The first methyl antimony linked dimeric tetrathiafulvalene and tetraselenafulvalenes

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Abstract—In quest of novel organic donors, dimeric tetrathiafulvalene (TTF) and tetraselenafulvalenes (TSFs) linked by a single or double methyl antimony bridge, MeSb(TTF)\(_2\) (1), (MeSb)\(_2\)(TSF)\(_2\) (cis-2 and trans-2), and MeSb(TSF)\(_2\) (3), have been synthesized. Singly bridged 1 and 3 show three pairs of redox waves, whereas doubly bridged cis-2 and trans-2 show two pairs of redox waves similarly to TSF. The X-ray structural analyses of neutral crystals, 1, cis-2 and trans-2, have succeeded. In their structures, antimony and chalcogen atoms form close intermolecular contacts useful in constructing supramolecular networks.

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Many chemical modifications of TTF (tetrathiafulvalene) have been carried out with the aim of exploring new metallic and superconducting cation radical salts. Among them, dimeric TTF molecules\(^2\) are expected to display a multiredox character by through-bond or through-space interactions between two TTF units and enhance the intermolecular interactions by the extended \(\pi\)-conjugation. For this purpose, main group elements such as sulfur,\(^3\) selenium,\(^4\) tellurium,\(^4\) silicon,\(^5\) phosphorus,\(^5\) and mercury\(^6\) have been employed to link two TTF units (Scheme 1). Recently, doubly bridged dimeric TTF with phenyl phosphorus linkage was reported.\(^6\) These heteroatoms are expected to form supramolecular networks in the crystals of their cation radical salts.

From the viewpoint of conducting materials, these dimeric systems have not been so suitable for the cooperation between supramolecular interactions and conducting pathways. Intermolecular interactions are of essential importance in delocalizing conduction electrons and stabilizing a metallic state. For this reason, we focus on the dimeric TTF system linked by methyl antimony(III) bridge(s). The antimony atom offers a possibility for electronic delocalization through intramolecular Sb\(\cdots\)Sb and Sb\(\cdots\)S contacts.\(^7\) Compared with the bulky aryl group, the small methyl group is suitable for the formation of intermolecular interactions. Moreover, antimony(III) atom is useful for electrocrystallization due to its more positive potential to antimony(V) species compared with other homologous elements. In addition, replacement of sulfur atoms with selenium atoms, which is a powerful method for the

Scheme 1. Dimeric TTF systems.

Scheme 2. Synthesis of dimeric TCFs.
enhancement of intermolecular interactions, has been performed.² In the present letter, we report synthesis, redox properties, and crystal structures of methyl antimony(III)-linked dimeric TCF (tetrachalcogenafulvalene) derivatives, MeSb(TTF)₂ (1), (MeSb)₂(TSF)₂ (cis-2 and trans-2) and MeSb(TSF)₂ (3).

The one-pot synthesis of the present compounds is outlined in Scheme 2. Methylantimonydiiodide (MeSbI₃) was used for the linkage of two TCF units. Compound 1 was obtained by the monolithiation of TTF with 1 equiv of LDA followed by a reaction with 0.5 equiv of MeSbI₃.¹⁰ Similarly, the treatment of selectively bislithiated TSF with 1 equiv of MeSbI₃ afforded compounds 2 (a cis/trans mixture) together with compound 3.¹² It should be noted that the treatment of TSF with 1 equiv of LDA followed by a reaction with 0.5 equiv of MeSbI₃ also afforded 2 (a cis/trans mixture) as a main product. This result suggests the predominant formation of 2,3-bislithiated TSF even if the reaction is carried out under the monolithiation condition.¹⁰ Subsequently, cis and trans isomers 2 were completely separated into each isomer by a gel-permeation chromatography eluted with CS₂ by a 6 time recycle. The cis/trans ratio was nearly 1/5 from the isolated yields. The subtle change of the peak height detected with 278 nm absorption, when cis/trans mixture had been stored in CS₂ solution for a long period at room temperature during the separation, would indicate the interconversion between cis-2 and trans-2. The cis/trans separation was only successful by the use of CS₂ as the eluent. In the absence of light, cis-2 and trans-2 which had been stored in CS₂ solution for several days afforded the crystals of cis-2 and trans-2, respectively. In comparison with 1, selenium compounds cis-2, trans-2 and 3 are less soluble in common organic solvents. However, it is not problematic for the study of electrochemical behaviour and electrocrystallization for preparing cation radicals.

Redox properties of 1–3 and their parent TTF and TSF are presented in Table 1 and Figure 1. Singly linked compounds 1 and 3 show three pairs of reversible redox waves and the first and second stages are successive. In addition, compounds 1 and 3 show the first wave slightly more negative than those of the parent TTF and TSF, respectively, exhibiting an improved electron donor character. It is difficult for the present results to provide further information about each redox steps. This behaviour, however, is similar to those of bis(tetrathiafulvalenyl)sulfide [(TTF)₂S] and its selenium analogue [(TTF)₂Se], except that the third one is irreversible in the case of [(TTF)₂S] and [(TTF)₂Se].³ The first and second couples of [(TTF)₂S] and [(TTF)₂Se] correspond to reversible one-electron processes to mono- and di-cat-ionic species (TTF⁻⁻C-TTF⁺ and TTF⁺⁻C-TTF⁺: C = chalchogen) and the third step is an irreversible two-electron process up to tetracation C(TTF)⁺⁺. If taking account of this explanation, a very small separation between the first and second steps in 1 and 3 suggests that the bridging antimony atom in 1 and 3 brings about an electronic coupling between two TCF units in 1 and 3 to some extent.

In contrast, the doubly bridged compounds cis-2 and trans-2 exhibit two pairs of reversible waves like parent TSF, and their electron donating abilities are inheritable from TSF. These two steps are quite similar to those of X₃(MeS₂TTF)₂ (X = Te)⁴b and contrastive to the case of X₂(Me₂TTF)₂ (X = PPh) that exhibits strictly separated four oxidation waves indicating the interaction between two TTF units.⁶ Compared with 1 and 3, the absence of further oxidation stages of cis-2 and trans-2

![Figure 1. Cyclic voltammograms for (a) 1 and 3 and (b) cis-2 and trans-2.](image-url)

Table 1. Redox potentials/V

<table>
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<tr>
<th>Compounds</th>
<th>E₁/₂</th>
<th>E₂/₃</th>
<th>E₁/₃</th>
<th>E₂/₃ - E₁/₂</th>
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<td></td>
<td>0.53</td>
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<tr>
<td>TSF</td>
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<td>0.49</td>
<td>0.40</td>
<td></td>
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<td>0.01</td>
<td>0.40</td>
<td>0.12</td>
</tr>
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<td>0.44</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>trans-2</td>
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<td>0.17</td>
<td>0.49</td>
<td>0.12</td>
</tr>
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</table>

*a Versus Ag/AgNO₃ in PhCN with 0.1 M n-Bu₄NPF₆, grassy carbon working electrode, scan rate 25, 50, 100 mV s⁻¹. The potentials of TTF and TSF were measured for comparison under the identical condition. The listed values are average for the three scan rates.
would suggest that the coupling of two TCF units in 1 and 3 comes from not the interactions via methyl antimony linkage but the approach of two TCF units by the bent of single methyl antimony linkage. In the case of cis-2 and trans-2, the rigid central diantimony ring would prevent the approach of two TSF units, and divide the molecule into two nearly independent halves.

Recrystallization of 1, cis-2, and trans-2 from some organic solvents afforded single crystals suitable for X-ray structure analysis.\(^\text{10,12,13}\) Compound 1 crystallizes in the monoclinic system with the space group \(Pc\). The molecular and crystal structures of 1 are shown in Figure 2. The whole molecule is crystallographically independent and the unit cell consists of two molecules. In contrast to a chair conformation of the neutral TTF,\(^\text{14}\) each TTF unit of 1 is almost planar and these two TTF planes is nearly perpendicular to each other [95.31(4)°]. The angles around the pyramidal antimony atom are 95.1(2)° for C(3)–Sb(1)–C(13), 94.7(2)° for C(9)–Sb(1)–C(13), and 94.3(2)° for C(3)–Sb(1)–C(9), whose values are slightly smaller than those reported for the tertiary stibine \(\text{Ph}_3\text{Sb}\) [95.1(3)–98.0(3)°].\(^\text{15}\) In the crystal, the antimony atom constructs two Sb⋯S intermolecular interactions within the sum of the van der Waals radii Sb⋯S (3.80 Å); the one is Sb(1)⋯S(7) [3.730(2) Å] and the other is Sb(1)⋯S(7) [3.730(2) Å]. Similarly, there are other remarkable interactions; short S⋯S contacts [3.573(3) Å for S(4)⋯S(6)] and some (C)H⋯S contacts shorter than the sum of the van der Waals radii. As a result, these interactions form the three-dimensional network in the crystal.

Two geometrical isomers cis-2 and trans-2 show entirely different types of crystal structures: the orthorhombic system with the space group \(Pnma\) for cis-2 and the triclinic system with the space group \(P1\) for trans-2. The molecular and crystal structures of cis-2 are shown in Figure 3. A mirror plane passes through the molecule along the molecular long axis and the half moiety is crystallographically independent. The central diantimony ring is much distorted into a boat conformation with the dihedral angle of 67.1(2)° between the Sb(1)–C(3)–C(30)–Sb(10) and Sb(1)–C(7)–C(70)–Sb(10) planes.

Figure 2. Crystal structure of 1. (a) Molecular structure and (b) packing diagram viewed along the \(b\)-axis. Dotted lines indicate short intermolecular contacts: p for Sb(1)⋯S(7) and r for S(4)⋯S(6).

Figure 3. Crystal structure of cis-2. (a) Molecular structure, (b) packing diagram viewed along the \(b\)-axis, (c) projection on the \(bc\)-plane. Dotted lines indicate Se⋯Se short contacts.
would be suppressed by the oxidation in cation radical salts, and molecular stacks with extended intramolecular interactions through chalcogen–chalcogen or chalcogen–antimony contacts are expected. The present molecules are the most fundamental and some peripheral modifications of the TCF core are possible. We propose the methyl antimony-bridged TCF systems are promising candidates to open the next generation in molecular conductors. The preparation of conducting cation radical salts with various inorganic anions is currently in progress.

Acknowledgements

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References and notes

10. To a solution of TTF (0.51 g, 2.5 mmol) in dry THF (12 ml) was slowly added a freshly prepared solution of LDA (2.7 mmol) in THF–hexane (5 ml) at −78 °C, and the resulting solution was stirred for 4 h at the same temperature. Then MeSbCl2 (0.52 g, 1.3 mmol) in dry THF (5 ml) was added dropwise to the solution and the
resulting mixture was allowed to warm up to room temperature. The mixture was filtered through Celite and extracted with toluene (100 ml). After removal of the solvent, the resulting residue was subjected to a gel-permeation chromatography (JAI polystyrene-gel columns 1H + 2H, eluted with CS2, detected with 278 nm absorption) to afford 1 (0.19 g, 29%) as yellow solids. The crude products were isolated as pink solids. The crude products were purified by a solvent was evaporated, and the resulting residue was extracted with CS2 (200 ml) and filtered through Celite. The solvent was removed from the filtrate and the residue was roughly separated by flash column chromatography eluted with CS2 after a 6 time recycle to afford 2.0 mmol) in THF–hexane (4.0 ml) at temperature was allowed to rise up to the resulting solution was stirred for 1 h at the mixture was cooled again to temperature. After the addition of MeOH (5.0 ml), the reaction mixture was allowed to warm up to room temperature. cis-2 (0.43 g, 1.1 mmol) in dry THF (3.0 ml) was added rapidly, and the reaction mixture was allowed to warm up to room temperature. After the addition of MeOH (5.0 ml), the solvent was evaporated, and the resulting residue was extracted with CS2 (200 ml) and filtered through Celite. The solvent was removed from the filtrate and the residue was roughly separated by flash column chromatography on silica gel with Cs2. At this stage, compound 3 (0.015 g) was isolated as pink solids. The crude products 2 containing unidentified by-products were purified by a gel-permeation chromatography eluted with Cs2–THF (1:1, v/v) to give cis and trans mixture 2 (0.074 g, 14%) as orange solids. Subsequently, the small amounts of cis and trans isomers 2 were separated by a gel-permeation chromatography eluted with Cs2 after a 6 time recycle for the characterization of its basic properties. The cis/trans ratio was nearly 1/5 from the isolated yields. Slow evaporation of the Cs2–hexane (1:1, v/v) solution of cis-2 and the Cs2–CH2Cl2 (1:1, v/v) solution of trans-2 gave orange block and orange plate suitable for X-ray analysis, respectively. Selected data: cis-2, Mp. 257–270 °C (decomp.); 1H NMR (300 MHz; CDCl3/CS2 = 1/1), δ 7.15 (s, 4H), 1.44 (s, 6H); m/z (FAB-MS), 1056 (M+); Anal. Caled for C14H10Sb2Se8: C, 17.00; H, 0.99; Se, 68.76. Found: C, 17.01, H, 0.97; Se, 68.53.

12. To a solution of TsF (0.4 g, 1.0 mmol) in dry THF (8 ml) was slowly added a solution of freshly prepared LDA (2.0 mmol) in THF–hexane (4.0 ml) at −90 °C, and the temperature was allowed to rise up to −78 °C and the resulting solution was stirred for 1 h at −78 °C. Then the mixture was cooled again to −100 °C, and MeSbI2 (0.43 g, 1.1 mmol) in dry THF (3.0 ml) was added rapidly, and the reaction mixture was allowed to warm up to room temperature. After the addition of MeOH (5.0 ml), the solvent was evaporated, and the resulting residue was extracted with Cs2 (200 ml) and filtered through Celite. The solvent was removed from the filtrate and the residue was chromatographed with Cs2 and Cs2–THF, 1H NMR (300 MHz; CDCl3/CS2 = 1/1), δ 7.16 (s, 4H), 1.40 (s, 6H); m/z (FAB-MS), 1056 (M+). Compound 3, mp. 167–168 °C (decomp.); 1H NMR (300 MHz; CDCl3/CS2 = 1/1), δ 7.36 (s, 2H), 7.14 (d, 4H), 1.32 (s, 3H); m/z (FAB-MS), 919 (M+); Anal. Caled for C14H10Sb2Se8; C, 7.00; H, 0.99; Se, 68.76. Found: C, 17.01, H, 0.97; Se, 68.53.

13. Crystal data for 1: C13H9Sb2, MW = 543.44, monoclinic, space group Pn, a = 13.233(10), b = 5.648(4), c = 13.663(10) A˚ , β = 114.70(1)°, V = 927(1) A˚ 3, T = 297 K, μ = 2.376 mm−1, Z = 2, 7601 reflections measured, 3797 unique (Rint = 0.036). Final R indices [I > 2σ(I)]: R1 = 0.0335, wR2 = 0.0880. For cis-2: C14H10Sb4Se16, MW = 1053.41, orthorhombic, space group Pnma, a = 10.321(5), b = 13.085(7), c = 16.696(9) A˚ , V = 2254(2) A˚ 3, T = 297 K, μ = 15.306 mm−1, Z = 4, 18441 reflections measured, 2687 unique (Rint = 0.0404). Final R indices [I > 2σ(I)]: R1 = 0.0275, wR2 = 0.0796. For trans-2: C28H20Sb4Se16CS2, MW = 2182.96, triclinic, space group P1, a = 8.990(3), b = 11.611(4), c = 11.839(4) A˚ , α = 97.738(6)°, β = 90.959(5)°, γ = 96.954(4)°, V = 1214.9(6) A˚ 3, T = 297 K, μ = 14.293 mm−1, Z = 1, 9892 reflections measured, 5491 unique (Rint = 0.0494). Final R indices [I > 2σ(I)]: R1 = 0.0759, wR2 = 0.2154. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers CCDC 280850–280852.