 3.99 Å. These values are rather larger than those in ordinary columnar structures. The terminal ethylene group in the molecule A shows anomalously large thermal parameters (B_{eq} values for the ethylene carbon atoms are 10 and 16 Å^2 for the molecule A, 4.2 and 5.1 Å^2 for the molecule B). It would be correlated to the loose donor packing in the column. There is no intra-column chalcogen•••chalcogen distance shorter than van der Waals distances. On the other hand, in the side-by-side direction, many short intermolecular chalcogen•••chalcogen distances are observed.

In Column B, the stacking arrangement is very similar to the one in the Bechgaard salt. The donor molecules are interrelated by an inversion center and weakly dimerized. Interplanar distances are 3.56 and 3.69 Å. Short chalcogen•••chalcogen contacts exist in either stacking and side-by-side direction.

Table 1 shows the calculated intermolecular overlap integrals among HOMO's. With respect to the intra-column interactions, values for Column A are smaller than those for Column B, which corresponds to the difference in interplanar distances and overlapping modes. On the other hand, the inter-column interactions for Column A are larger than intra-column ones. The interaction p1 for Column A is as large as the intra-column interaction a1, and the interaction c is about a half of the a1. These values suggest two-dimensionality of the layer constructed by Column A. Actually, tight-binding band calculation shows a cylindrical Fermi surface (Fig. 2).

Table 1. Overlap Integrals of HOMO's ($\times 10^{-3}$)

		Column A	Column B
intra-column	a1	11.01	23.69
	a2	14.26	22.76
inter-column	p1	10.73	5.39
	p2	1.42	3.70
	c	-4.26	0.69

On the other hand, inter-column interactions for Column B (p1, p2) are about 1/5 of intra-column interactions. This ratio is larger than that for the Bechgaard salt (1/10). And the band calculation shows an open but distorted Fermi surface.

After all, (TMET-STF)$_2$ClO$_4$ has two different types of columns; the one is two-dimensional and the other is quasi one-dimensional. It is the first case that such a unique structure is

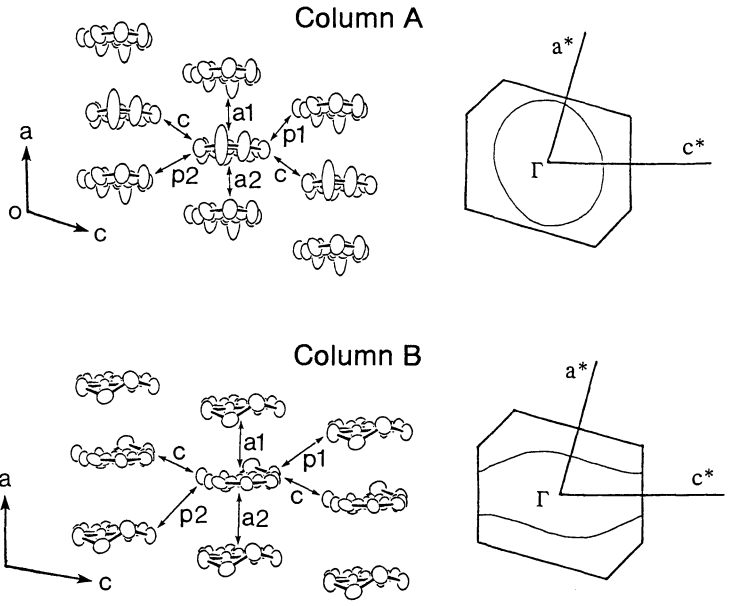


Fig. 2. Calculated Fermi surfaces for Column A and Column B.

found in the molecular conductors.

This salt shows metallic behavior down to 22 K followed by a transition to a semiconductor (Fig. 3). The anisotropy of the resistivity is rather small ($\rho_{\perp a}/\rho_{//a} \approx 3.5$). At present, the nature of the metal-semiconductor transition is not clear. One possible origin of the transition is the instability interrelated to the quasi one-dimensional Fermi surface associated with Column B. This phenomenon is very fascinating especially in relation with the magnetic property (for example, a possibility of the spin density wave (SDW) formation and its influence on the two-dimensional conduction electrons). Further study is in progress.

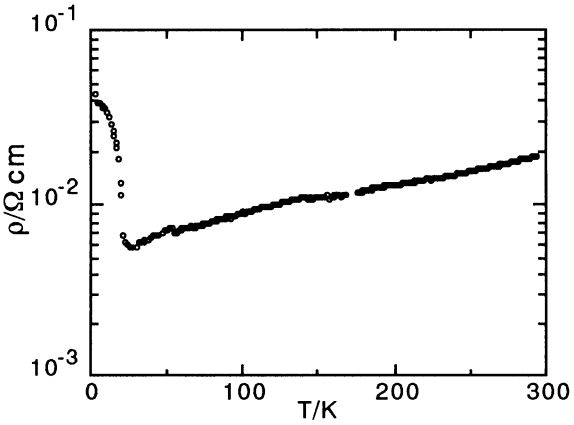


Fig.3. Temperature dependence of electrical resistivity along the a axis for the 2:1 salt, measured by a standard four-probe method.

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6) **4**: Yellow crystals; MS (EI) m/z 270 (M^+, 100%), 226 ($M^+ - CS$, 19%), 189 ($M^+ - Se$, 55%), 66 (55%), 65 (40%); ^1H NMR (500 MHz, $CDCl_3$) δ 2.86 (m, 4H), 2.37 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 223.3 (s), 146.0 (s), 33.7 (t), 25.7 (t).
7) **5**: Black powder; ^1H NMR (500 MHz, $CDCl_3$) δ 3.59 (q, 2H, J = 7.4 Hz), 3.28 (m, 4H), 2.60 (m, 2H), 1.66 (t, 3H, J = 7.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 227.2 (s), 159.2 (s), 40.1 (t), 33.5 (t), 28.4 (t), 12.0 (q).
8) TMET-STF: Red crystals; MS (EI) m/z 430 (M^+, 100%), 402 ($M^+ - C_2H_4$, 62%), 314 ($C_5H_6Se_2C{=}CS_2^+$, 35%), 282 ($C_5H_6Se_2C{=}CS^+$, 97%), 238 ($C_5H_6Se_2C^+$, 70%).
9) The 1:1 salt is an insulator. The crystal data of the 1:1 salt are: $C_{28}H_{25}Se_4S_8Cl_3O_8$, FW= 1168.18, triclinic, space group $P\bar{1}$, a = 10.236 (3), b = 11.477 (4), c = 9.168 (4) Å, α = 97.58 (3), β = 109.49 (2), γ = 102.71 (3)°, V = 965.5 (5) $Å^3$, Z = 1, D_{calc} = 2.01 g/cm^3. Independent 2436 reflections ($2\theta \leq 60°$, $|Fo| \geq 4\sigma(|Fo|)$) were used for calculation. The final R-value is 0.098. The crystal consists of one-dimensional columns of dimerized donor molecules. The donor column is separated from each other by anion-solvent array. Looking from the stacking direction, the donor stack and the anion array are arranged like a checker board. Solvent molecule is on the inversion center and disordered.
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