Preparation and Properties of Tetrathiafulvalene (ttf) and Tetramethyltetraselenafulvalene † Salts of Tin(IV) Halide Anions and *X*-Ray Crystal Structure of $[ttf]_3[SnCl_6]$ ‡

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Tetrathiafulvalene (ttf) reacts with SnX_4 (X = Cl or Br) in MeCN to give $[ttf]_2[SnX_6]$. The corresponding tetramethyltetraselenafulvalene (tmtsf) salt also is obtained as an acetonitrile solvate, $[tmtsf]_2[SnCl_6]\cdot MeCN$, by the reaction of tmtsf with $SnCl_4$ in MeCN. On the other hand, electrocrystallization of ttf and tmtsf in the presence of SnX_6^{2-} (X = Cl or Br) or $[SnMe_2Cl_3]^-$ in MeCN or in $CHCl_2CH_2Cl$ affords $[ttf]_3[SnX_6]$, $[ttf]_3[SnMe_2Cl_4]$, or $[tmtsf][SnMe_2Cl_3]$. Electrical resistivities of these salts as compacted samples fall in the range 1.6×10^1—9.9×10^4 Ω cm at 25 °C. The stacking of the ttf and tmtsf moieties is discussed on the basis of electronic reflectance spectra. A single-crystal *X*-ray analysis of the salt $[ttf]_3[SnCl_6]$ has revealed a layer structure consisting of ttf trimers. The tetragonal crystal, space group *P4/mbm*, has cell dimensions $a = 11.807(1)$, $c = 11.861(2)$ Å, and $Z = 2$. Block-diagonal least-squares refinement, based on 876 independent reflections with $|F_o| > 3\sigma(F)$, yielded an *R* factor of 0.040.

Tetrathiafulvalene (ttf) is known to react with electron acceptors to give low-dimensional organic compounds with high electrical conductivities.[1] Thus, a variety of ttf salts with organic acceptors such as tetracyanoquinodimethane (tcnq) [1,2] and with simple anions such as Cl^-, Br^-, and ClO_4^- [1,3] has been reported. Rather less attention has, however, been focused on the ttf salts with metal halide anions;[4,5] only a few ttf salts with $CuCl_4^{2-}$, $CuBr_3^-$, $AuCl_2^-$, $AuCl_4^-$, and $HgCl_3^-$ which show a semiconducting property (resistivity, $\rho = 10^2$—10^5 Ω cm) have been prepared so far.[6,7] On the other hand, tetramethyltetraselenafulvalene (tmtsf) salts with the composition $[tmtsf]_2X$, where X is ClO_4, ReO_4, PF_6, AsF_6, and TaF_6, have been reported to exhibit a metallic behaviour and to undergo transition to a superconducting state at *ca.* 1 K.[8] The electrical properties of ttf salts and related compounds may thus be greatly influenced by the nature of the counter anions.

Metal halide anions generally assume several different geometries and oxidation states, and in particular tin(II, IV) halide anions easily undergo redox reactions between tin(II)/tin(IV). It seems, therefore, to be of interest to investigate the structure and electrical properties of salts formed by the reaction of tin(II, IV) halide anions with ttf and analogous donors. This paper reports the synthesis and electrical properties of several ttf and tmtsf salts of tin(IV) halide anions (X = Br or Cl) which can be obtained by electrocrystallization and/or by conventional chemical reactions. The stacking of ttf or tmtsf in the salts has been determined by electronic reflectance spectroscopy and an *X*-ray crystallographic analysis of $[ttf]_3[SnCl_6]$ is described.

Experimental

Materials.—The compounds ttf,[9] tmtsf,[10] and $[ttf]_3[BF_4]_2$ [11] were synthesized and purified according to the literature, as were $[NBu^n_4]_2[SnX_6]$,[12] $[NBu^n_4][SnX_3]$ (X = Cl or Br),[13] $[SCH_2CH_2CH_2SC{=}NMe_2][SnMe_2Cl_3]$,[14] and $[SCH_2CH_2SC{=}NMe_2][SnMe_2Br_3]$.[15] All the synthetic reactions to obtain ttf and tmtsf salts were carried out under dry nitrogen.

$[ttf]_2[SnX_6]$ [X = Cl (1a) *or* Br (1b)]. To an MeCN (20 cm^3) solution of ttf (50 mg, 0.25 mmol) was added $SnCl_4$ (65 mg, 0.25 mmol) in MeCN (1 cm^3). The mixture was allowed to stand in a refrigerator overnight. The resulting precipitate of salt (1a) was filtered off and dried *in vacuo* (yield 88%). Similarly, salt (1b) was obtained by the reaction of $SnBr_4$ with ttf in MeCN (yield 67%).

$[ttf]_3[SnX_6]$ [X = Cl (2a) *or* Br (2b)]. Tetrathiafulvalene (50 mg, 0.25 mmol) was oxidized on a platinum electrode with a constant current (8 μA) in MeCN (15 cm^3) containing $[NBu^n_4]_2[SnCl_6]$ (820 mg, 1.0 mmol) for 14 d. Black plates of salt (2a) developed on both the electrode and the wall of the electrolysis cell and were collected, washed with dry MeCN, and dried *in vacuo* (yield 60% based on ttf). Salt (2b) was obtained similarly by the use of $[NBu^n_4]_2[SnBr_6]$ in place of $[NBu^n_4]_2[SnCl_6]$. These salts were obtained as microcrystals also by the reaction of $[ttf]_3[BF_4]_2$ with $[NBu^n_4][SnX_3]$ (X = Cl or Br) in MeCN.

$[ttf]_3[SnMe_2Cl_4]$ (3). To a hot MeCN (40 cm^3) solution of $[ttf]_3[BF_4]_2$ (100 mg, 0.13 mmol) was added $[SCH_2CH_2CH_2SC{=}NMe_2][SnMe_2Cl_3]$ (110 mg, 0.25 mmol) and $SnMe_2Cl_2$ (56 mg, 0.25 mmol) dissolved in hot MeCN (10 cm^3). The mixture was allowed to stand in a refrigerator overnight to afford black plates of salt (3), which were filtered off and dried *in vacuo* (yield 58%). A similar reaction of ttf with $[SCH_2CH_2SC{=}NMe_2][SnMe_2Br_3]$ and $SnMe_2Br_2$ afforded a known compound $[ttf]Br_{0.7}$.[16] Black plates of salt (3) were also obtained by electrocrystallization of an MeCN (10 cm^3) solution containing ttf (50 mg, 0.25 mmol) and $SnMe_2Cl_2$ (660 mg, 3.0 mmol) as well as $[NEt_4]Cl$ (250 mg, 1.5 mmol).

$[tmtsf]_2[SnCl_6]\cdot MeCN$ (4).—To a hot MeCN (10 cm^3) solution of tmtsf (100 mg, 0.22 mmol) was added $SnCl_4$ (290 mg, 1.1 mmol). After refluxing for 15 min, the solution was allowed to stand in a refrigerator overnight to afford a black precipitate of salt (4), which was filtered off and dried *in vacuo* (yield 49% based on tmtsf). The involvement of MeCN in the crystals was confirmed by the ^1H n.m.r. spectrum and elemental analysis.

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† 2-(1′,3′-Dithiol-2′-ylidene)-1,3-dithiole and 2-(4′,5′-dimethyl-1′,3′-diselenol-2′-ylidene)-4,5-dimethyl-1,3-diselenole.

‡ *Supplementary data available* (No. SUP 23790, 6 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical data and melting points of the salts

	Salt	M.p. (decomp.) (°C)	Analysis[a] (%) C	H
(1a)	[ttf]$_2$[SnCl$_6$]	260	19.6 (19.5)	1.25 (1.1)
(1b)	[ttf]$_2$[SnBr$_6$]	250	14.4 (14.3)	0.95 (0.8)
(2a)	[ttf]$_3$[SnCl$_6$]	235	22.8 (22.9)	1.45 (1.3)
(2b)	[ttf]$_3$[SnBr$_6$]	230	17.85 (17.85)	1.2 (1.0)
(3)	[ttf]$_3$[SnMe$_2$Cl$_4$]	180	26.55 (26.6)	2.15 (2.0)
(4)	[tmtsf]$_2$[SnCl$_6$]·MeCN[b]	170	21.05 (20.85)	2.4 (2.15)
(5)	[tmtsf][SnMe$_2$Cl$_3$]	178	20.7 (20.5)	2.8 (2.6)

[a] Calculated values in parentheses. [b] N, 1.4 (1.1%).

[tmtsf][SnMe$_2$Cl$_3$] (5). Tetramethyltetraselenafulvalene (50 mg, 0.11 mmol) dissolved in CHCl$_2$CH$_2$Cl (10 cm^3) containing [NEt$_4$]Cl (170 mg, 1.0 mmol) and SnMe$_2$Cl$_2$ (440 mg, 2.0 mmol) was electrochemically oxidized under the same conditions as described for salt (2a) to yield black needles of (5), whose composition was confirmed by the ^{1}H n.m.r. spectrum of the salt dissolved in concentrated HNO$_3$ as well as by the elemental analysis.

The elemental analyses and melting points of the ttf and tmtsf salts obtained are summarized in Table 1.

Physical Measurements.—The electrical resistivities of the salts were measured on compacted pellets by the conventional two-probe technique. Electronic absorption spectra in dimethyl sulphoxide were recorded on a Union SM-401 spectrophotometer, electronic powder reflectance spectra with a Hitachi 340 spectrophotometer equipped with a Hitachi NIR (near i.r.) or R-10A (u.v. and visible) integrating sphere unit.

X-*Ray Crystal Structure Analysis.*—Preliminary oscillation and Weissenberg photographs of black plates of salt (2a) prepared by electrocrystallization indicated a tetragonal system and three possible space groups: $P\bar{4}b2$, $P4bm$, and $P4/mbm$. The latter was found to be correct on the basis of the successful analysis. Accurate cell constants were determined by least-squares treatment of the angular co-ordinates of 48 independent reflections with 2θ 20—35°, measured on a Rigaku four-circle automated diffractometer with Mo-K_α (λ = 0.710 69 Å) radiation.

Crystal data. C$_{18}$H$_{12}$Cl$_6$S$_{12}$Sn, (2a), M = 944.4, tetragonal, space group $P4/mbm$, a = 11.807(1), c = 11.861(2) Å, U = 1 653.5(6) Å^3, D_m(flotation) = 1.90 g cm^{-3}, Z = 2, D_c = 1.897(1) g cm^{-3}, F(000) = 928, μ(Mo-K_α) = 16.5 cm^{-1}.

A single crystal with dimensions *ca.* 0.60 × 0.20 × 0.09 mm was used for the data collection. Intensity data were collected by using graphite-monochromatized Mo-K_α radiation and the ω—2θ scan technique at a 2θ scan rate of 4° min^{-1}. The scan width in ω was (1.0 + 0.34tanθ)° and 30-s background counts were taken on either side of each scan. Five standard reflections were monitored before every 50 measurements. No significant intensity variation was observed throughout the data collection. The intensities were corrected for Lorentz and polarization effects, but not for absorption. A total of 1 170 independent intensities in the range 2θ < 55° were measured, of which 876 reflections with $|F_o| > 3\sigma(F)$ were used in the solution and refinement of the structure.

Table 2. Atomic co-ordinates (× 10^4; H, × 10^3) for [ttf]$_3$[SnCl$_6$] (2a) with estimated standard deviations in parentheses

Atom	x	y	z
Sn	0	0	0
Cl(1)	0	0	2 057(2)
Cl(2)	2 036(2)	337(2)	0
S(1)	1 215(1)	2 031(1)	3 641(1)
S(5)	4 130(2)	870(2)	3 628(4)
C(1)	1 772(5)	2 423(5)	2 353(4)
C(3)	2 069(4)	2 931(4)	4 427(6)
C(7)	4 602(8)	398(8)	2 342(15)
C(9)	5 000	0	4 428(14)
H(1)	143(6)	208(6)	167(4)
H(7)	443(10)	57(10)	149(11)

Structure determination. A Fourier map phased by the tin atom at the origin gave the positions of the chlorine and sulphur atoms. Another Fourier map based on these atoms gave the positions of all the carbon atoms. By assuming the space group $P4/mbm$, four cycles of block-diagonal least-squares refinement of the positional and isotropic thermal parameters for tin, chlorine, sulphur, and carbon resulted in $R(=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ = 0.217. Further least-squares cycles with anisotropic thermal parameters converged to R = 0.044. With anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for hydrogen atoms found in a difference-Fourier map, the final four cycles of refinement gave R = 0.040 and $R'\{=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ = 0.054. The weighting scheme $1/w = \sigma^2(F_o) + 0.006(F_o)^2$ was used. The final difference-Fourier map showed no positive maxima > 1 e Å^{-3} except 1.1 e Å^{-3} in the vicinity of the tin atom. Atomic scattering factors for Sn^{4+}, Cl$^-$, and neutral S, C, and H were employed.[17] The final atomic co-ordinates 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 1 and 2 were drawn by the local version of the ORTEP-II program.[18]

Results and Discussion

Reactions of ttf with SnX$_4$ *and of* [ttf]$_3$[BF$_4$]$_2$ *with* SnX$_3^-$ *and* [SnMe$_2$Cl$_3$]$^-$ (X = Cl *or* Br).—The reaction of ttf with SnX$_4$ (X = Cl or Br) gave [ttf]$_2$[SnX$_6$], suggesting the occurrence of a redox reaction (i). This is consistent with a low potential

$$2\text{ttf}^0 + 2\text{SnX}_4 \longrightarrow 2\text{ttf}^{\cdot+} + \text{SnX}_2 + \text{SnX}_6^{2-} \quad \text{(i)}$$

for oxidation of ttf to the ttf$^{\cdot+}$ radical cation [$E^\ominus$ = +0.33 V *vs.* saturated calomel electrode (s.c.e.)].[19] On the other hand, [ttf]$_3$[BF$_4$]$_2$ reacted with SnX$_3^-$ (X = Cl or Br) to afford [ttf]$_3$[SnX$_6$]. The stoicheiometry for the formation of SnX$_6^{2-}$ may be expressed by equation (ii), which involves the

$$2\text{ttf}^{\cdot+} + 4\text{SnX}_3^- \longrightarrow 2\text{ttf}^0 + 3\text{SnX}_2 + \text{SnX}_6^{2-} \quad \text{(ii)}$$

oxidation of SnX$_3^-$ by the ttf$^{\cdot+}$ radical cation, although the reaction mechanism is not known. The [ttf]$_3$[BF$_4$]$_2$ salt formally involves the ttf$^{\cdot+}$ radical cation as well as neutral ttf^0. In addition, [SnMe$_2$Cl$_3$]$^-$ undergoes partial disproportionation to an equilibrium mixture of SnMe$_2$Cl$_2$ and [SnMe$_2$Cl$_4$]$^{2-}$ [equation (iii)].[14] Thus, there may be

$$2[\text{SnMe}_2\text{Cl}_3]^- \rightleftharpoons \text{SnMe}_2\text{Cl}_2 + [\text{SnMe}_2\text{Cl}_4]^{2-} \quad \text{(iii)}$$

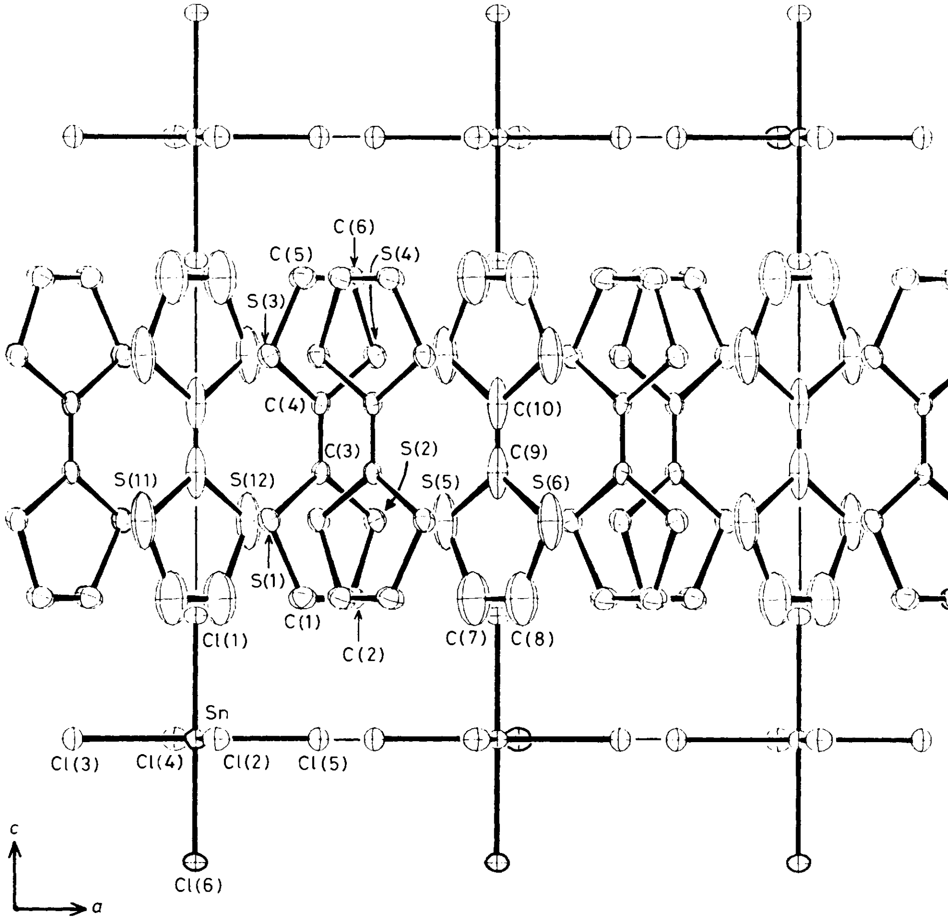


Figure 1. Crystal structure of [ttf]$_3$[SnCl$_6$] (2a) projected along *b*

several possible products of the reaction of [ttf]$_3$[BF$_4$]$_2$ with [SnMe$_2$Cl$_3$]$^-$, such as [ttf][SnMe$_2$Cl$_3$] and [ttf]$_2$-[SnMe$_2$Cl$_4$]. The reaction in the presence of SnMe$_2$Cl$_2$, however, gave [ttf]$_3$[SnMe$_2$Cl$_4$]. The isolation of such a single product may be due to its low solubility in MeCN compared with other possible products. It is therefore expected that products with different compositions will be isolated when the reaction is conducted under other conditions, such as a different solvent or synthetic method. Thus, [tmtsf][SnMe$_2$Cl$_3$] was obtained by electrocrystallization.

X-*Ray Crystal Structure of Salt* (2a).—Figures 1 and 2 show the crystal structure of salt (2a) projected along the *b* and *c* axes, respectively, together with the atom labelling. The bond distances and angles as well as selected contact distances are listed in Table 3. The octahedral SnCl$_6$$^{2-}$ anion is located on (0,0,0) and on ($\frac{1}{2}$,$\frac{1}{2}$,0). The Sn–Cl distances [2.437(2), 2.439(2) Å] are slightly longer than those (2.402—2.423 Å)[20] reported for other salts with this anion such as K$_2$[SnCl$_6$] and [NH$_4$]$_2$[SnCl$_6$]. The ttf molecules are arranged so that their planes are perpendicular to the *c* plane. Since the (220) plane is a crystallographic mirror, the ttf molecules constitute a trimeric unit with the parallel planes separated by the same distance and adjacent trimers perpendicular to each other to satisfy the tetragonal symmetry. The (002) plane also is a mirror. Thus, the centres of the ttf molecules are located on this plane to form a layer of ttf (Figure 1). Although the central ttf molecules within the trimer are strictly planar, the remaining two molecules deviate by +0.02 Å for all the sulphur atoms and by −0.01 Å for all the carbon atoms from the mean plane. The interplanar spacing within the trimer is 3.490 Å, which is almost equal to the closest intermolecular sulphur–sulphur distance, but longer than the interplanar distance of the ttf$^{\cdot+}$ radical cation dimer in [ttf]Br (3.34 Å),[3] [ttf]I$_3$ [3.40(1) Å],[21] and [ttf]ClO$_4$ (3.41 Å).[22] The spacing between the ttf planes, however, is somewhat shorter than those of other mixed-valence ttf salts with columnar structures; 3.588(4) Å for [ttf]Cl$_{0.92}$,[23] 3.572(2) Å for [ttf]Br$_{0.71-0.76}$,[16] and 3.554 Å for [ttf]I$_{0.71}$.[24] The short interplanar distance in the present salt may be due to the formation of a ttf trimer with no columnar structure. Some information about the oxidation state of the ttf molecules is obtainable from their charge-sensitive parameters. The structural data of salt (2a) and some other ttf salts are listed in Table 4, which reveals that the exocyclic C=C double bond (a) is lengthened, whereas the C–S bonds (b) are shortened compared with those in neutral ttf. These bond distances in salt (2a) are close to those in [ttf][tcnq] and [ttf]I$_{0.71}$, suggesting partial oxidation of the ttf molecules in (2a).

The closest sulphur–sulphur distance between adjacent ttf trimers located perpendicular to each other is 3.705 Å, very close to the sum of the van der Waals radii (3.70 Å).[25] Thus, the electrical conduction in salt (2a) (resistivity: 410 Ω cm at 25 °C, see later) may at least occur through the layer consisting of ttf trimers which form a network through the sulphur–sulphur contacts.

The closest sulphur–chlorine distance is 3.367(2) Å which is shorter than the sum of the van der Waals radii (3.65 Å).[25]

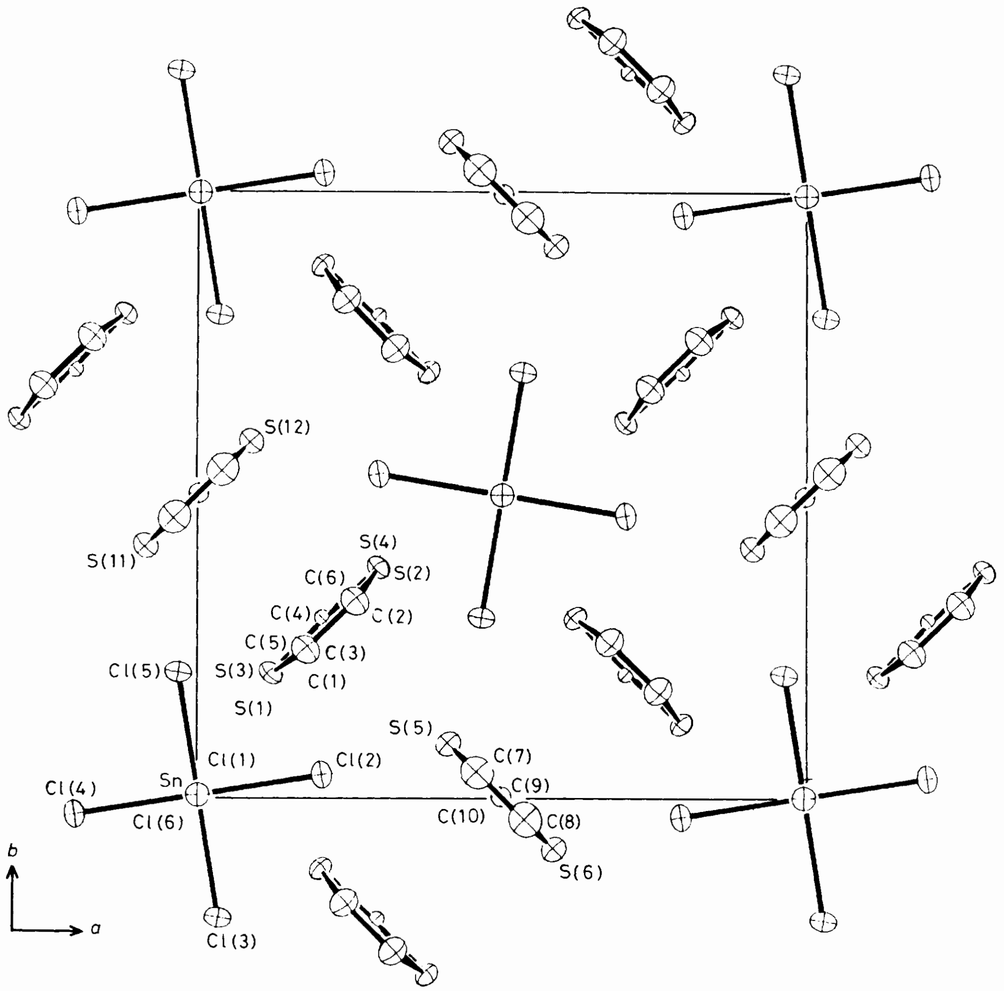


Figure 2. Crystal structure of $[\mathrm{ttf}]_3[\mathrm{SnCl_6}]$ (2a) projected along *c*

Table 3. Selected distances (Å) and angles (°) for $[\mathrm{ttf}]_3[\mathrm{SnCl_6}]$ (2a) with estimated standard deviations in parentheses

Sn–Cl(1)	2.439(2)	S(5)–C(9)	1.736(10)
Sn–Cl(2)	2.437(2)	C(1)–C(2)	1.345(9)
S(1)–C(1)	1.726(6)	C(3)–C(4)	1.360(9)
S(1)–C(3)	1.737(5)	C(7)–C(8)	1.326(10)
S(5)–C(7)	1.717(16)	C(9)–C(10)	1.357(24)
S(1) · · · C(1)	3.367(2)	S(5) · · · S(11)	3.493(2)
S(1) · · · S(5)	3.705(2)		
Cl(1)–Sn–Cl(2)	90	C(1)–S(1)–C(3)	95.1(3)
C(7)–S(5)–C(9)	95.8(6)	S(1)–C(1)–C(2)	117.3(4)
S(1)–C(3)–C(4)	122.5(3)	S(5)–C(7)–C(8)	117.4(13)
S(5)–C(9)–C(10)	123.2(5)	S(1)–C(3)–S(2)	115.0(4)
S(5)–C(9)–S(6)	113.7(10)		

Since the sulphur atoms of the $\mathrm{ttf}^{\cdot +}$ radical cation may be polarized positively [26] and the chlorine atoms of $\mathrm{SnCl_6}^{2-}$ are negatively charged, there should be a significant electrostatic interaction between these atoms. A similar close contact between sulphur and chlorine atoms has been found in $[\mathrm{ttf}][\mathrm{HgCl_3}]$ [3.276(8) Å].[6]

Electronic Spectra.—Figure 3 shows the electronic reflectance spectra of salts (1a) and (2a) together with the absorption spectrum of (1a) in dimethyl sulphoxide (dmso). Although a dmso solution of (2a) exhibits a similar spectrum to that of (1a), the highest-energy band around 30 000 cm^{-1} is more intense. This is due to the involvement of neutral ttf^0 besides the $\mathrm{ttf}^{\cdot +}$ radical cation in salt (2a). The reflectance spectra of salts (1a) and (2a) show bands around 20 000 and 30 000 cm^{-1}, both of which are ascribed to local electronic excitation

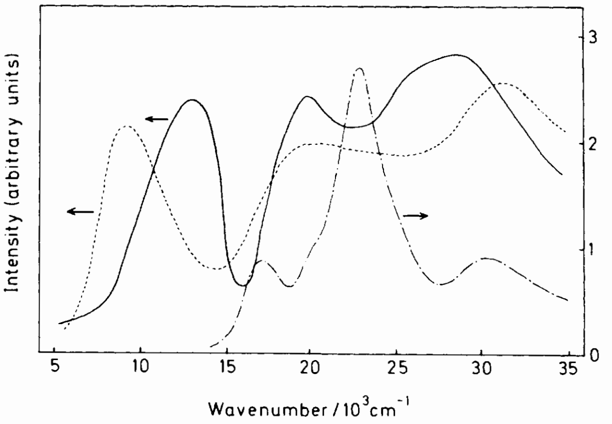
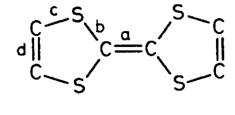


Figure 3. Powder reflectance spectra of salts (1a) (——) and (2a) (– – – –), and absorption spectrum of (1a) in dimethyl sulphoxide (— · — ·)

Table 4. Bond distances (Å) of the ttf molecule [*mmm* (D_{2h}) point-group symmetry imposed]



	ttf[a]	[ttf][tcnq][b]	$[ttf]_3[SnCl_6]$[c]	$[ttf]I_{0.71}$[d]	$[ttf]I_3$[e]	$[ttf][HgCl_3]$[f]
a	1.349(3)	1.369(4)	1.357(24), 1.360(9)	1.350	1.382(7)	1.41(1)
b	1.757(2)	1.743(4)	1.736(10), 1.737(5)	1.732	1.719(8)	1.72(1)
c	1.726(4)	1.736(5)	1.717(16), 1.726(6)	1.721	1.728(11)	1.71(1)
d	1.314(3)	1.323(4)	1.326(10), 1.345(9)	1.336	1.322(11)	1.31(1)

[a] T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 1973, 471. [b] T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr., Sect. B*, 1974, **30**, 763. [c] This work. [d] Ref. 24. [e] Ref. 21. [f] Ref. 6.

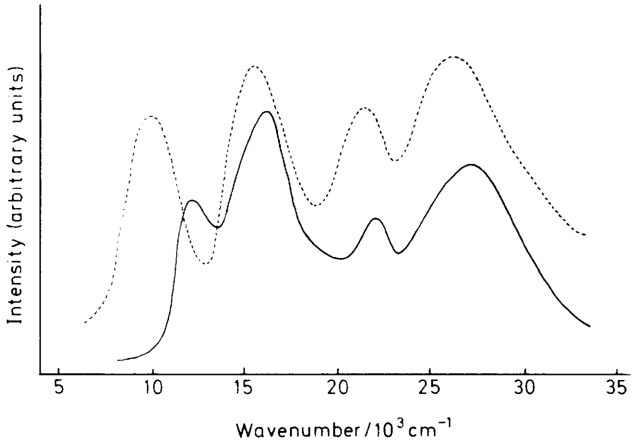


Figure 4. Powder reflectance spectra of salts (4) (——) and (5) (– – – –)

(l.e.) of the $ttf^{\cdot +}$ radical cations or neutral ttf^0, by analogy with the powder absorption spectrum of [ttf]Cl.[27] Another band at 13 100 cm^{-1} of (1a) is reasonably assigned to the charge transfer (c.t.) transition between the $ttf^{\cdot +}$ radical cations, while the band at 9 100 cm^{-1} of (2a) is assigned to the c.t. transition between ttf^0 and $ttf^{\cdot +}$; [27] no c.t. band between the $ttf^{\cdot +}$ radical cations is observed for (2a). Thus, the ttf moiety of salt (2a) in the solid state seems to involve only a $ttf^{\cdot +}/ttf^0$ pair. As described in the preceding section, the ttf moiety in (2a) exists as a trimer in which the two interplanar distances are identical with each other. In view of this result and the electronic spectrum, the stacking of ttf in (2a) should be as $ttf^{\cdot +}/ttf^0/ttf^{\cdot +}$.

The reflectance spectrum of salt (1b) displayed a band at 13 200 cm^{-1} due to the $ttf^{\cdot +}$ dimer, whereas (2b) and (3) exhibited a band at 8 900 and 9 000 cm^{-1}, respectively, assignable to the $ttf^{\cdot +}/ttf^0$ c.t., indicating that the ttf stacking in (2b) and (3) is essentially the same as that in (2a). Preliminary oscillation and Weissenberg photographs of a single crystal of (3) indicate that this salt crystallizes in the tetragonal system with cell constants very close to those of (2a), suggesting that the counter anion should have a *C*4 axis. Thus, the methyl groups of *trans*-$[SnMe_2Cl_4]^{2-}$ may be rotating in the crystal of (3).

Figure 4 illustrates the powder reflectance spectra of salts (4) and (5), in which the lowest-frequency bands, 12 000 cm^{-1} for (4) and 10 000 cm^{-1} for (5), can be assigned to a c.t. transition between the tmtsf$^{\cdot +}$ radical cations, by analogy with the assignment of the spectra of (1a) and (1b). Thus, the tmtsf moiety of these salts in the solid state exists as a dimer, and the dimeric structure of (5) may be more stabilized than that of (4).

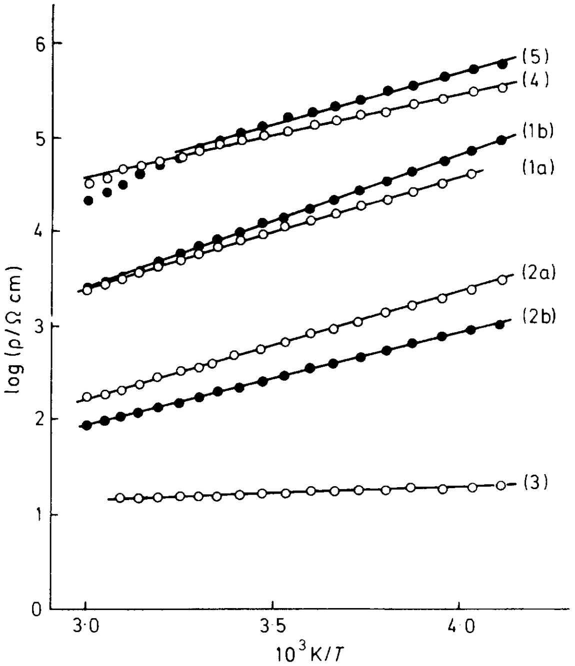


Figure 5. Temperature dependence of the resistivities of the salts

Table 5. Electrical resistivities (ρ) and activation energies (E_a) of the salts; eV ≈ 1.60 × 10^{-19} J

Salt	$\rho_{25\,°C}/\Omega$ cm	E_a/eV
(1a)	6.6×10^3	0.24
(1b)	8.1×10^3	0.28
(2a)	4.1×10^2	0.23
(2b)	1.9×10^2	0.20
(3)	1.6×10	0.028
(4)	7.6×10^4	0.18
(5)	9.9×10^4	0.22

Electrical Resistivity.—The temperature dependence of the resistivities (ρ) of compacted samples of the salts is shown in Figure 5. All the salts behave as a typical semiconductor in the range 240—300 K. The resistivities at 25 °C ($\rho_{25\,°C}$) and activation energies (E_a) calculated from $\rho = \rho_0\exp(E_a/kT)$ are summarized in Table 5. The $\rho_{25\,°C}$ values of salts (1a) and (1b) are of the order of 10^3 Ω cm, which is in the range of resistivities reported for ttf salts with other metal halide anions.[6,7] Such rather small resistivities may reasonably be explained in terms of a columnar stacking of the dimeric ttf$^{\cdot+}$ radical cations evidenced by the reflectance spectra. Salts (2a) and (2b) exhibit smaller resistivities than (1a) and (1b). The *X*-ray crystal structure of (2a) shows that the ttf molecule and its radical cation do not form a one-dimensional column but exist as trimeric units, forming a layer through which two-dimensional electrical conduction seems to occur. Salt (3) exhibits much smaller $\rho_{25\,°C}$ and E_a values than (2a), although a similar ttf stacking may be assumed in these salts, based on the reflectance spectra. The tmtsf salts show rather large resistivities, probably because of the columnar structure of the more distant tmtsf$^{\cdot+}$ dimers.

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Received 3rd *June* 1983; *Paper* 3/899