X-Ray Crystal Structures and Properties of Tris(tetrathiafulvalenium) Tetrachlorodimethylstannate(IV) and Tetrathiafulvalenium Trichlorodimethylstannate(IV) [†]

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A single-crystal X-ray structure analysis has been performed for $[ttf]_3[SnMe_2Cl_4]$ obtained by electrocrystallization of tetrathiafulvalene (ttf) in the presence of $SnMe_2Cl_2$ and $[NEt_4]Cl$ in acetonitrile. The crystals are tetragonal, space group $P4/mbm$, with $Z = 2$, $a = 11.725(1)$, and $c = 12.194(3)$ Å. Block-diagonal least-squares refinement, based on 847 independent reflections with $|F_o| > 3\sigma(F)$, converged at $R = 0.052$. The ttf molecules exist as trimers, located perpendicularly to each other, forming a two-dimensional network with somewhat close sulphur–sulphur contacts among the trimers. The $[SnMe_2Cl_4]^{2-}$ anions are disordered with respect to the Sn–Me and Sn–Cl bonds. An X-ray structure analysis of $[ttf][SnMe_2Cl_3]$ obtained by the reaction of $[ttf]_3[BF_4]_2$ with $SnMe_2Cl_2$ and $[NEt_4]Cl$ in acetonitrile has shown that both $ttf^{\bullet+}$ radical cations and $[SnMe_2Cl_3]^-$ anions exist as dimers. The crystals are triclinic, space group $P\bar{1}$, with cell dimensions $a = 9.348(1)$, $b = 10.475(1)$, $c = 8.451\,7(9)$ Å, $\alpha = 92.47(1)$, $\beta = 102.53(1)$, $\gamma = 109.27(1)°$, and $Z = 2$. Least-squares refinement, based on 3 196 independent reflections with $|F_o| > 3\sigma(F)$, converged at $R = 0.048$.

Recently we reported the preparations and electrical properties of some tetrathiafulvalene (ttf) salts of halogenostannate(IV) anions and the X-ray crystal structure of $[ttf]_3[SnCl_6]$.[1] This salt contains a two-dimensional layer structure of ttf molecules with intermolecular sulphur–sulphur van der Waals contacts, and exhibits a rather small resistivity (410 Ω cm at 25 °C as a compacted sample). Thus, an electrical current path through the layer has been suggested. The $[ttf]_3[SnMe_2Cl_4]$ salt also has been reported to display a smaller resistivity (16 Ω cm at 25 °C as a compacted sample) than $[ttf]_3[SnCl_6]$.[1]

Here, we have undertaken to clarify the mechanism of electrical conduction in the ttf salts of chlorostannate(IV) anions based on a structural viewpoint. This paper reports the X-ray crystal structures of $[ttf]_3[SnMe_2Cl_4]$ and $[ttf][SnMe_2Cl_3]$. Their electrical resistivities as well as electronic reflectance and X-ray photoelectron spectra are discussed.

Experimental

Preparation of $[ttf]_3[SnMe_2Cl_4]$ (**1**) *and* $[ttf][SnMe_2Cl_3]$ (**2**).—Salts (**1**) and (**2**) were prepared by the reaction of $[ttf]_3[BF_4]_2$[2] (0.14 g, 0.18 mmol) in acetonitrile (60 cm^3) with $SnMe_2Cl_2$ (1.23 g, 3.6 mmol) and $[NEt_4]Cl$ (0.075 g, 0.45 mmol) in the same solvent (15 cm^3) under a nitrogen atmosphere. The mixture was allowed to stand at room temperature for 3 d, giving a mixture (0.057 g) of black square plates of salt (**1**) (density 1.79 g cm^{-3}) and black cubes of (**2**) (density 2.02 g cm^{-3}), which were readily separated in 1,3-dibromopropane (density 1.98 g cm^{-3}). The crystals of (**1**) (0.048 g) and of (**2**) (0.009 g) were collected, washed with diethyl ether, and dried *in vacuo*. Salt (**1**) obtained here was identical with black square plates afforded by the electrocrystallization of ttf[3] in the presence of $SnMe_2Cl_2$ and $[NEt_4]Cl$ as electrolyte in acetonitrile.[1]

Table 1. Summary of crystal data and experimental details of the structural study of salts (**1**) and (**2**)

	Salt (**1**)	Salt (**2**)
Formula	$C_{20}H_{18}Cl_4S_{12}Sn$	$C_8H_{10}Cl_3S_4Sn$
Crystal system	Tetragonal	Triclinic
Space group	$P4/mbm$	$P\bar{1}$
a/Å	11.725(1)	9.348(1)
b/Å	11.725(1)	10.475(1)
c/Å	12.194(3)	8.451 7(9)
α/°		92.47(1)
β/°		102.53(1)
γ/°		109.27(1)
U/Å^3	1 676.4(5)	756.7(2)
M	903.6	459.4
Z	2	2
D_c/g cm^{-3}	1.790(1)	2.016(1)
D_m(flotation)/g cm^{-3}	1.79	2.02
Crystal dimensions/mm	0.25 × 0.25 × 0.06	0.40 × 0.24 × 0.20
μ/cm^{-1}	15.2	21.3
$F(000)$	869	446
Scan range/°	$0.9 + 0.34\tan\theta$	$1.0 + 0.35\tan\theta$
2θ limits/°	3—55	4—55
Reflections: total	1 178	3 556
observed $\lvert F_o\rvert > 3\sigma(F)$	847	3 196

Details common to both determinations: Mo-K_α radiation, λ = 0.710 69 Å; graphite monochromator.

Physical Measurements.—Electronic powder reflectance[1] and X-ray photoelectron spectra[4] were recorded as described elsewhere. The electrical resistivities of the salts as compacted samples were measured by the conventional two-probe technique.[1]

X-*Ray Crystal Structures of Salts* (**1**) *and* (**2**).—Cell constants (Table 1) were obtained from a least-squares fit of the angular co-ordinates of 25 reflections with 2θ values from 21 to 36° for salt (**1**) and from 30 to 41° for (**2**), which were measured on

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[†] Tetrathiafulvalene = 2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole.

Supplementary data available: structure factors are available from the editorial office.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[\text{ttf}]_3[\text{SnMe}_2\text{Cl}_4]$ (**1**)							
Sn	0	0	0	C(Me2)	1 761(15)	316(18)	0
Cl(1)	0	0	2 132(2)	C(1)	1 775(7)	2 432(7)	2 421(5)
Cl(2)	2 190(4)	342(5)	0	C(3)	2 076(5)	2 925(5)	4 445(6)
S(1)	1 226(1)	2 007(1)	3 684(1)	C(7)	4 576(12)	423(12)	2 309(35)
S(5)	4 125(2)	875(2)	3 667(7)	C(9)	5 000	0	4 445(39)
(*b*) $[\text{ttf}][\text{SnMe}_2\text{Cl}_3]$ (**2**)							
Sn	3 613.1(3)	877.8(3)	1 372.9(3)	C(1)	5 541(6)	1 092(5)	3 330(6)
Cl(1)	1 756(1)	−222(1)	3 155(2)	C(2)	1 880(6)	−149(5)	−755(6)
Cl(2)	5 535(2)	1 925(2)	−558(2)	C(3)	−1 443(6)	5 185(5)	1 013(6)
Cl(3)	3 254(2)	3 060(1)	1 717(2)	C(4)	−304(6)	6 411(5)	1 483(6)
S(1)	−1 189(1)	3 846(1)	2 016(1)	C(5)	3 519(7)	3 757(6)	6 564(7)
S(2)	1 300(1)	6 501(1)	3 036(2)	C(6)	2 363(8)	2 552(6)	6 088(8)
S(3)	3 253(1)	5 121(1)	5 637(2)	C(7)	604(5)	4 802(4)	3 272(5)
S(4)	745(2)	2 508(1)	4 602(2)	C(8)	1 448(5)	4 202(4)	4 386(5)

computer-controlled Rigaku four-circle diffractometers at Kwansei Gakuin University and at the Crystallographic Research Centre, Osaka University, respectively. Intensity data were collected on the same diffractometers. No intensity decay was observed during the data collections. Data were corrected for background, attenuators, and Lorentz and polarization effects in the usual fashion. No absorption correction was made. Experimental conditions are listed in Table 1.

Although for salt (**1**) three possible tetragonal space groups, *P*$\bar{4}$*b*2, *P*4*bm*, and *P*4/*mbm*, were indicated by oscillation and Weissenberg photographs, the space group *P*4/*mbm* led to a successful analysis, as was the case for $[\text{ttf}]_3[\text{SnCl}_6]$.[1] For salt (**1**) a Fourier map phased on the tin atom at the origin gave the positions of the chlorine and sulphur atoms. The carbon atoms of the SnMe groups, however, were not found in Fourier maps after the following refinements. A block-diagonal least-squares refinement, based on the position of the methyl-carbon atom calculated from the assumed Sn–C distance of 2.1 Å,[5,6] with an occupancy of 0.5, and disorder of methyl groups and chlorine atoms on the *c* plane, converged. Refinement with anisotropic thermal parameters for all the non-hydrogen atoms led to residual indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.052$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.070$. The weighting scheme $1/w = \sigma^2(F_o) + 0.0007(F_o)^2$ was used.

The structure of salt (**2**) was solved by conventional Patterson and Fourier techniques. By assuming the space group *P*$\bar{1}$, refinement with anisotropic thermal parameters for all the non-hydrogen atoms led to $R = 0.048$ and $R' = 0.062$, using the weighting scheme $1/w = \sigma^2(F_o) + 0.001(F_o)^2$. No attempt was made to refine hydrogen atoms at any stage of both analyses. Atomic scattering factors used were taken from ref. 7.

The final atomic co-ordinates with standard deviations for (**1**) and (**2**) are given in Table 2. Crystallographic calculations were performed on an ACOS 900S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. Figures were drawn by the local version of the ORTEP II program.[8]

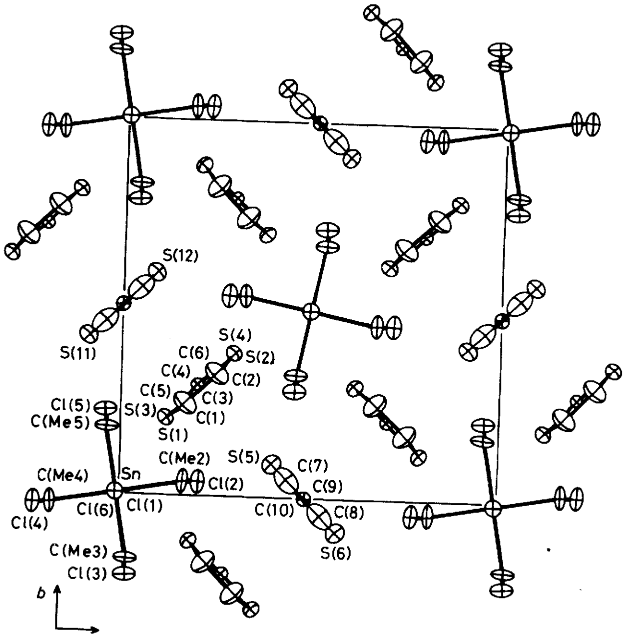

Figure 1. Projection of the crystal structure of $[\text{ttf}]_3[\text{SnMe}_2\text{Cl}_4]$ (**1**) along *c*

Results and Discussion

The Crystal Structure and Properties of Salt (**1**).—Figures 1 and 2 illustrate the crystal structure of salt (**1**) together with the atom-labelling scheme. Bond distances and angles as well as relevant intermolecular atom–atom distances are listed in Table 3. The tin atom of the distorted octahedral $[\text{SnMe}_2\text{Cl}_4]^{2-}$ anion occupies (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,0), as found in $[\text{ttf}]_3[\text{SnCl}_6]$.[1] An interesting feature of the present salt is the presence of disorder of the methyl groups and chlorine atoms which are located on the *c* plane, as is apparent from Figure 1. The $[\text{SnMe}_2\text{Cl}_4]^{2-}$ anion in its tetramethyl- and tetraethyl-ammonium salts was suggested on the basis of vibrational and Mössbauer spectroscopies to assume a *trans* geometry.[9,10] This geometry is also exhibited by $[\text{Hpy}]_2[\text{SnMe}_2\text{Cl}_4]$ (py = pyridine) as confirmed by *X*-ray crystallographic analysis.[11] Thus, in the present salt the linear Me–Sn–Me and Cl–Sn–Cl skeletons seem to be disordered. The Sn–C(Me) [2.098(18) Å] and Sn–Cl distances [2.599(5) and 2.600(3) Å] are close to those of the pyridinium salt [Sn–C(Me) 2.109(9), Sn–Cl 2.603(2), and 2.625(2) Å].[11] The rather long Sn–Cl distances in the pyridinium salt stem from the Cl ••• H–N hydrogen bonding,[11] while the long Sn–Cl bond in salt (**1**) may be due to the

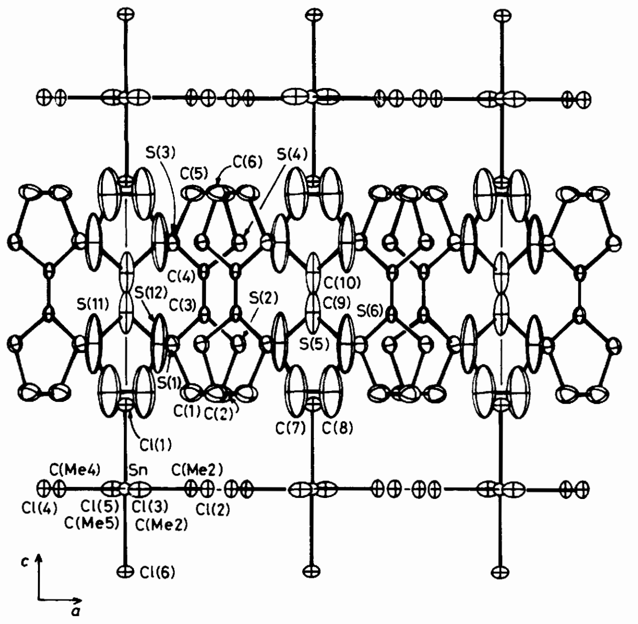

Figure 2. Projection of the crystal structure of $[ttf]_3[SnMe_2Cl_4]$ (**1**) along *b*

Table 3. Selected distances (Å) and angles (°) for $[ttf]_3[SnMe_2Cl_4]$ (**1**) with estimated standard deviations in parentheses

Sn–Cl(1)	2.600(3)	S(5)–C(9)	1.734(26)
Sn–Cl(2)	2.599(5)	C(1)–C(2)	1.346(12)
Sn–C(Me2)	2.098(18)	C(3)–C(4)	1.354(10)
S(1)–C(1)	1.733(7)	C(7)–C(8)	1.404(20)
S(1)–C(3)	1.736(6)	C(9)–C(10)	1.354(67)
S(5)–C(7)	1.818(40)		
S(1) • • • Cl(1)	3.344(2)	S(1) • • • S(11)	3.498(3)
S(1) • • • S(5)	3.649(3)		
Cl(1)–Sn–Cl(2)	90	S(1)–C(3)–C(4)	112.3(5)
Cl(1)–Sn–C(Me2)	90	C(7)–S(5)–C(9)	98.8(15)
Cl(2)–Sn–C(Me2)	1.3(6)	S(5)–C(7)–C(8)	114.3(29)
C(1)–S(1)–C(3)	95.2(4)	S(5)–C(9)–S(6)	113.6(27)
S(1)–C(1)–C(2)	117.2(5)	S(5)–C(9)–C(10)	123.2(13)
S(1)–C(3)–S(2)	115.2(4)		

electrostatic interaction between Cl(1) and S(1) [3.344(2) Å]. This interaction may force the methyl groups to be located on the *c* plane, which results in disorder of these groups and of the chlorine atoms because of the presence of the four-fold axis along the *c* axis.

The arrangement of ttf molecules in the crystal is essentially the same as that found in $[ttf]_3[SnCl_6]$. The ttf molecules constitute a trimeric unit, in which their (cofacial) planes parallel to the *c* axis are almost overlapped and are separated by the same distance. The adjacent trimeric units are perpendicular to each other to satisfy the tetragonal symmetry, and the centres of the ttf molecules occupy the (002) plane forming a layer of ttf (Figure 2).

The ttf molecules at the ends within the trimeric unit are almost planar, with C(3), C(4), and the sulphur atoms 0.03—0.08 Å below (toward the central molecule) and the other carbon atoms 0.07 Å above the least-squares best plane. All the atoms of the central ttf molecule have extremely large thermal parameters. This is due to the fact that this molecule is rather loosely located compared with the other two ttf molecules in the trimeric unit which are more rigidly positioned through the sulphur–chlorine electrostatic interaction mentioned above. Although the bond distances in the central ttf molecule are not precisely determined because of the large thermal parameters of the atoms, those in the two other ttf molecules are very close to the corresponding distances in $[ttf]_3[SnCl_6]$. The C(3)–C(4) distance [1.354(10) Å] is almost the same and C(3)–S(1) [1.736(6) Å] is shorter compared with those [1.349(3) and 1.752(2) Å, respectively] of neutral ttf.[12] The interplanar spacing within the trimer is 3.499(2) Å, which is also very close to that of $[ttf]_3[SnCl_6]$ [3.493(2) Å]. These values are longer than interplanar spacings of the $ttf^{\bullet +}$ radical cation dimer (3.34—3.43 Å) in [ttf]Br,[13] $[ttf]I_3$,[14] $[ttf][ClO_4]$,[15] and $[ttf][HgCl_3]$[16] and shorter than those (3.554—3.607 Å) of mixed-valence ttf salts having an eclipsed columnar structure, such as $[ttf]Br_{0.76}$,[17] $[ttf]I_{0.71}$,[18] and $[ttf][SCN]_{0.57}$.[19]

The closest sulphur–sulphur distance between the adjacent ttf trimer units is 3.649(3) Å, which is not only somewhat shorter than the sum of the van der Waals radii of sulphur atoms (3.70 Å)[20] but also shorter than that found in $[ttf]_3[SnCl_6]$ (3.705 Å).[1] The difference between the sulphur–sulphur contacts in these two salts may reflect the electrical conduction; the specific resistivity (16 Ω cm at 25 °C as a compacted sample) and the activation energy for conduction (0.028 eV) obtained for salt (**1**) are appreciably smaller than those (410 Ω cm, 0.23 eV) for $[ttf]_3[SnCl_6]$.[1] Such a correlation supports the existence of electrical conduction through the two-dimensional layer consisting of ttf trimers with the network due to the sulphur–sulphur contacts.

Table 4. Binding energies (eV) of the Sn $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ electrons of some chlorostannate(IV) salts observed in *X*-ray photoelectron spectra

Salt	Sn $3d_{\frac{3}{2}}$	Sn $3d_{\frac{5}{2}}$
$[ttf]_3[SnMe_2Cl_4]$ (**1**)	494.0	485.5
$[\overline{S(CH_2)_2SC}{=}NMe_2]_2[SnMe_2Cl_4]$[a]	494.3	486.0
$[ttf]_3[SnCl_6]$[b]	493.8	485.5
$[NBu^n{}_4]_2[SnCl_6]$[b]	495.0	486.5
$[ttf][SnMe_2Cl_3]$ (**2**)	493.9	485.3
$[\overline{S(CH_2)_3SC}{=}NMe_2]_2[SnMe_2Cl_4]$[c]	494.5	486.0

[a] T. Tanaka and T. Abe, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 569. [b] Ref. 1. [c] T. Tanaka, K. Tanaka, and T. Yoshimitsu, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 112.

The S(1)–Cl(1) distance [3.344(2) Å] also is shorter than the sum of the van der Waals radii of sulphur and chlorine (3.65 Å), indicating electrostatic interaction between these atoms, as in $[ttf]_3[SnCl_6]$.[1] Table 4 lists the binding energies of Sn $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ electrons for the chlorostannate(IV) anion salts as determined from *X*-ray photoelectron spectra. The binding energies for salt (**1**) and $[ttf]_3[SnCl_6]$ are smaller than those for $[\overline{S(CH_2)_3SC}{=}NMe_2]_2[SnMe_2Cl_4]$ and $[NBu^n{}_4]_2[SnCl_6]$, respectively. This means that the tin atoms in the ttf salts are more reduced than in the latter salts, suggesting a partial, although slight, transfer of negative charge from $ttf^{\bullet +}/ttf^0$ to the chlorostannate(IV) anions. This is consistent with the mentioned sulphur–chlorine contacts.

The Crystal Structure and Properties of Salt (**2**).—A projection of the unit-cell contents of salt (**2**) is shown in Figure 3. The crystal structure consists of dimeric units of ttf and of $[SnMe_2Cl_3]^-$. The bond distances, angles, and selected intermolecular atom–atom distances are summarized in Table 5. The ttf molecule is almost planar, with all the sulphur atoms

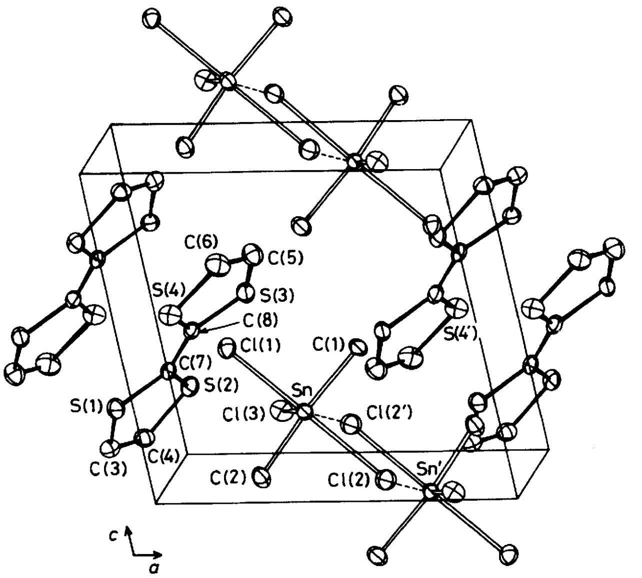

Figure 3. Projection of the crystal structure of [ttf][SnMe$_2$Cl$_3$] (**2**) along the *c** axis

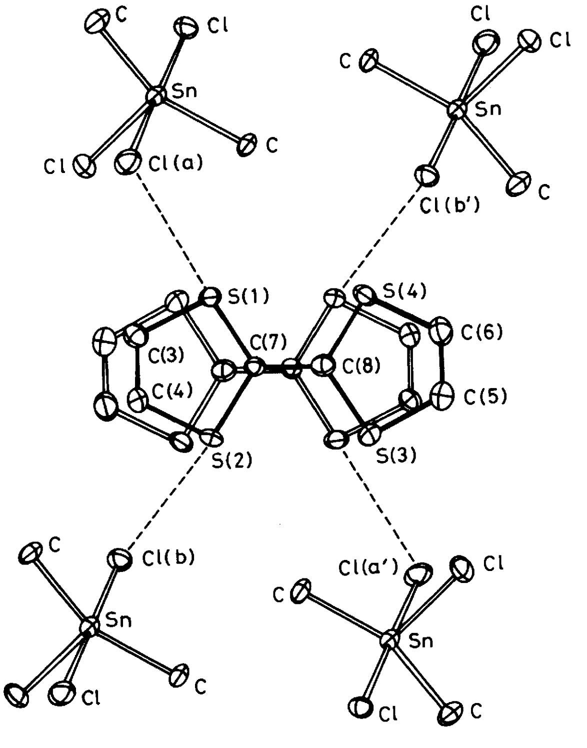

Figure 4. Molecular overlap of the (ttf)$_2{}^{2+}$ dimer and sulphur–chlorine interactions in [ttf][SnMe$_2$Cl$_3$] (**2**)

Table 5. Selected distances (Å) and angles (°) for [ttf][SnMe$_2$Cl$_3$] (**2**) with estimated standard deviations in parentheses

Sn–Cl(1)	2.564(1)	S(2)–C(7)	1.718(4)
Sn–Cl(2)	2.687(2)	S(3)–C(5)	1.720(7)
Sn–Cl(3)	2.432(2)	S(3)–C(8)	1.720(4)
Sn–C(1)	2.108(5)	S(4)–C(6)	1.730(7)
Sn–C(2)	2.106(4)	S(4)–C(8)	1.710(4)
S(1)–C(3)	1.726(6)	C(3)–C(4)	1.346(6)
S(1)–C(7)	1.722(4)	C(5)–C(6)	1.338(8)
S(2)–C(4)	1.738(5)	C(7)–C(8)	1.400(7)
S(1) • • • Cl(a)	3.292(8)	S(2) • • • Cl(b)	3.311(7)
Sn • • • Cl(2′)	3.367(6)		
Cl(1)–Sn–Cl(2)	177.57(5)	S(3)–C(8)–C(7)	122.2(3)
Cl(1)–Sn–Cl(3)	93.2(1)	S(4)–C(8)–C(7)	122.2(3)
Cl(2)–Sn–Cl(3)	89.0(1)	C(3)–S(1)–C(7)	94.9(2)
Cl(1)–Sn–C(1)	89.8(2)	C(4)–S(2)–C(7)	94.6(2)
Cl(1)–Sn–C(2)	90.6(2)	C(5)–S(3)–C(8)	95.4(2)
Cl(2)–Sn–C(1)	90.7(2)	C(6)–S(4)–C(8)	95.1(2)
Cl(2)–Sn–C(2)	87.9(2)	S(1)–C(7)–S(2)	116.3(3)
Cl(3)–Sn–C(1)	102.4(2)	S(1)–C(3)–C(4)	117.1(4)
Cl(3)–Sn–C(2)	103.2(2)	S(2)–C(4)–C(3)	117.1(4)
C(1)–Sn–C(2)	154.2(2)	S(3)–C(8)–S(4)	115.6(3)
S(1)–C(7)–C(8)	121.0(3)	S(3)–C(5)–C(6)	116.8(5)
S(2)–C(7)–C(8)	122.7(3)	S(4)–C(6)–C(5)	117.1(5)

and C(7) and C(8) 0.008—0.026 Å below (toward the other molecule of the dimer) and the other carbon atoms 0.019—0.028 Å above the least-squares plane. The C(7)–C(8) [1.400(7) Å], C(7)–S(1,2) and C(8)–S(3,4) distances [1.718(4) Å, average], which are sensitive to the oxidation state of the ttf molecule, are similar to the corresponding distances in [ttf][HgCl$_3$] [1.41(1) and 1.71(1) Å][16] and [ttf]I$_3$ [1.382(7) and 1.719(8) Å, respectively].[14] Thus, the ttf molecule in salt (**2**) may exist as the radical cation.

The molecular overlap of the ttf$^{\bullet+}$ radical cation in the dimer is nearly eclipsed with a significant lateral shift (0.621 Å) along the in-plane molecular axis, as illustrated in Figure 4. It has been pointed out that dimeric (ttf)$_2{}^{2+}$ cations prefer an eclipsed overlap configuration.[21–23] A nearly eclipsed overlap mode of the ttf$^{\bullet+}$ radical cation was reported for some salts containing (ttf)$_2{}^{2+}$ dimers, such as those of ClO$_4{}^-$,[15] Br$^-$,[17] and tetracyano-2,5-difluoroquinodimethane.[24] The overlap of the ttf$^{\bullet+}$ radical cations with appreciable lateral shift in the present salt is presumably due to the static interaction between the sulphur atom of ttf and the nearby chlorine atom of the [SnMe$_2$Cl$_3$]$^-$ anion: S(1)–Cl(a) 3.292(8) Å and S(2)–Cl(b) 3.311(7) Å (Figure 4). Each dimer is appreciably separated with the nearest interatomic sulphur–sulphur contact S(2) • • • S(4′) 6.553(3) Å. Such a separation of (ttf)$_2{}^{2+}$ dimers in the crystal is consistent not only with the appearance of a band at 12 100 cm^{-1} in the powder reflectance spectrum assignable to the (ttf)$_2{}^{2+}$ dimer transition[25] but also with a large electrical resistivity (1.3 × 10^7 Ω cm at 25 °C as a compacted sample).

The [SnMe$_2$Cl$_3$]$^-$ anion assumes a distorted trigonal-bipyramidal geometry, which is essentially the same as in its quinolinium salt.[6] Bond distances between the tin and two axial chlorine atoms [2.564(1) and 2.687(2) Å] are significantly longer than the equatorial Sn–Cl bond [2.432(2) Å]. This may be due to the static interaction between the axial chlorine and sulphur atoms, as described above. A transfer of some negative charge from the ttf$^{\bullet+}$ radical cation to the [SnMe$_2$Cl$_3$]$^-$ anion also is suggested from the binding energies of Sn 3*d* electrons (see Table 4). It is noteworthy that two [SnMe$_2$Cl$_3$]$^-$ anions are arranged to form a dimeric unit; a chlorine atom of an adjacent anion is located at a distance of 3.367(6) Å from the tin atom. This configuration around the tin atom is similar to that found for the quinolinium salt [Sn • • • Cl 3.486(7) Å].[6] Such a dimeric geometry was also found in InMe$_2$Cl [In • • • Cl 3.450(9) Å][26] and SnMe$_2$Cl$_2$ (Sn • • • Cl 3.54 Å).[27] The C(1)–Sn–C(2) angle [154.2(2)°] for salt (**2**) is considerably larger than not only the value (120°) expected from the equatorial carbon atoms in the trigonal bipyramidal geometry around the tin atom but also that of the anion of [SnMe$_2$Cl(terpy)][SnMe$_2$Cl$_3$] (terpy = 2,2′:6′,2″-terpyridyl) [140(2)°].[5] This may result from a repulsion between the methyl group of $[SnMe_2Cl_3]^-$ and that of the adjacent anion through dimer formation.

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