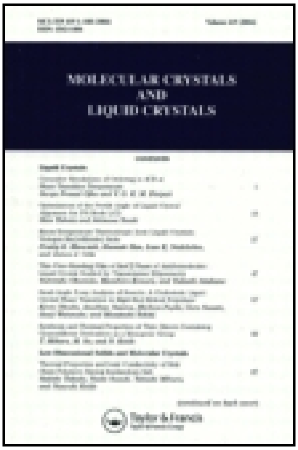

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Crystal Structures and Electrical Properties of TTF Salts with TIN(IV) Chloride Anions

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CRYSTAL STRUCTURES AND ELECTRICAL PROPERTIES OF TTF SALTS WITH TIN(IV) CHLORIDE ANIONS

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Abstract Several TTF salts with tin(IV) chloride anions have been prepared: $[TTF][SnR_2Cl_3]$ (R = Me and Et), $[TTF]_2[SnR_2Cl_4]$ (R = Cl and Ph), $[TTF]_3[SnR_2Cl_4]$ (R = Cl, Me, and Et), and $[TTF]_{3.3}[SnPh_2Cl_4]$. They behave as semiconductors with electrical resistivities (ρ) in the range $1\times(10 - 10^9)$ Ω cm as compacted pellets at 25 °C. X-Ray crystal analyses have revealed that $[TTF][SnMe_2Cl_3]$ ($\rho_{25^\circ C} = 1.3 \times 10^7$ Ω cm) consists of both the dimeric $(TTF^{\cdot +})_2$ and $(SnMe_2Cl_3^-)_2$, and that $[TTF]_3[SnR_2Cl_4]$ (R = Cl, Me, and Et) ($\rho_{25^\circ C} = 16 - 410$ Ω cm) contain the TTF trimeric units which are located perpendicularly to each other, forming a two-dimensional sheet with somewhat close sulfur-sulfur contact among the trimers.

INTRODUCTION

Metal halide anions may be of interest as counter parts to prepare tetrathiafulvalene (TTF) radical cation salts since the stacking of TTF radical cations (and molecules) in the salts may be influenced by the geometry and the formal charge of counter anions. In this connection, TTF radical cation salts with mercury, copper, and gold halide anions have been reported so far.[1,2] Here, we report the preparation and electrical resistivities of several TTF salts with tin(IV) hexachloride and diorganotin(IV) chloride anions. The resistivities are discussed based on electronic reflectance spectra and X-ray crystallographic analysis.

EXPERIMENTAL

The reaction of $[TTF]_3[BF_4]_2$ with $SnCl_4$ in acetonitrile gave $[TTF]_2[SnCl_6]$ (1) and $[TTF]_3[SnCl_6]$ (5). The reactions of $[TTF]_3[BF_4]_2$ with SnR_2Cl_2 (R = Me and Et) in the presence of $[PPh_3CH_2Ph]Cl$ in acetonitrile yielded $[TTF][SnR_2Cl_3]$ (R = Me (2) and Et (3)) and $[TTF]_3[SnR_2Cl_4]$ (R = Me (6) and Et (7)). A similar reaction of $[TTF]_3[BF_4]_2$ with $SnPh_2Cl_2$ afforded $[TTF]_2[SnPh_2Cl_4]$ (4). Electrolysis of TTF in acetonitrile containing $[NBu^n{}_4]_2[SnCl_6]$ or $[PPh_3CH_2Ph]Cl/SnR_2Cl_2$ (R = Me and Et) as a supporting electrolyte afforded also salts 5 – 7. On the other hand, the electrolysis of TTF in acetonitrile in the presence of $[PPh_3CH_2Ph]Cl/SnPh_2Cl_2$ gave $[TTF]_{3.3}[SnPh_2Cl_4]$ (8).

X-Ray crystallographic analyses have been performed for the following salts.

Crystal data:

2: Triclinic, space group $P\bar{1}$, a = 9.348(1), b = 10.475(1), c = 8.4517(9) Å, α = 92.47(1), β = 102.53(1), γ = 109.27(1)°, V = 756.7(2) Å^3, Z = 2.

5: Tetragonal, space group $P4/mbm$, a = 11.807(1), c = 11.861(2) Å, V = 1653.5(6) Å^3, Z = 2.

6: Tetragonal, space group $P4/mbm$, a = 11.725(1), c = 12.194(3) Å, V = 1676.4(5) Å^3, Z = 2.

7: Tetragonal, space group $I4cm$, a = 11.710(3), c = 25.242(7) Å, V = 3461(2) Å^3, Z = 4.

RESULTS AND DISCUSSION

Electrical specific resistivities (ρ) of the salts measured for compacted pellets at 25 °C and activation energies (E_a) calculated from the equation $\rho = \rho_0 \exp(E_a/kT)$ are listed in the Table, which shows also the band maxima of powder electronic reflectance spectra of the salts. All the salts

TABLE Electrical properties and powder electronic reflectance spectra of the TTF salts

Salt	$\rho_{25°C}$	E_a	charge transfer band / 10^3 cm^{-1}	
	Ω cm	eV	$\mathrm{TTF}^{\cdot+}/\mathrm{TTF}^{\cdot+}$	$\mathrm{TTF}^{\cdot+}/\mathrm{TTF}^{0}$
$[TTF]_2[SnCl_6]$ (**1**)[a]	6.6×10^3	0.24	12.5	
$[TTF][SnMe_2Cl_3]$ (**2**)[b]	1.3×10^7	0.31	12.1	
$[TTF][SnEt_2Cl_3]$ (**3**)	2.1×10^8	0.53	12.5	
$[TTF]_2[SnPh_2Cl_4]$ (**4**)	9.0×10^8	0.60	12.8	
$[TTF]_3[SnCl_6]$ (**5**)[a]	4.1×10^2	0.23		9.0
$[TTF]_3[SnMe_2Cl_4]$ (**6**)[b]	1.6×10	0.028		9.0
$[TTF]_3[SnEt_2Cl_4]$ (**7**)	4.2×10	0.13		8.8
$[TTF]_{3.3}[SnPh_2Cl_4]$ (**8**)	2.9×10^3	0.28	12.8	8.8

a) Ref. 3. b) Ref. 4.

behave as typical semiconductors in the temperature range measured; -20 — +40 °C.

The crystal structure of **2** consists of both dimeric $(\mathrm{TTF}^{\cdot+})_2$ and $(SnMe_2Cl_3^-)_2$, as shown in Fig. 1. Since the $(\mathrm{TTF}^{\cdot+})_2$ dimers are located separately, the salt exhibits a large resistivity. The powder reflectance spectrum of **2** exhibits a band around 12100 cm^{-1} which is assignable to the $\mathrm{TTF}^{\cdot+}/\mathrm{TTF}^{\cdot+}$ transition (see Table).[5] Salt **4** also seems to have the crystal structure consisting of the $(\mathrm{TTF}^{\cdot+})_2$ dimers located separately to each other, based on the reflectance spectrum and its large electrical resistivity. On the other hand, the resistivity of **1** is considerably small, although it is likely to contain the dimeric $(\mathrm{TTF}^{\cdot+})_2$ units based on the reflectance spectrum. Thus, the dimeric units seem to construct a columnar structure with somewhat short spacing between them. The X-ray analysis of **1** is now in progress.

The structure of **5** involves $TTF^{+\bullet}/TTF^{0}/TTF^{+\bullet}$ trimeric units with the eclipsed overlap, which are arranged perpenducularly to each other with the sulfur-sulfur contact of 3.705(2) Å between the trimers to form a two-dimensional TTF-sheet.[3] Salt **6** also has essentially the same arrangement of TTF molecules as **5**. They involve the trimeric unit with the eclipsed TTF-overlap having the molecular spacing of 3.499(2) Å. The tin atom of $[SnMe_2Cl_4]^{2-}$ is located on (0,0,0) and(1/2,1/2,0) with a disorder with respect to the methyl groups and chlorine atoms on the *c* plane (Fig. 2). Furthermore, this salt contains somewhat short sulfur-sulfur contact (d = 3.649(2) Å) between the trimeric units compared with the sum of the van der Waals radii of sulfur

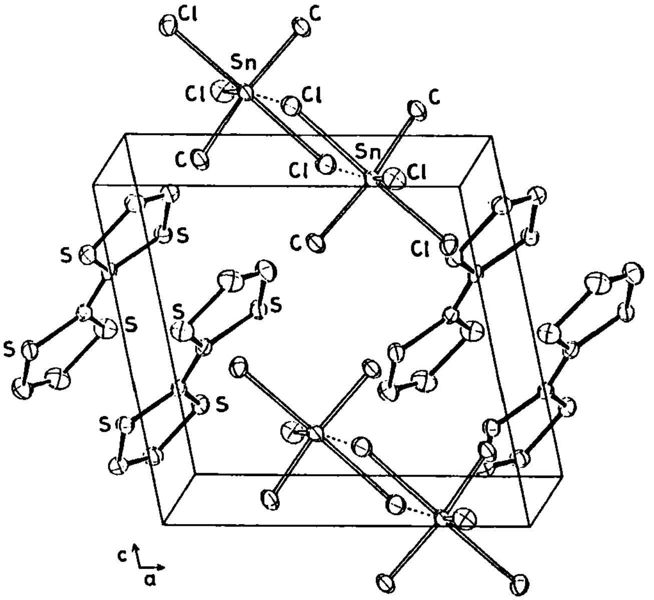

FIGURE 1. Crystal structure of $[TTF][SnMe_2Cl_3]$ (**2**) projected along the b* axis. Thermal ellipsoids are drawn at the 30% probability level.

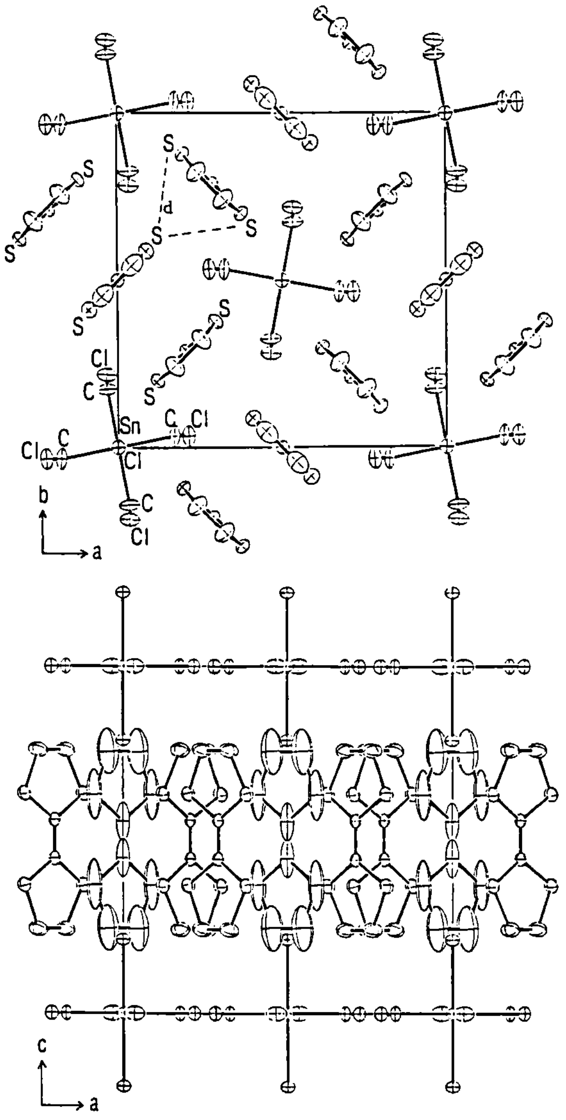

FIGURE 2. Crystal structure of $[TTF]_3[SnMe_2Cl_4]$ (**6**) projected along *c* and *b* axes. Thermal ellipsoids are drawn at the 30% probability level.

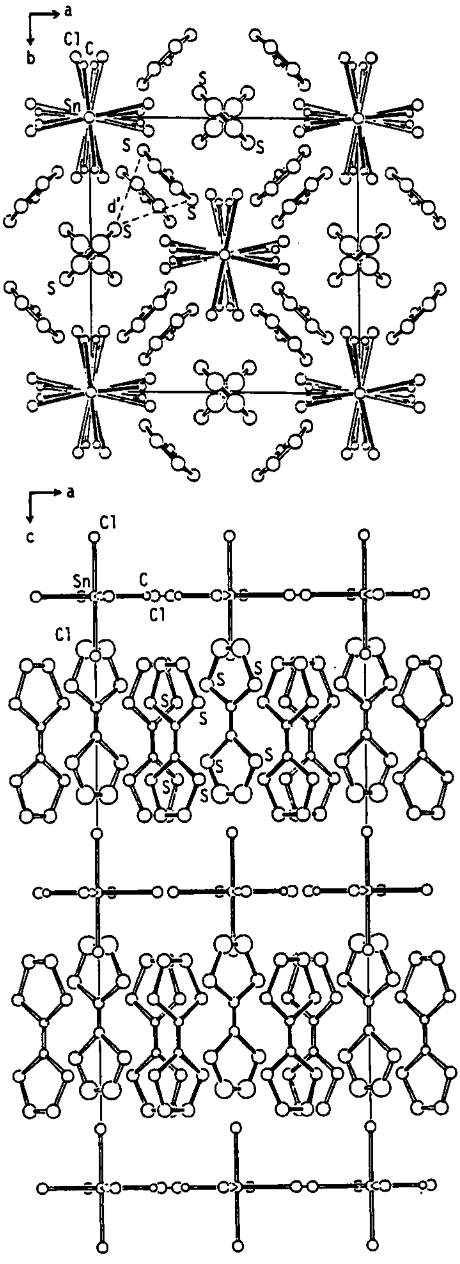

FIGURE 3. Crystal structure of $[TTF]_3$-$[SnEt_2Cl_4]$ (7) projected along c and b axes. Atoms are drawn with the arbitrary isotropic thermal factors.

atoms (3.7 Å), which results in a two-dimensional TTF-sheet parallel to the c plane. Salt 7 also crystallizes in the tetragonal system, and the molecular packing is similar to that of 6, as shown in Fig. 3; the ethyl groups and chlorine atoms are disordered on the c plane and TTF molecules form a trimeric unit with the molecular spacing of 3.46(2) Å. The overlap of cofacial TTF molecules within the unit deviates from the eclipsed mode with a lateral shift (0.79 Å) along the c axis. This salt also constructs a two-dimensional TTF-sheet parallel to the c plane, with sulfur-sulfur contacts (d' = 3.69(2) Å) between the trimers. Salts 5 – 7 exhibit much smaller resistivities than 2. This suggests the electrical conduction through the two-dimensional TTF-sheets in salts 5 – 7. These salts show a broad reflectance band around 9000 cm^{-1} (see Table) due to the electronic transition between $TTF^{+\bullet}$ and TTF^{0}. Moreover, we have revealed a very similar crystal structure consisting of the TTF trimeric units in $[TTF]_3[PtCl_6]$ which was obtained from the diffusion reaction of TTF with $[NBu^n{}_4]_2$-$[PtCl_6]$ in acetonitrile.[7] Thus, metal chloride dianions with an octahedral geometry may stabilize the crystals in the tetragonal system, where the molecular packing consists of the TTF trimeric units.

Salt 8 shows two reflectance bands around 12800 and 8800 cm^{-1}, which are assignable to $TTF^{+\bullet}/TTF^{+\bullet}$ and $TTF^{+\bullet}/TTF^{0}$ transitions, respectively. Thus, 8 may assume a columnar structure, based on its relatively small resistivity. Similar spectral behaviors and resistivities ($\rho_{25°C}$ = $1\times(10^{2}-10^{4})$ Ω cm) have been observed in TTF salts with bis(oxalato)platinate(II) and -cuprate(II) anions[8] and with $[MX_4]^{2-}$ anions (M = Cd and Zn; X = Cl, Br, and I).[9]

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