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Syntheses and Electrical Resistivities of TTF and TSF Salts with Tris(oxalato)silicate, -germanate, and -stannate

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Several tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) salts of tris(oxalato)silicate, -germanate, and -stannate, $(TTF)_x[M(C_2O_4)_3]\cdot nCH_3CN$ $(x = 2$ *and* $n = 0.5$ *for* $M = Si$ *and Ge, and* $x = 2.8$ *and* $n = 0$ *for* $M = Sn)$ *and* $(TSF)_2[M(C_2O_4)_3]\cdot nCH_3CN$ $(n = 0$ *for* $M = Si$, *Sn and* $n = 0.5$ *for* $M = Ge)$, *have been prepared by the reaction of* $(TTF)_3(BF_4)_2$ *or* $(TSF)_3(BF_4)_2$ *with* $[R_4N]_2[M(C_2O_4)_3]$ $(R = Et$ *or n-Bu) in acetonitrile.*

Electrocrystallization for the $TTF-[Et_4N]_2[Sn(C_2O_4)_3]$ *and* $TSF-[Et_4N]_2[Ge(C_2O_4)_3]$ *systems in acetonitrile afforded* $(TTF)_{2.8}[Sn(C_2O_4)_3]\cdot 0.5CH_3CN$ *and* $(TSF)_2[Ge(C_2O_4)_3]$, *respectively. Electrical resistivities of the TTF salts as compacted samples at 25 °C fall in the range* 10^4-10^5 Ω *cm and those of the TSF salts in the range* 10^3-10^4 Ω *cm.*

Electronic reflectance spectra of the TTF and TSF salts show bands at 13300–13600 cm^{-1} *and 11400–12500* cm^{-1} *due respectively to the* $(TTF^{\dagger})_2$ *and* $(TSF^{\dagger})_2$ *dimers. In addition,* $(TTF)_{2.8}[Sn(C_2O_4)_3]$ *exhibited a band at 8900* cm^{-1}, *ascribed to a charge transfer transition between neutral TTF and the* $TTF^{\dagger}$ *radical cation. All the salts display weakly diamagnetic properties, consistent with the appearance of anisotropic weak ESR signals attributable to the* $TTF^{\dagger}$ *and* $TSF^{\dagger}$ *radical cations.*

Introduction

Low-dimensional organic crystals containing the radical cations of tetrathiafulvalene (TTF), tetraselenafulvalene (TSF), and their derivatives have been investigated extensively [1]. Among these, tetramethyltetraselenafulvalene (TMTSF) salts with cubic inorganic anions, $(TMTSF)_2X$ ($X^- = ClO_4^-$, ReO_4^-, PF_6^-, SbF_6^-, and TaF_6^-), have been shown to exhibit metallic conductivities and to transfer to a superconducting state around 1 K under atmospheric or high pressures [2]. On the other hand, there have been reported some TTF salts with planar metal chelate anions [3–7], such as bis(dithiolene)metal anions, whose electrical resistivities fall in the range of semiconductors more than 1×10^3 Ω cm [3–6]. Thus we have undertaken the present study on TTF and TSF salts with cubic metal chelate anions as no such salts have been reported so far.

This paper reports the preparations and electrical resistivities of TTF and TSF salts with tris(oxalato)metallate anions, $M(OX)_3^{2-}$ ($M = Si$, Ge, and Sn; $OX^{2-} = C_2O_4^{2-}$). The stack of these salts in the crystalline state are discussed on the basis of electronic and ESR spectra, and on magnetic susceptibilities.

Experimental

Materials

Tetrathiafulvalene (TTF) [8], tetraselenafulvalene (TSF) [9], tetrathiafulvalenium tetrafluoroborate, $(TTF)_3(BF_4)_2$ [10], and tetraselenafulvalenium tetrafluoroborate, $(TSF)_3(BF_4)_2$ [11], were prepared according to the literature. Bis(tetrabutylammonium) tris(oxalato)silicate, $[n\text{-}Bu_4N]_2[Si(OX)_3]$, and bis(tetraethylammonium) tris(oxalato)germanate and -stannate, $[Et_4N]_2[Ge(OX)_3]$ and $[Et_4N]_2[Sn(OX)_3]$, were obtained by the modified literature methods [12].

Preparation of Tetrathia- and Tetraselenafulvalenium Tris(oxalato)metallates

An acetonitrile (10 cm^3) solution of $[n\text{-}Bu_4N]_2[Si(OX)_3]$ (150 mg, 0.19 mmol) was added to an acetonitrile (50 cm^3) solution of $(TTF)_3(BF_4)_2$ (140 mg, 0.18 mmol) under nitrogen atmosphere and the mixture was allowed to stand at 4 °C overnight. The resulting black microcrystals of $(TTF)_2[Si(OX)_3]\cdot 0.5CH_3CN$ (**1**) were collected by filtration and dried *in vacuo*, 75% yield. The involvement of acetonitrile was confirmed by the ^1H NMR spectrum. The reaction of $[Et_4N]_2[Ge(OX)_3]$ with $(TTF)_3(BF_4)_2$ in acetonitrile similarly afforded dark brown microcrystals of $(TTF)_2[Ge(OX)_3]\cdot 0.5CH_3CN$ (**2**) in an 83% yield, whereas black microcrystals of $(TTF)_{2.8}[Sn(OX)_3]$ (**3a**) were obtained in a 64%

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yield by the reaction of $[Et_4N]_2[Sn(OX)_3]$ with $(TTF)_3(BF_4)_2$ in the same solvent. On the other hand, $(TSF)_3(BF_4)_2$ reacted with $[n\text{-}Bu_4N]_2[Si(OX)_3]$, $[Et_4N]_2[Ge(OX)_3]$, and $[Et_4N]_2[Sn(OX)_3]$ in acetonitrile to give $(TSF)_2[Si(OX)_3]$ (**4**), $(TSF)_2[Ge(OX)_3]\cdot0.5CH_3CN$ (**5b**), and $(TSF)_2[Sn(OX)_3]$ (**6**) as black microcrystals, in 68, 47, and 59% yields, respectively.

Electrocrystallization

An acetonitrile (10 cm^3) solution both containing TTF (24 mg, 0.12 mmol) and $[Et_4N]_2[Sn(OX)_3]$ (300 mg, 0.47 mmol) was subjected to controlled current ($I = 5$ μA) electrolyses in a cell with two platinum (0.3 mm ϕ) electrodes under nitrogen atmosphere for 10 days. Black microcrystals of $(TTF)_{2.8}[Sn(OX)_3]\cdot0.5CH_3CN$ (**3b**) thus produced on the anode were collected and dried *in vacuo* (6 mg). The electrolysis of an acetonitrile solution containing TSF and $[Et_4N]_2[Ge(OX)_3]$ under the same conditions afforded black microcrystals of $(TSF)_2[Ge(OX)_3]$ (**5a**). Electrocrystallization from an acetonitrile solution containing TSF and $[n\text{-}Bu_4N]_2[Si(OX)_3]$ or $[Et_4N]_2[Sn(OX)_3]$, however, gave **4** or **6**, which is the same product as that obtained in the reaction of $(TSF)_3(BF_4)_2$ with $[n\text{-}Bu_4N]_2[Si(OX)_3]$ or $[Et_4N]_2[Sn(OX)_3]$ in acetonitrile.

Analyses and melting points of the salts obtained are summarized in Table I.

Physical Measurements

Electrical resistivities (ρ) were measured for compacted samples (about 10 mg) in the −25 to +30 °C range by the conventional two-probe method, as described previously [13]. Electronic absorption spectra were recorded on a Union SM-401 spectrophotometer. Electronic powder reflectance spectra were measured with a Hitachi 340 spectrophotometer equipped with a Hitachi NIR (near IR) or R-10A (UV and visible) integrating sphere unit. X-ray photoelectron spectra were measured as described elsewhere [14]. Magnetic susceptibilities were measured by the Gouy method at room temeprature. ESR measurements were carried out using a JEOL-2X spectrometer.

Results and Discussion

Electrical Resistivities and Electronic Spectra

Temperature dependence of the specific resistivities of the TTF and TSF salts indicated that all the salts behave as a typical semiconductor in the temperature range measured (−25 to +30 °C). Table II lists the specific resistivities of the TTF and TSF salts at 25 °C ($\rho_{25\,°C}$) and the activation energies (E_a) determined from the equation $\rho = \rho_0 \exp(E_a/kT)$, where ρ_0, k, and T stand for a constant value, Boltzmann's constant, and the temperature, respectively,

TABLE I. Analyses and Melting Points of TTF and TSF Salts.*

No.	Salt	Found (Calcd.) %			M.p. (dec.) °C
		C	H	N	
1	$(TTF)_2[Si(OX)_3]\cdot0.5CH_3CN$	31.91 (31.64)	1.53 (1.33)	0.96 (0.97)	>195
2	$(TTF)_2[Ge(OX)_3]\cdot0.5CH_3CN$	29.89 (29.89)	1.47 (1.25)	0.79 (0.91)	>200
3a	$(TTF)_{2.8}[Sn(OX)_3]$	28.55 (28.68)	1.32 (1.18)		>185
3b	$(TTF)_{2.8}[Sn(OX)_3]\cdot0.5CH_3CN$	29.06 (29.31)	1.72 (1.31)	0.43 (0.72)	>180
4	$(TSF)_2[Si(OX)_3]$	19.80 (20.09)	1.08 (0.75)		>300
5a	$(TSF)_2[Ge(OX)_3]$	19.01 (19.29)	1.04 (0.72)		>300
5b	$(TSF)_2[Ge(OX)_3]\cdot0.5CH_3CN$	19.94 (20.00)	1.03 (0.85)	0.56 (0.61)	>300
6	$(TSF)_2[Sn(OX)_3]$	18.55 (18.53)	1.06 (0.69)		>300

*3b and 5a were prepared by electrocrystallization, and others by the reaction of $(TTF)_3(BF_4)_2$ and $(TSF)_3(BF_4)_2$ with $[M(OX)_3]$ salts in acetonitrile.

TABLE II. Electrical Resistivity (ρ), Activation Energy (E_a), and Reflectance Spectra of the TTF and TSF Salts.

Salt	$\rho_{25\,°C}/\Omega$ cm	E_a/eV	LE band/10^3 cm^{-1}			CT band/10^3 cm^{-1}	
						$D^{+\cdot}/D^{+\cdot}$ [a]	$D^{+\cdot}/D^{0}$ [a]
1	2.9×10^5	0.35	28.4	b	19.1	13.3	
2	2.1×10^5	0.47	28.7	23.3	19.3	13.6	
3a	3.9×10^4	0.43	27.3	b	19.4	13.6	8.9
3b	1.2×10^5	0.41	27.7	b	19.2	12.8	8.9
4	1.3×10^3	0.27	27.9	b	16.5	11.4	
5a	2.9×10^4	0.28	27.8	b	16.1	12.3	
5b	8.2×10^4	0.32	27.0	22.6	16.4	11.8	
6	1.0×10^3	0.25	27.6	b	16.7	12.5	

[a] D = TTF or TSF. [b] The position has not been determined, it being obscured by the high frequency bands.

as well as their electronic reflectance spectra. The resistivities of the TTF salts obtained in this work (10^4–10^5 Ω cm at 25 °C) fall in the same range as those of TTF salts with bis(dithiolene)metal complexes [3–6], which have been suggested to adopt the columnar structure of the TTF$^{+\cdot}$ radical cation in the crystals. The TSF salts obtained exhibit resistivities and activation energies smaller than the corresponding TTF salts. This is consistent with the lower charge transfer (CT) energy between the TSF$^{+\cdot}$ radical cations than between the TTF$^{+\cdot}$ radical cations, as described below. The involvement of acetonitrile molecules in the crystals causes an appreciable increase in the resistivity (Table II). Differential thermal analyses of the salts containing acetonitrile molecules showed no desolvation of acetonitrile, even at around 150 °C. Thus, acetonitrile molecules may be located stably in the crystal lattice.

Figure 1 shows the powder reflectance spectra of **1** and **3a**, together with the electronic absorption spectrum of **1** in acetonitrile. The solution spectrum exhibits bands at 29 500, 22 900 and 17 200 cm^{-1}, due to the TTF$^{+\cdot}$ radical cation [15]. Thus, the bands appeared in the 17 000–35 000 cm^{-1} region of the reflectance spectrum of **1** may be ascribed to the local excitation (LE) of TTF$^{+\cdot}$, some of which are shifted to high frequencies on the salt formation. Such high frequency shifts have also been reported for the powder absorption spectrum of (TTF)Cl [16] and the polarized absorption spectrum of (TTF)ClO$_4$ [17]. The band at 13 300 cm^{-1} observed in the reflectance spectrum of **1** can reasonably be assigned to an intermolecular CT transition in a TTF$^{+\cdot}$ dimer [16, 17]. Salt **2** exhibited a spectrum very similar to **1** (Table II).

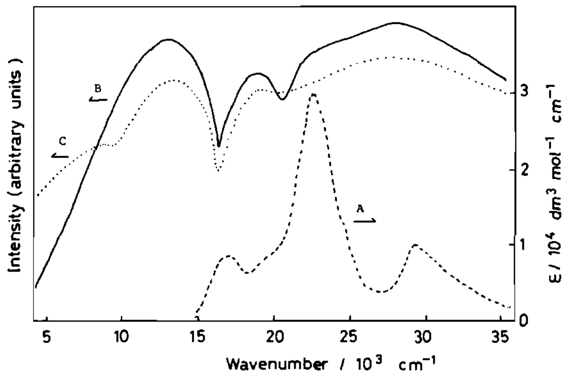

Fig. 1. The absorption spectrum of **1** in acetonitrile (A), and the powder reflectance spectra of **1** (B) and **3a** (C).

The spectrum of **3a** in acetonitrile showed an absorption maxima at 31 300 cm^{-1}, characteristic of neutral TTF in addition to three bands of TTF$^{+\cdot}$, whose frequencies are almost the same as those of **1** shown in Fig. 1. The powder reflectance spectrum of **3a** shows a band at 8900 cm^{-1}, assignable to a CT transition between the TTF$^{+\cdot}$ radical cation and neutral TTF [18], as well as that due to a CT transition between the TTF$^{+\cdot}$ radical cations at 13 600 cm^{-1}. Salt **3b** also exhibits the bands due to the CT transitions, not only between two TTF$^{+\cdot}$ radical cations, but also between the TTF$^{+\cdot}$ radical cation and neutral TTF (Table II). Thus, **3a** and **3b** are suggested to involve the stack of TTF$^{+\cdot}$/TTF$^{+\cdot}$/TTF^{0} in the crystalline state. This is contrast to [TTF]$_3$-[SnCl$_6$], which contains the TTF$^{+\cdot}$/TTF^{0}/TTF$^{+\cdot}$ stack, as confirmed by the electronic reflectance spectrum and X-ray crystallographic analysis [19].

All the TSF salts obtained here have the composition as simple salts, (TSF)$_2$[M(OX)$_3$] (M = Si, Ge, and Sn), with or without inclusion of acetonitrile. The powder reflectance spectra of those salts are very similar to the corresponding TTF simple salts, although all the LE and CT bands of the TSF salts appeared in lower frequencies than those of the TTF salts (Table II). Thus, the present TSF salts may involve a TSF$^{+\cdot}$ radical cation dimer in the crystalline state. The binding energies of Sn 3d$_{3/2}$ and 3d$_{5/2}$ electrons for **3a** (494.1 ± 0.2 and 485.6 ± 0.2 eV, respectively) and for **6** (494.2 ± 0.2 and 485.9 ± 0.2 eV, respectively) determined from the X-ray photoelectron spectra were very close to those of

$[Et_4N]_2[Sn(OX)_3]$ (494.5 ± 0.2 and 485.8 ± 0.2 eV, respectively). In view of this result, no appreciable charge transfer may occur between the $[Sn(OX)_3]^{2-}$ anion and the $TTF^{\dot{+}}$ or $TSF^{\dot{+}}$ radical cation.

Magnetic Susceptibilities and ESR Spectra

Except for **3b** and **5a**, whose amounts required for the measurement of magnetic susceptibilities have not been obtained by electrocrystallization, all the TTF and TSF salts exhibit diamagnetic properties at room temperature, as shown in Table III. The magnetic susceptibilities obtained for the TTF and TSF salts are very close to those of the corresponding tetraalkylammonium salts; $[n\text{-}Bu_4N]_2[Si(OX)_3]$ (-1.0×10^{-4} emu mol^{-1}), $[Et_4N]_2[Ge(OX)_3]$ (-3.7×10^{-4} emu mol^{-1}), and $[Et_4N]_2[Sn(OX)_3]$ (-4.0×10^{-4} emu mol^{-1}), respectively. This is consistent with the fact that the $TTF^{\dot{+}}$ and $TSF^{\dot{+}}$ radical cations exist as dimers in the crystalline state as described above, except for **3a** and **3b**, which may involve the stack of $TTF^{\dot{+}}/TTF^{\dot{+}}/TTF^0$ in the crystalline state.

TABLE III. Molar Magnetic Susceptibilities (χ_M)[a] and ESR g Values[b] of the TTF and TSF Salts.

Salt	χ_M/emu mol^{-1}	g_{max}	g_{int}	g_{min}
1	-1.4×10^{-4}	2.012	2.007	2.002
2	-4.1×10^{-4}	2.016	2.007	2.002
3a	-4.1×10^{-4}	2.016	2.007	2.002
4	-1.7×10^{-4}	2.067	2.022	1.995
5b	-3.8×10^{-4}	2.036	2.019	1.999
6	-4.0×10^{-4}	2.059	2.022	1.997

[a]Measured at room temperature. [b]Measured at 77 K.

ESR spectra of the TTF and TSF salts (polycrystalline samples) at 77 K gave three kinds of weak signals with anisotropic g values (Table III). Those values indicate that all the spins observed are associated with the $TTF^{\dot{+}}$ and $TSF^{\dot{+}}$ radical cations, which assume dimers through rather weak spin-pairing. The TTF salts, **1**, **2**, and **3a**, have almost the same g values, which are also close to those of $(TTF)_3(BF_4)_2$ ($g_{max} = 2.0145$, $g_{int} = 2.0074$, $g_{min} = 2.0020$) [11], $(TTF)Cl_{0.9}$ ($g_{max} = 2.0127$, $g_{int} = 2.009$, $g_{min} = 2.0026$) [11], $(TTF)I_{1.88}$ ($g_{max} = 2.015$, $g_{int} = 2.007$, $g_{min} = 2.002$) [11], $(TTF)[CuS_4C_4(CF_3)_4]$ ($g_{max} = 2.015$, $g_{int} = 2.007$, $g_{min} = 2.002$) [20]. On the other hand, the TSF salts, **4**, **5b**, and **6**, as well as $(TSF)_3(BF_4)_2$ ($g_{max} = 2.0551$, $g_{int} = 2.0196$, $g_{min} = 1.9954$) [11] exhibit not only a somewhat wide variation in the anisotropic g values (in particular g_{max}) with changing the counter anion, but also about five times broader signals than the TTF analogs. Such broad signals of the TSF salts may arise from an increasingly rapid spin–lattice relaxation associated with an effective spin–orbit coupling in the heavier Se atoms [21, 22].

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