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Crystal Structures and Electrical Properties of Tetrakis(methylseleno)-tetrathiafulvalene (TSeC$_1$-TTF) and Two Phases of (TSeC$_1$-TTF)I$_3$

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The crystal structure and the electrical property of TSeC$_1$-TTF as well as those of the new complex (TSeC$_1$-TTF)I$_3$ with two kinds of phases are reported. The crystal structure of TSeC$_1$-TTF was determined to be monoclinic, space group $P2_1/a$, a=7.728(1), b=20.952(4), c=5.315(1) Å, and β=90.57(2)° having a unit cell volume of 860.6(3) Å^3. By an electrochemical method and a diffusion method, TSeC$_1$-TTF gave two forms of single crystals of (TSeC$_1$-TTF)I$_3$. The crystal data of one form; monoclinic, space group $P2_1/n$, a=24.359(1), b=11.831(3), c=7.842(6) Å, β=96.71(4)°, V=2244(1) Å^3 and those of the other; monoclinic, space group $P2_1/a$, a=23.174(5), b=11.727(3), c=8.960(5) Å, β=110.54(2)°, V=2280(1) Å^3. The former complex has lower resistivity, 4.1×10^4 Ω cm, compared with the latter one 1.1×10^8 Ω cm. The dimerization is more noticeable in the latter complex than in the former one.

For the purpose of developing organic molecules directed toward organic conductors, a family of TYC$_n$-TTF (Y=S, Se, and Te, n=1—18), shown in Fig. 1, has been prepared and the crystal structures and properties have been widely investigated.[1—3] As a part of the investigation, a variety of the charge-transfer complexes based on the TYC$_n$-TTF family have also been obtained,[4] and some of them show relatively high conductivities. In this paper the crystal structures and electrical properties of the donor TSeC$_1$-TTF and the new complex (TSeC$_1$-TTF)I$_3$ with two kinds of phases are presented.

Experimental

The synthesis of TSeC$_1$-TTF compound was reported in the preceding paper.[5] Two kinds of single crystals of TSeC$_1$-TTF were prepared by slow cooling method using different solvents after several days. Dark-red block-like single crystals of (TSeC$_1$-TTF) were grown in hexane solution with higher resistivity 8.5×10^7 Ω cm and higher melting point 106.3 °C, (TSeC$_1$-TTF)(H). On the other hand, red needle-like single crystals (TSeC$_1$-TTF) were grown in a mixed solvent of hexane and benzene with lower resistivity 1.0×10^6 Ω cm and lower melting point 92.5 °C, (TSeC$_1$-TTF)(L). Needle-like single crystals of (TSeC$_1$-TTF)I$_3$ were obtained by a diffusion method using iodine as an acceptor in a benzene solution after several days, which were black-colored needle-like crystals and the typical size was 0.01×0.6×0.01 mm^3, (TSeC$_1$-TTF)I$_3$(N). On the other hand, block-like single crystals of (TSeC$_1$-TTF)I$_3$ were obtained by an electrochemical method, (TSeC$_1$-TTF)I$_3$(B). In this method, tetrabutylammonium triiodide (TBAI$_3$) (50 mg) and TSeC$_1$-TTF (14.7 mg) were dissolved in a mixed solvent of THF and acetonitrile with a ratio of 1:10 with gentle heating under an argon atmosphere. Electrochemical oxidation was carried out with a constant current of 1 μA at a constant temperature (25 °C) on a vibration-free table. After 20 days, the anode was covered with a black-colored block-like microcrystalline material. The typical size of the crystals is 0.01×0.02×0.02 mm^3, which is too small for a conductivity measurement.

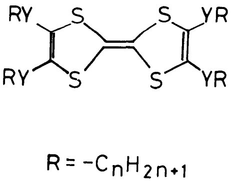

Fig. 1. The molecular structure of TYC$_n$-TTF (Y=Selenium for TSeC$_n$-TTF, Y=sulfur for TTC$_n$-TTF and Y=tellurium for TTeC$_n$-TTF).

The X-ray diffraction data collection was carried out with a Rigaku automated four-circle X-ray diffractometer AFC-5R and AFC-5 for the donor molecule (TSeC$_1$-TTF)(H) and the complexes of (TSeC$_1$-TTF)I$_3$(N) and (TSeC$_1$-TTF)I$_3$(B), respectively. For the compound of (TSeC$_1$-TTF)(H) the crystal data is: Se$_4$S$_4$C$_{10}$H$_{12}$, F.W. 575.84, monoclinic, space group $P2_1/a$, a=7.728(1), b=20.952(4), c=5.315(1) Å, β=90.57(2)°, V=860.6(3) Å^3, Z=2, D_{calc}=2.22 g cm^{-3} and μ(Mo $K\alpha$)=95.97 cm^{-1}. Intensity data was measured by the θ–2θ scan technique on the diffractometer with graphite monochromatized Mo $K\alpha$ radiation (2θ<60°). 2830 unique reflections were measured. The structure was solved by the direct method using MULTAN 78 program system[6] and refined by the block-diagonal least-squares procedure using 1391 independent reflections with $|F_o|>3\sigma(|F_o|)$. After absorption correction the refinement was converged to a final R value of 0.063. For the complex (TSeC$_1$-TTF)I$_3$(N) the crystal data is: Se$_4$S$_4$C$_{10}$H$_{12}$I$_3$, F.W. 956.54, monoclinic, space group $P2_1/a$, a=23.174(5), b=11.727(3), c=8.960(5) Å, β=110.54(2)°, V=2280(1) Å^3, Z=4, D_{calc}=2.788 g cm^{-3} and μ(Mo $K\alpha$)=107.38 cm^{-1}. Intensity data were measured by the θ–2θ scan technique on the diffractometer with graphite monochromatized Mo $K\alpha$ radiation (2θ<60°). 5928 unique reflections were measured. The structure was solved by the direct method using MULTAN 78 program system[6] and refined by the block-diagonal least-squares procedure using 1440 independent reflections with $|F_o|>3\sigma(|F_o|)$. After absorption correction the refinement was converged to a final R value of 0.069. For the complex (TSeC$_1$-TTF)I$_3$(B), the crystal data is: Se$_4$S$_4$C$_{10}$H$_{12}$I$_3$, F.W. 956.54, monoclinic, space group $P2_1/n$, a=24.359(7), b=11.831(3), c=7.842(6) Å, β=96.71(4)°, V=

2245(2) Å^3, Z=4, D_{calc}=2.83 g cm^{-3}, and μ(Mo $K\alpha$)=109.09 cm^{-1}. Intensity data was measured by the θ–2θ scan technique on the diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($2\theta<60°$). 6904 unique reflections were measured. The structure was solved according to the Patterson method and refined by the block-diagonal least-squared procedure using 1857 independent reflections ($|F_o|>3\sigma(|F_o|)$). After absorption correction the refinement was converged to a final R value of 0.063. For all these analyses, anisotropic thermal parameters were adopted for all nonhydrogen atoms, and the hydrogen atoms were refined isotropically.[7]

The electrical resistivities were measured by a two probe method. The electrical contacts to the specimen crystals were made with gold paint. Only for (TSeC$_1$-TTF)I$_3$(B) polycrystalline samples were used, because the single crystal size was too small to measure the resistivity.

Results and Discussion

TSeC$_1$-TTF. The atomic coordinates for (TSeC$_1$-TTF)(H) are listed in Table 1. The molecular and crystal structures are shown in Figs. 2 and 3. Along the c-axis, the TSeC$_1$-TTF molecules are stacked with overlapping as shown in Fig. 3(c), where the distance between the two C$_2$S$_4$ molecular planes is 3.481(3) Å. The shortest intermolecular Se–Se contact is 3.670(1) Å which is much shorter than the sum of the van der Waals radii (4.00 Å). The shortest intermolecular S–S contact is 3.663(3) Å, which is still shorter than the sum of the van der Waals radii (3.70 Å). The shortest intermolecular S–Se contact is 3.890(2) Å, which is a little longer than the sum of the van der Waals radii (3.85 Å). The molecule has a special structure which is neither of the chair nor boat form and is of similar to that of TSeC$_4$-TTF's.[2] The four terminal Se–C bonds of a molecule are almost perpendicular to each other. Such kind of molecular shape leads to the electrical resistivities of 7.3×10^8/4.1×10^9/8.5×10^7 (Ω cm), which is slightly anisotropic.

Table 1. Positional Parameters (×10^4) and Equivalent (Isotropic Thermal Parameters of (TSeC$_1$-TTF)(H)

	X	Y	Z	B_{eq}/Å^2
Se1	2470 (1)	1366 (0)	−1950 (2)	3.4
Se2	−1282 (1)	2035 (0)	232 (2)	3.7
S1	1785 (2)	277 (1)	2012 (4)	3.0
S2	−1445 (3)	858 (1)	3855 (4)	3.2
C1	67 (9)	233 (4)	4162 (13)	2.5
C2	1146 (9)	1011 (3)	676 (13)	2.4
C3	−297 (9)	1268 (4)	1498 (13)	2.6
C4	4535 (13)	868 (6)	−1748 (22)	6.4
C5	−911 (14)	2572 (5)	3212 (17)	4.8

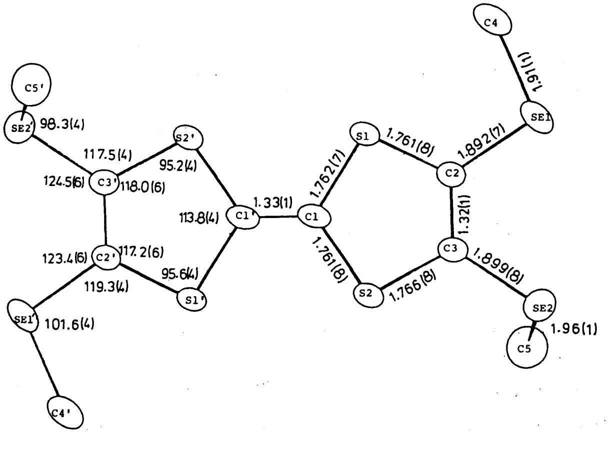

Fig. 2. ORTEP[8] drawing of TSeC$_1$-TTF(H) showing bond lengths and bond angles.

It should be noted here that TSeC$_1$-TTF, by using different solvent, gives two kinds of single crystal with the same chemical composition and the same density but displaying very different physical properties. One is block-like dark red single crystal with higher melting point and higher resistivity [(TSeC$_1$-TTF)(H)]; and the other one is needle-like red single crystal with lower melting point and lower resistivity [(TSeC$_1$-TTF)(L)]. The difference in resistivity is about 2 orders. The crystal data are still quite different. However, the structure analysis for the single crystal with lower melting point [(TSeC$_1$-

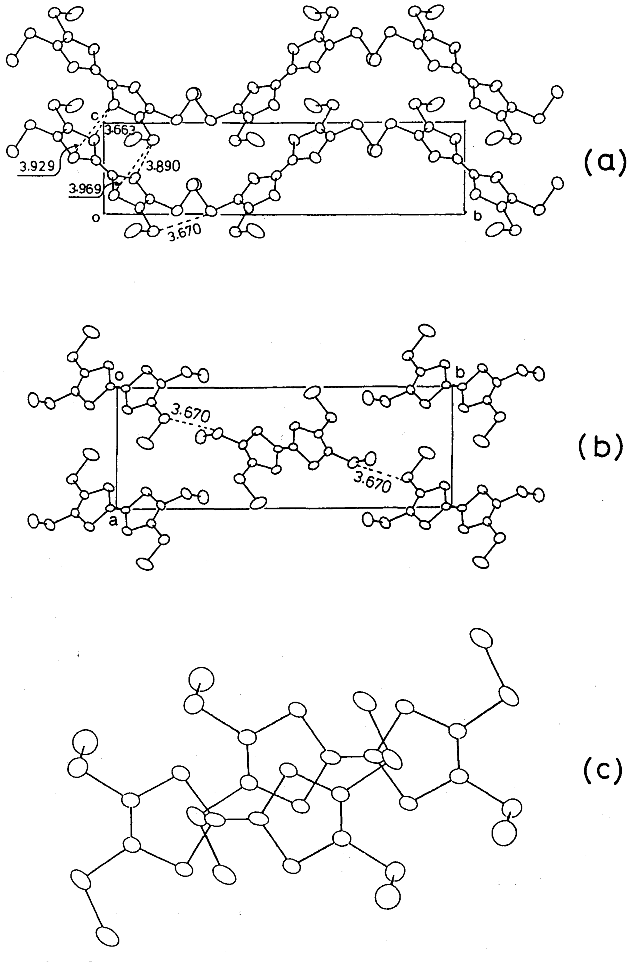

Fig. 3. The crystal structure of TSeC$_1$-TTF(H) projected along the a-axis (a), projected along the c*-axis (b), and the mode of overlapping of TSeC$_1$-TTF (c).

Table 2. Crystal Data and Resistivities

	TSeC$_1$-TTF(L)	TSeC$_1$-TTF(H)	(TSeC$_1$-TTF)I$_3$(B)	(TSeC$_1$-TTF)I$_3$(N)
T_m/°C	92.5	106.3		
ρ_{RT}/Ω cm	1.03×10^6	8.5×10^7	4.1×10^{4}[a)]	1.1×10^8
	Red	Dark red	Black	Black
	needle-like	block-like	block-like	needle-like

a) The resistivity was measured by using polycrystalline samples.

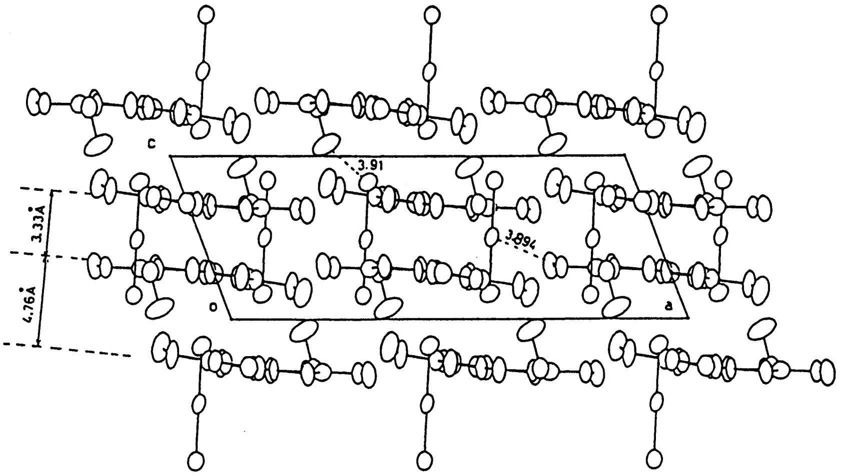

Fig. 4. Crystal structure of (TSeC$_1$-TTF)I$_3$(N) projected along the b-axis.

TTF)(L)] is somehow difficult. To elucidate the interesting problem of the donor molecule itself, some more detailed works are going on.

Comparing with TTC$_1$-TTF and TTeC$_1$-TTF,[9] the magnitude of resistivity of TSeC$_1$-TTF(H) is just in between of them. In TTC$_1$-TTF the central C_6S_8 moiety is nonplanar and the molecular structure has a boat form. Because of the weak intermolecular interactions between adjacent C_6S_8 moieties and the absence of discernible intermolecular overlaps between adjacent π systems, the resistivity is as high as 2.9×10^{10} Ω cm, which is much higher than that of TSeC$_1$-TTF in high or low phase. For TTeC$_1$-TTF[10] the magnitude of the resistivity, 8.1×10^4 Ω cm, is the lowest in the TYC$_1$-TTF group (Y=S, Se, and Te). The central $C_6S_4Te_4$ moiety of TTeC$_1$-TTF is planar unlike TTC$_1$-TTF and TSeC$_1$-TTF. TTeC$_1$-TTF molecules are stacked to form a column structure with the interplanar distance of 3.76 Å. Tellurium atoms between neighboring columns form zigzag chains along the stacking axis of TTeC$_1$-TTF molecules. The distance between those two Te atoms is 3.644(2) Å, which is significantly shorter than the van der Waals distance (4.12 Å).

(TSeC$_1$-TTF)I$_3$(N). The atomic coordinates for the crystal of (TSeC$_1$-TTF)I$_3$(N) are listed in Table 3. The crystal structure is shown in Figs. 4 and 5. Along the c-axis, TSeC$_1$-TTF molecules are stacked in the dimerized form with overlapping as shown in Fig. 5(b). The distances between the two optimal planes of the central C_2S_4 parts of a dimer and between those of two dimers are 3.33 and 4.76 Å, respectively. The shortest intermolecular Se–Se contact within the dimer is 3.845(6) Å (Fig. 4(b)), which is much shorter than the sum of the van der Waals radii (4.00 Å). The shortest

Table 3. Positional Parameters ($\times10^4$) and Equivalent Isotropic Thermal Parameters of (TSeC$_1$–TTF)I$_3$(N)

	X	Y	Z	B_{eq}/Å^2
I1	1397 (1)	6944 (2)	5064 (3)	5.9
I2	1928 (1)	7074 (2)	8511 (3)	6.6
I3	871 (1)	6803 (2)	1576 (3)	8.0
Se4	693 (1)	13639 (3)	2486 (5)	6.8
Se5	−2326 (1)	8428 (3)	3210 (5)	7.2
Se6	−1382 (2)	6171 (3)	2944 (5)	7.0
Se7	1584 (2)	11394 (3)	2085 (6)	8.4
S8	−439 (4)	8078 (8)	3051 (13)	8.2
S9	−197 (3)	11750 (8)	2908 (12)	7.6
S10	−1219 (3)	9983 (8)	3267 (12)	7.4
S11	566 (4)	9856 (8)	2625 (14)	8.6
C12	−507 (12)	9550 (32)	3007 (40)	8.4
C13	836 (12)	11255 (22)	2440 (36)	5.3
C14	−1558 (13)	8615 (27)	3149 (37)	6.5
C15	−1200 (12)	7764 (27)	3089 (40)	6.9
C16	−82 (12)	10318 (28)	2915 (42)	7.5
C17	14 (14)	14320 (31)	2845 (43)	8.3
C18	475 (12)	12045 (24)	2602 (39)	6.4
C19	−1481 (20)	6011 (30)	691 (47)	10.7
C20	−2550 (14)	9937 (27)	3303 (47)	8.5
C21	1770 (17)	9835 (32)	1643 (54)	10.9

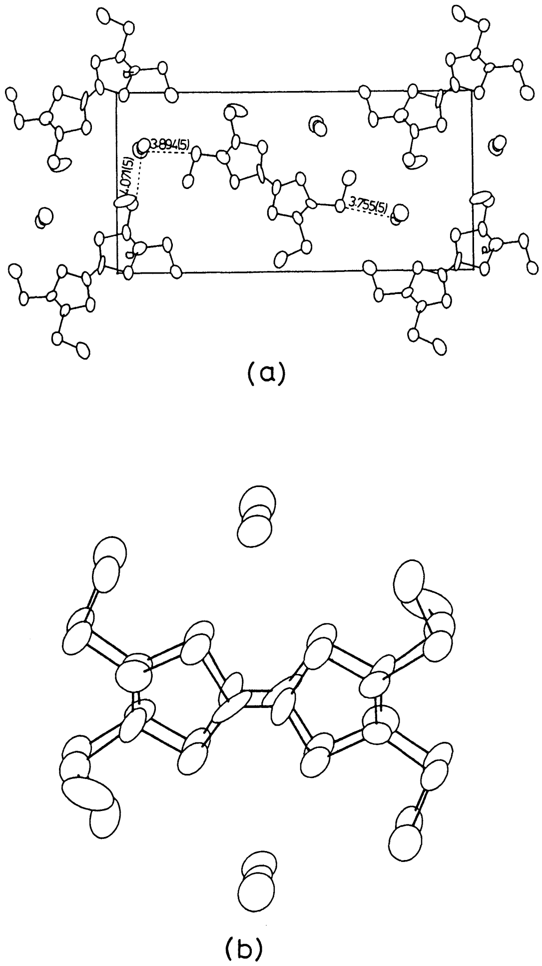

Fig. 5. Crystal structure of ($TSeC_1$-TTF)I_3(N) projected along the c*-axis (a) (only half of the molecules in a cell are shown here) and the mode of overlapping of $TSeC_1$-TTF (b).

intermolecular S–S contact within the dimer is 3.4(1) Å, which is still much shorter than the sum of the van der Waals radii (3.70 Å). The shortest distance between the donor molecule and the acceptor molecule I_3, that is the Se–I contact, is 3.755(5) Å (Fig. 5(a)), which is still much shorter than the sum of the van der Waals radii (4.15 Å). The donor molecule $TSeC_1$-TTF in the complex has a slightly bent structure (Fig. 6), the dihedral angles between the optimal plane of the central C_2S_4 part and the planes of the two C_2Se_2 parts are 6.51(9) and 1.8(4)°, respectively, and only one Se–C bond is obviously perpendicular to the connected C_2Se_2 part. Although the distances between Se and Se, and S and S are 3.845(6) and 3.40(1) Å within the dimer, which are much shorter than the respective sum

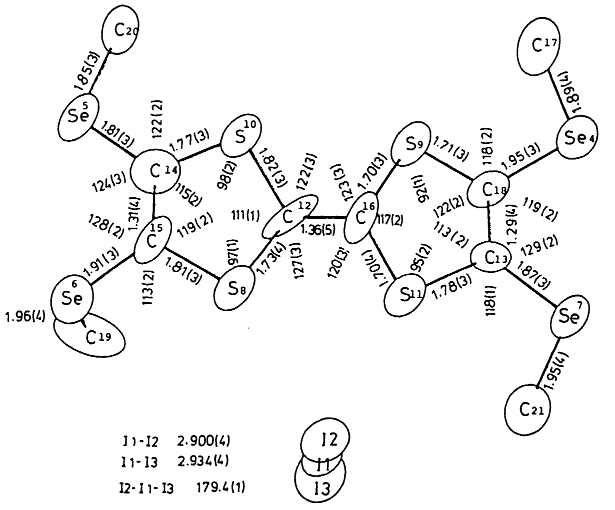

Fig. 6. ORTEP drawing of ($TSeC_1$-TTF)I_3 in the complex ($TSeC_1$-TTF)I_3(N) showing bond lengths and bond angles.

Table 4. Positional Parameters (×10^4) and Equivalent Isotropic Thermal Parameters of ($TSeC_1$-TTF)I_3(B)

	X	Y	Z	B_{eq}/Å^2
I1	1530 (1)	2050 (1)	983 (2)	3.8
I2	873 (1)	1593 (2)	3832 (3)	5.1
I3	2191 (1)	2397 (2)	−1798 (3)	5.3
Se4	−1283 (1)	−8998 (2)	5 (4)	3.9
Se5	488 (1)	−1517 (2)	3566 (4)	3.7
Se6	−2196 (1)	−6783 (2)	−1105 (4)	3.9
Se7	1368 (1)	−3641 (2)	4960 (4)	3.8
S8	−311 (3)	−3450 (5)	2057 (8)	3.3
S9	448 (3)	−5285 (5)	3181 (8)	3.2
S10	−469 (3)	−7091 (5)	1359 (8)	3.3
S11	−1210 (3)	−5215 (5)	408 (8)	3.1
C12	657 (10)	−3918 (18)	3729 (28)	3.0
C13	−1118 (11)	−7439 (20)	378 (31)	3.8
C14	−568 (9)	−5651 (18)	1388 (26)	2.2
C15	302 (11)	−3087 (19)	3191 (28)	3.6
C16	−166 (11)	−4887 (20)	2109 (28)	3.4
C17	−1513 (13)	−6595 (19)	−43 (30)	4.6
C18	−111 (11)	−894 (23)	2075 (40)	5.6
C19	−1557 (14)	−9281 (24)	2248 (37)	6.4
C20	1715 (11)	−5076 (26)	4891 (37)	5.3
C21	−2524 (13)	−5299 (24)	−696 (41)	6.1

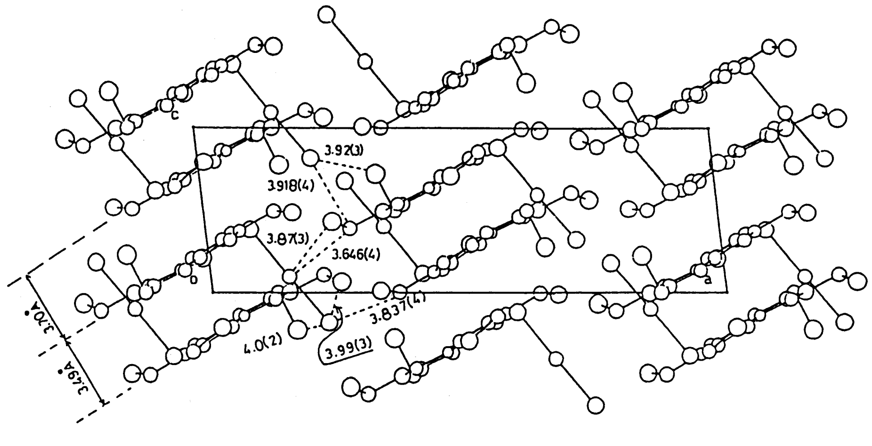

Fig. 7. Crystal structure of (TSeC$_1$-TTF)I$_3$(B) projected along the b-axis.

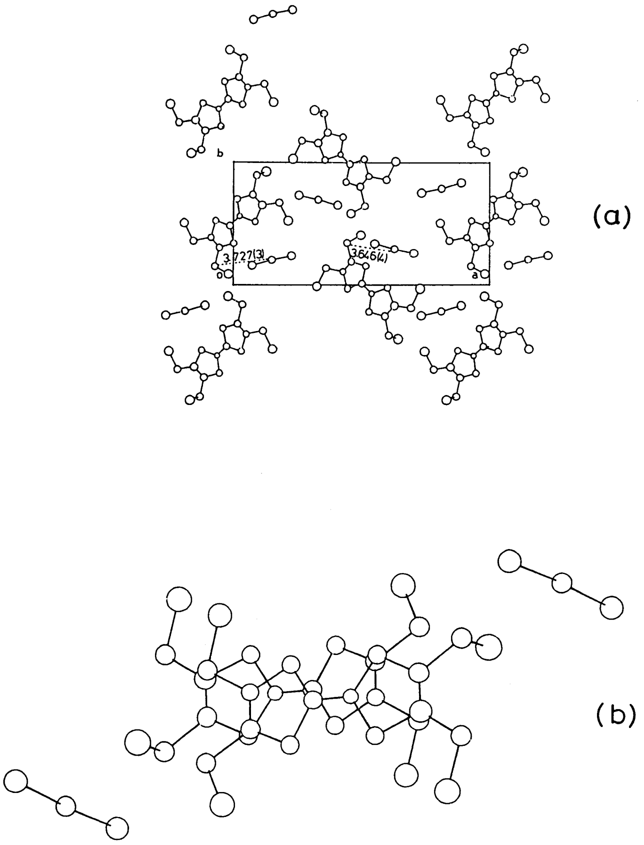

Fig. 8. Crystal structure of (TSeC$_1$-TTF)I$_3$(B) projected along the c*-axis (a) (only half of the molecules in a cell are shown here) and the mode of overlapping of TSeC$_1$-TTF (b).

of the van der Waals radii, the electrical conductivity is mainly dominated by the dimerized structure. Therefore, the resistivity appeared as high as 1.1×10^8 Ω cm, which is in the same order as that of the donor TSeC$_1$-TTF(H) (8.5×10^7 Ω cm) and higher than that of the donor in another phase (TSeC$_1$-TTF)(L) (1.0×10^6 Ω cm).

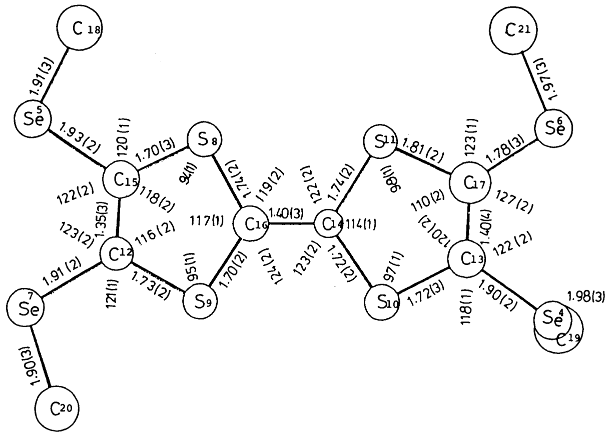

Fig. 9. ORTEP drawing of TSeC$_1$-TTF in the complex (TSeC$_1$-TTF)I$_3$(B) showing bond lengths and bond angles.

(TSeC$_1$-TTF)I$_3$(B). The atomic coordinates for the single crystal (TSeC$_1$-TTF)I$_3$(B) are listed in Table 4. The crystal and molecular structures are shown in Figs. 7, 8, and 9. The donor molecule has a bent structure, and the planes of the two C$_2$Se$_2$ parts are slightly bent towards the same direction from the optimal plane of central C$_2$S$_4$ part, where the dihedral angles between the optimal plane of the central C$_2$S$_4$ part and the planes of the two C$_2$Se$_2$ part are 2.0(2) and 4.2(2)°, respectively; and only one Se–C bond is obviously perpendicular to the connected C$_2$Se$_2$ part. Along the c-axis, the TSeC$_1$-TTF molecules are stacked in one-dimensional way with overlapping as shown in Figs. 7 and 8, and the distances between the two molecular planes are 3.49(1) and 3.70(2) Å, respectively. The difference between them is not so large as comparing with that of (TSeC$_1$-TTF)I$_3$(N). Thus, the degree of dimerization is relatively small. The shortest intermolecular Se–Se contact is 3.637(5) Å which is much shorter than the sum of the van der Waals radii. The shortest intermolecular S–S contact is 3.52(1) Å which is still much shorter than the sum of the van der Waals radii. Although the shortest interplane distance, 3.49(1) Å, is longer than that of ($TSeC_1$-TTF)I_3(N) (3.33 Å) and the overlapped area (Fig. 8(b)) is smaller than that of ($TSeC_1$-TTF)I_3(N), the resistivity is as low as $4.1\times10^3\,\Omega\,\mathrm{cm}$ even for the polycrystalline samples, because the degree of dimerization of this complex is much smaller than that of the complex ($TSeC_1$-TTF)I_3(N).

Comparing with the iodine complex of TTC_1-TTF, (TTM-TTF)$I_{2.47}$,[11] the resistivities of ($TSeC_1$-TTF)I_3 (N) and ($TSeC_1$-TTF)I_3(B) are much higher than that of (TTM-TTF)$I_{2.47}$, $7-10\times10^{-3}\,\Omega\,\mathrm{cm}$. Anyhow, the relatively high resistivities of ($TSeC_1$-TTF)I_3(N) and ($TSeC_1$-TTF)I_3(B) should also be originated in the simple salt formation.

In summary, we have obtained two kinds single crystals for the donor molecules $TSeC_1$-TTF, ($TSeC_1$-TTF)(H), and ($TSeC_1$-TTF)(L). For the single crystal ($TSeC_1$-TTF)(H), the crystal structure has been analyzed. We have also obtained two kinds of single crystals of a 1:1 triiodide of $TSeC_1$-TTF, ($TSeC_1$-TTF)I_3(N), and ($TSeC_1$-TTF)I_3(B), depending on the preparation methods. Both of the crystal structures have been solved, and we found out some specific factors to understand their properties. We have measured the electrical properties for the complexes of a 1:1 triiodide of $TSeC_1$-TTF in the two different phases. Although the relatively high resistivities of these materials should be originated in the simple salt formation, the degree of dimerization still play a very important role to determine the electrical properties.

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