Electrical Properties and Configurations of TTF and TSF Salts with *cis*-Dialkylbis(oxalato)stannate(IV) Anions

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Abstract

TTF and TSF salts with $[cis\text{-}R_2Sn(C_2O_4)_2]^{2-}$, $[\text{TTF or TSF}]_{2.0-4.0}$ $[cis\text{-}R_2Sn(C_2O_4)_2]$ (R = Me and Et; $C_2O_4^{2-}$ = the oxalate anion) were prepared by the reaction of $[\text{TTF or TSF}]_3[BF_4]_2$ with $[cis\text{-}R_2Sn(C_2O_4)_2]^{2-}$ in acetonitrile, and by electrolysis of TTF or TSF in acetonitrile solutions containing $[NBu^n_4]_2[cis\text{-}R_2Sn(C_2O_4)_2]$ as electrolytes. All the salts behave as typical semiconductors with electrical resistivities of $1\times(10^1–10^7)$ Ω cm at 25°C as compacted pellets. TTF or TSF molecules (D) in the complex salts are stacked in a column with $D^{\dot{+}}/D^{\dot{+}}$ and $D^{\dot{+}}/D^0$ interactions in the solids, as discussed on the basis of electronic reflectance spectra. Electronic interactions between TTF and TSF moieties and the polarized $[cis\text{-}R_2Sn(C_2O_4)_2]^{2-}$ anions were observed in the infrared spectra.

Introduction

Several tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) salts with metal-complex anions have been prepared, and their low-dimensional structures and electrical properties have been investigated [1]. Recently, we have reported the preparation and electrical conductivities of TTF and TSF salts with tris(oxalato)metallate anions (metal = Si(IV), Ge(IV), and Sn(IV)) [2] and bis(oxalato)metallate anions (metal = Pt(II) and Cu(II)) [3]. In the former anions with bulky hexa-coordinate structures, $TTF^{\dot{+}}$ or $TSF^{\dot{+}}$ simple salts containing only the radical cation have mainly been obtained, whereas complex salts containing both the $TTF^{\dot{+}}$ (or $TSF^{\dot{+}}$) radical cation and neutral TTF^0 (or TSF^0) have been obtained in the latter anions with planar structures. On the other hand, polarizable bulky hexa-coordinated anions may be of interest as a counterpart to prepare TTF and TSF salts in the viewpoints of stacking modes of the donor molecules and their interactions with the anions.

This paper reports the preparation of TTF and TSF salts with *cis*-dialkylbis(oxalato)stannate(IV) anions (alkyl = Me and Et) and their electrical resistivities. Configurations of the anions and TTF or TSF stacks and their electronic interactions are discussed on the basis of electronic reflectance, infrared, and X-ray photoelectron spectra.

Experimental

Preparation of $[NBu^n_4]_2[R_2Sn(C_2O_4)_2]$ *(R = Me and Et)*

To an acetone (30 cm^3) solution containing tetrabutylammonium bromide (1.93 g, 6.0 mmol) and oxalatosilver(I) (2.0 g, 6.6 mmol) was added an acetone (10 cm^3) solution of dichlorodimethyltin(IV) (0.66 g, 3.0 mmol) with stirring at 0 °C. The mixture was stirred at room temperature for 4 h, followed by the filtration to remove silver chloride and silver bromide. The filtrate was dried under reduced pressures to give crude $[NBu^n_4]_2[Me_2Sn(C_2O_4)_2]$, which was recrystallized from a mixture of acetone and diethyl ether, affording white crystals (1.4 g), 53% yield, mp. 114 °C. *Anal.* Found: C, 55.44; H, 9.59; N, 3.33%. Calcd. for $C_{38}H_{78}N_2O_8Sn$: C, 56.37; H, 9.71; N, 3.46%.

$[NBu^n_4]_2[Et_2Sn(C_2O_4)_2]$ was similarly prepared by the reaction of a mixture of tetrabutylammonium bromide and oxalatosilver(I) with dichlorodiethyltin(IV) in acetone, 50% yield, mp. 92–94 °C. *Anal.* Found: C, 56.86; H, 10.06; N, 3.23. Calcd. for $C_{40}H_{82}N_2O_8Sn$: C, 57.35; H, 9.87; N, 3.34%.

Preparation of the TTF and TSF salts

An acetonitrile (35 cm^3) solution containing $[TTF]_3[BF_4]_2$ [4] (50 mg, 86 μmol) and $[NBu^n_4]_2[Me_2Sn(C_2O_4)_2]$ (35 mg, 43 μmol) was allowed to stand in a refrigerator for 2 h under nitrogen atmosphere. The resulting dark brown precipitate of $[TTF]_2[Me_2Sn(C_2O_4)_2]\cdot0.67MeCN$ (**1a**) was filtered and dried *in vacuo*, 98% yield based on $[NBu^n_4]_2[Me_2Sn(C_2O_4)_2]$. Similarly, the reaction of $[TTF]_3[BF_4]_2$ with $[NBu^n_4]_2[Et_2Sn(C_2O_4)_2]$ in acetonitrile afforded $[TTF]_{2.5}[Et_2Sn(C_2O_4)_2]\cdot0.2MeCN$ (**2a**) in a 90% yield.

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$[TSF]_2[Me_2Sn(C_2O_4)_2]$ (**3a**) and $[TSF]_2[Et_2Sn(C_2O_4)_2]$ (**4a**) were analogously obtained in 90 and 95% yields, respectively, by the reaction of $[TSF]_3[BF_4]_2$ [5] with the corresponding oxalato–stannate anion salts. The TTF and TSF salts were obtained by electrocrystallization; an acetonitrile (10 cm^3) solution containing TTF (50 mg, 0.24 mmol) and $[NBu^n_4]_2[Me_2Sn(C_2O_4)_2]$ (810 mg, 1.0 mmol) was electrolyzed in a cell consisting of a platinum wire (anode) and a graphite rod (cathode) under a constant current (5 μA) for 3 weeks to afford $[TTF]_{2.5}[Me_2Sn(C_2O_4)_2]\cdot 0.67MeCN$ (**1b**) (20 mg). $[TTF]_{3.3}[Et_2Sn(C_2O_4)_2]$ (**2b**), $[TSF]_{4.0}[Me_2Sn(C_2O_4)_2]$ (**3b**), and $[TSF]_{2.2}[Et_2Sn(C_2O_4)_2]$ (**4b**) were similarly obtained by electrocrystallization from an acetonitrile solution containing TTF or TSF and the oxalato–stannates.

Mole ratios of the $TTF^{+\cdot}$ radical cation to neutral TTF^0 in the salts obtained were determined by both electronic absorption spectra in acetonitrile and elemental analyses. The involvement of solvent molecules in the salts was confirmed by ^1H NMR spectra in conc. HNO_3.

Properties and analytical data for the salts are summarized in Table I.

Physical Measurements

Powder electronic reflectance [2], infrared [6], ^1H NMR [6], and X-ray photoelectron spectra [7] were recorded as described elsewhere. Electrical resistivities were measured as compacted pellets by the conventional two-probe method [8].

Results and Discussion

Electrical Resistivity

All the salts obtained behave as typical semiconductors; plots of log ρ (ρ = specific resistivities) *vs.* $1/T$ gave linear relationships in the 243–308 K range, while some deviations from linearity were observed for all the salts above *ca.* 308 K. The electrical resistivities at 298 K and activation energies (E_a) calculated for the temperature dependence of electrical conduction are summarized in Table II, which also lists relevant wavenumbers in the electronic reflectance and infrared spectra.

The $\rho_{298\ K}$ values of salts **1a**, **3a** and **4a** containing the $TTF^{+\cdot}$ or $TSF^{+\cdot}$ radical cation without neutral TTF^0 or TSF^0 are in the range $1 \times (10^3–10^5)$ Ω cm, similar to those of the TTF- and TSF-tris(oxalato)metallate anions (metal = Si(IV), Ge(IV), and Sn(IV)) [2]. Complex salts which contain both the $TTF^{+\cdot}$ or $TSF^{+\cdot}$ radical cation and neutral TTF^0 or TSF^0 exhibit small resistivities in the order of $1 \times (10^1–10^3)$ Ω cm except for **2a** involving solvent molecules. In particular, salt **3b** containing more neutral TSF^0 molecules displays a smaller resistivity. The $\rho_{298\ K}$ values of the complex salts are compared with the TTF or TSF complex salts with bis(oxalato)-platinate(II) and -cuplate(II) anions [3].

Configuration of the Dialkylbis(oxalato)stannate(IV) Anions (alkyl = Me and Et)

The ^1H NMR spectrum of $[NBu^n_4]_2[Me_2Sn(C_2O_4)_2]$ in chloroform-*d* showed an Sn-methyl proton

TABLE I. Properties and Analyses of the TTF and TSF Salts.

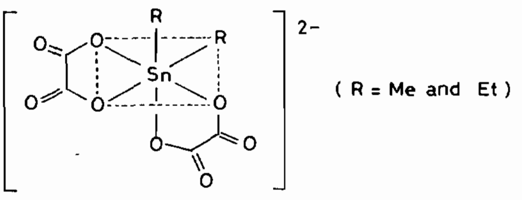
No.	Salt	Color	mp. (dec.)	Found (Calcd.) %		
			(°C)	C	H	N
1a	$[TTF]_2[Me_2Sn(C_2O_4)_2]\cdot 0.67MeCN$	Dark brown	>144	30.77 (30.42	2.42 2.10	0.95 1.11)
1b	$[TTF]_{2.5}[Me_2Sn(C_2O_4)_2]\cdot 0.67MeCN$	Black	>141	31.13 (31.13	2.23 2.11	1.18 1.13)
2a	$[TTF]_{2.5}[Et_2Sn(C_2O_4)_2]\cdot 0.2MeCN$	Dark brown	>141	32.21 (32.23	2.69 2.38	0.32 0.32)
2b	$[TTF]_{3.3}[Et_2Sn(C_2O_4)_2]$	Black	>121	32.16 (32.51	2.65 2.28)	
3a	$[TSF]_2[Me_2Sn(C_2O_4)_2]$	Dark green	>113	19.34 (19.50	1.52 1.27)	
3b	$[TSF]_{4.0}[Me_2Sn(C_2O_4)_2]$	Black	>111	18.20 (19.04	1.45 1.17)	
4a	$[TSF]_2[Et_2Sn(C_2O_4)_2]$	Dark green	>111	20.96 (21.13	1.86 1.60)	
4b	$[TSF]_{2.2}[Et_2Sn(C_2O_4)_2]$	Black	>137	20.92 (20.96	1.83 1.56)	

TABLE II. Electrical Resistivities ($\rho_{298\,K}$), Activation Energies (E_a) and Powder Reflectance and Infrared Spectra of the TTF and TSF salts.

Salt	$\rho_{298\,K}$ (Ω cm)	E_a (eV)	LE band of D[a] (10^3 cm^{-1})			CT band/10^3 cm^{-1}		ν(C=O)[b] (cm^{-1})
						D^{+}/D^{+} [a]	D^{+}/D^{0} [a]	
1a	3.2×10^5	0.30	29.4		18.9	12.8		1640
1b	1.4×10^3	0.20	27.8		19.1	12.8	8.5	1640
2a	2.0×10^6	0.31	29.4		19.9	13.5	8.8	1630
2b	3.4×10^2	0.26	29.4		19.2	12.5	9.1	1630
3a	1.8×10^4	0.28	25.0	22.7	16.4	11.8		1624
3b	8.9×10	0.15	27.8	23.7	16.5	12.2	9.0	1630
4a	6.8×10^3	0.20	27.8	22.2	16.7	11.8		1620
4b	7.2×10^2	0.13	28.6	20.3	16.1	11.8	8.8	1622

[a] D = TTF or TSF. [b] Frequencies of the most intense carbonyl stretching bands of the oxalato ligands, measured in Nujol mulls. *Cf.* 1650 cm^{-1} for $[NBu^n_4]_2[Me_2Sn(C_2O_4)_2]$ and 1640 cm^{-1} for $[NBu^n_4]_2[Et_2Sn(C_2O_4)_2]$.

signal at δ 0.29, which was accompanied with the satellites due to the spin-spin coupling with $^{117/119}Sn$ nuclei [$^2J(^{119}Sn–CH_3) = 78.6$ Hz and $^2J(^{117}Sn–CH_3) \simeq 75.6$ Hz]. The $^2J(^{117/119}Sn–CH_3)$ values of dimethyltin(IV) compounds are known to reflect the s-character of the Sn–C bond [9] which may be related with C–Sn–C angles [10]. The ^2J value obtained here is rather close to those of Me_2SnCl_2 with a tetrahedral geometry (68.9 Hz in carbon tetrachloride [10]), and bis(8-hydroxyquinolinato)-dimethyltin(IV) (71.2 Hz) [11] with the C–Sn–C angle of 110.7° [12]. The value is in contrast to the $^2J(^{119}Sn–CH_3)$ values of *trans*-$Me_2SnCl_2L_2$ [L = pyridine (112.0 Hz) [13], dimethyl sulfoxide (114.8 Hz) [14], hexamethylphosphoric triamide (121.1 Hz) [14]], *trans*-Me_2SnCl_2(N-substituted picolinaldimines) (111.5-114.6 Hz) [15], *trans*-Me_2SnCl_2(phen) (phen = substituted *o*-phenanthrolines (110.8–115.6 Hz) [16], and *trans*-dimethylbis(acetylacetonato)tin(IV) (99.5 Hz) [11, 17]. In view of these results, the present anion reasonably assumes the *cis*-configuration (**I**). The $[Et_2Sn(C_2O_4)_2]^{2-}$ anion exhibited the $^3J(^{119}Sn–CH_3)$ value of 126 Hz (at δ 0.99) in dimethyl sulfoxide-d_6*.



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Configuration of the TTF and TSF Salts

In the electronic reflectance spectra, bands at higher frequencies than 16 000 cm^{-1} observed for all the salts are ascribed to local excitations of the TTF^{+} or TSF^{+} radical cation (D^{+}) as well as the neutral TTF^0 or TSF^0 molecule (D^0) (D = TTF and TSF) [18]. In addition, **1a**, **3a** and **4a** exhibit bands at 12 800, 11 800 and 11 800 cm^{-1} respectively, which are due to the $(TTF^{+})_2$ or $(TSF^{+})_2$ radical cation dimers [19]. Since these salts have fairly large resistivities, the electronic interaction between the neighboring dimers may be small. The remaining salts display a band around 9000 cm^{-1} as well as a band around 12 000 or 13 000 cm^{-1} ascribed to the $(D^{+})_2$ dimers. The former band is assigned to the charge

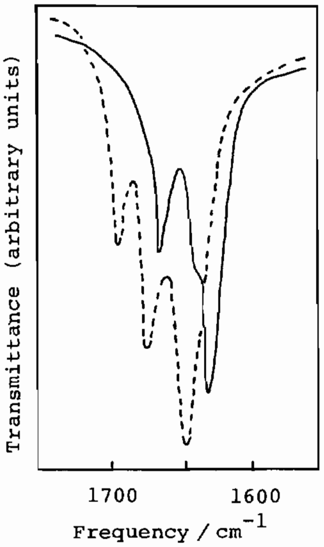

Fig. 1. Infrared spectra of $[NBu^n_4]_2[Me_2Sn(C_2O_4)_2]$ (– – –) and **1a** (——) in Nujol mulls.

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*The $^3J(^{119}Sn–CH_3)$ value was measured for $[PPh_3CH_2Ph)_2[Et_2Sn(C_2O_4)_2]$.

transfer transition between $D^{+\cdot}$ and D^0 [18]. Thus, these salts are suggested to assume a columnar structure containing both $D^{+\cdot}/D^{+\cdot}$ and $D^{+\cdot}/D^0$ arrangements, which is consistent with rather small resistivities of these salts (except for **2a** involving solvent molecules, as mentioned above).

The oxalato-metal complexes exhibit the characteristic three ν(C=O) bands near 1650 cm^{-1} [20]. As shown in Fig. 1, all the ν(C=O) bands of $[NBu^n_4]_2$-$[Me_2Sn(C_2O_4)_2]$ are shifted to low frequencies in **1a**. This is also the case with other TTF salts as well as the TSF salts (Table II), while no low frequency shift of ν(C=O) bands has been observed in the oxalato ligand of TTF– and TSF–$[M(C_2O_4)_3]$ salts (M = Si(IV), Ge(IV) and Sn(IV)) [2]. The low frequency shift of ν(C=O) in the present salts is suggestive of an interaction between negatively polarized carbonyl–oxygen and positively polarized sulfur of the TTF$^{+\cdot}$ radical cation [21]. The carbonyl–oxygen of $[cis\text{-}R_2Sn(C_2O_4)_2]^{2-}$ (R = Me and Et) may be negatively polarized by the electron-donation of the alkyl group in the *trans* position of the oxalato ligand.

Table III summarizes the binding energies of Sn $3d_{3/2}$ and $3d_{5/2}$ electrons of the TTF salts and tetrabutylammonium salts of $[cis\text{-}R_2Sn(C_2O_4)_2]^{2-}$ which were determined by X-ray photoelectron spectroscopy. The binding energies are essentially constant in all the salts, indicating that the interaction between TTF moieties and the $[R_2Sn(C_2O_4)_2]^{2-}$ anions is too weak to change the electronic state of the tin atom.

TABLE III. Binding Energies (eV) of the Sn $3d_{3/2}$ and $3d_{5/2}$ Electrons of some Dialkylbis(oxalato)stannates(IV).

Salt	Sn $3d_{3/2}$	Sn $3d_{5/2}$
$[NBu^n_4]_2[Me_2Sn(C_2O_4)_2]$	494.2	485.7
1a	494.2	485.7
1b	494.2	485.7
3a	494.2	485.7
$[NBu^n_4]_2[Et_2Sn(C_2O_4)_2]$	493.6	485.3
2a	493.2	484.8
4a	493.7	485.6

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