Inorganica Chimica Acta, 97 (1985) 201–204

Preparation and Properties of TTF and TSF Salts with Planar Platinum(II) and Copper(II) Oxalate Anions

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Received June 6, 1984

Abstract

Tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) salts with bis(oxalato)platinate, dichloro(oxalato)platinate, and bis(oxalato)cuprate anions were prepared by the reaction of $[TTF]_3[BF_4]_2$ or $[TSF]_3[BF_4]_2$ with the oxalatometallates, either in acetonitrile or in dimethyl sulfoxide. These salts contain neutral TTF^0 or TSF^0 as well as the $TTF^{\dot{+}}$ or $TSF^{\dot{+}}$ radical cation. Electronic reflectance spectra of the salts show a band due to dimeric $(TTF^{\dot{+}})_2$ or $(TSF^{\dot{+}})_2$ in the 13100–14000 or 10500–12300 cm^{-1} region, as well as a band due to a $TTF^{\dot{+}}/TTF^0$ or $TSF^{\dot{+}}/TSF^0$ charge transfer transition in the 8600–8900 cm^{-1} range. X-Ray photoelectron spectra of the TTF salts with oxalato-platinates indicate the occurrence of some negative charge transfer from the TTF moiety to the platinate anion. It is also suggested that the planar bis(oxalato)cuprate anions in the TTF and TSF salts exist as a dimer based on the ESR spectra. All the salts behave as semiconductors with the electrical resistivities in the order 10^2–10^4 Ω cm as compacted samples at 25 °C.

Introduction

Tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) are known to form electrically conductive salts with several metal complex anions containing organic ligands [1, 2]. Recently, we reported the preparation of TTF and TSF salts with tris(oxalato)-matallate anions (metal = Si(IV), Ge(IV), and Sn(IV)) having a bulky octahedral configuration, which behave as semiconductors with specific resistivities of 1 × (10^3–10^5) Ω cm as compacted samples at 25 °C [2]. On the other hand, the square-planar bis(oxalato)platinate anion as rubidium and potassium salts was reported to assume a columnar structure with a platinum–platinum interaction when partially oxidized and to exhibit a high electrical conductivity [3–5]. Sodium, potassium, and ammonium bis(oxalato)cuprates are also known as polymers with metal-to-ligand intermolecular contacts in the anionic moieties [6, 7]. Thus, it may be of interest to study the electrical conduction of TTF and TSF salts with these planar bis(oxalato)metallate anions in relation to the stackings of TTF or TSF and the anionic moieties.

This paper reports the preparation of TTF and TSF salts with planar bis(oxalato)platinate, dichloro(oxalato)platinate, and bis(oxalato)cuprate anions, and their electrical resistivities. The stacking of the TTF or TSF molecule, as well as the electronic interaction between TTF or TSF and the anionic moieties in the crystals, is discussed based on electronic reflectance, X-ray photoelectron and ESR spectra.

Experimental

Materials

TTF [8], TSF [9], $[TTF]_3[BF_4]_2$ [10], $[TSF]_3[BF_4]_2$ [11], $[NH_4]_2[Cu(C_2O_4)_2]$ [6], and $[NBu^n_4]_2[Pt(C_2O_4)_2]$ [12] ($C_2O_4^{2-}$ = the oxalate anion) were prepared according to literature methods. $[NBu^n_4]_2[Pt(C_2O_4)Cl_2]$ was obtained by the reaction of K_2PtCl_6 with $K_2C_2O_4$ at mol ratio 1:3 in water; the precipitate of $K_2[Pt(C_2O_4)_2]$ produced [12] was filtered and the filtrate was evaporated to a half-volume to give a red precipitate (1.4 g). The latter was collected by filtration and dissolved in water (10 cm^3), followed by the addition of an aqueous solution (10 cm^3) of $[NBu^n_4]Br$ (1.9 g). A precipitate formed was dissolved in dichloromethane. Removal of the solvent afforded a pale red powder, which was washed with diethyl ether to give the product (0.73 g), m.p. 114–119 °C. *Anal.* Calcd for $C_{34}H_{72}N_2O_4Cl_2Pt$; C, 48.68; H, 8.65; N, 3.34; Cl, 8.45%. Found: C, 48.31; H, 8.72; N, 3.41; Cl, 8.58%.

Preparation of TTF and TSF Salts

An acetonitrile (35 cm^3) solution containing $[TTF]_3[BF_4]_2$ (47 mg, 60 μmol) and $[NBu^n_4]_2$-

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0020-1693/85/$3.30

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

No.	Salt	Color	m.p. (dec.)/°C	Found (Calcd)[a]	
				%C	%H
1	$[TTF]_{2.7}[Pt(C_2O_4)_2]\cdot 0.5MeCN$	dark brown	>300	26.74 (26.99)	1.55 (1.31)
2	$[TTF]_{2.7}[Pt(C_2O_4)Cl_2]\cdot MeCN$	brown	>145	25.21 (25.63)	1.78 (1.47)
3	$[TTF]_3[Cu(C_2O_4)_2]\cdot 1.5Me_2SO$	brown	195–197	30.45 (30.96)	2.19 (2.18)
4	$[TSF]_{4.5}[Pt(C_2O_4)_2]$	dark green	>300	17.46 (17.44)	1.11 (0.85)
5	$[TSF]_{3.5}[Pt(C_2O_4)Cl_2]$	dark green	>300	15.95 (16.00)	1.09 (0.82)
6	$[TSF]_3[Cu(C_2O_4)_2]\cdot 2Me_2SO$	dark green	>300	19.16 (19.87)	1.52 (1.51)

[a] %N: 0.64 (0.74) for **1** and 1.55 (1.48) for **2**.

TABLE II. Electrical Resistivities ($\rho_{25\,°C}$), Activation Energies (E_a), and Powder Reflectance and ESR Spectra of the TTF and TSF Salts.

Salt	$\rho_{25\,°C}/\Omega$ cm	E_a/eV	LE band of D[a]			CT band/10^3 cm^{-1}		ESR parameter of D[a,b]		
			10^3 cm^{-1}			$D^{+\cdot}/D^{+\cdot}$ [a]	$D^{+\cdot}/D^0$ [a]	g_{max}	g_{int}	g_{min}
1	1.2×10^3	0.25	29.0	[c]	18.5	13.1	8.8	2.015	2.008	2.000
2	2.6×10^4	0.40	29.5	[c]	18.4	13.2	8.6		2.010	
3	9.3×10^3	0.18	29.4	24.8	20.0	14.0	8.9		2.006[d]	
4	7.2×10^2	0.18	27.9	24.9	16.6	12.3	8.8	2.061	2.018	1.998
5	5.8×10^2	0.10	27.5	22.5	16.5	11.8	8.8	2.065	2.024	1.998
6	2.1×10^3	0.12	27.9	22.7	16.7	10.5	8.7		2.009[d]	

[a] D = TTF or TSF. [b] Measured at 77 K. [c] Obscured by the higher frequency bands. [d] See the text for signals due to the $[Cu(C_2O_4)_2]^{2-}$ moiety.

$[Pt(C_2O_4)_2]$ (63 mg, 74 μmol) was allowed to stand in a refrigerator for several hours under nitrogen atmosphere. The resulting dark brown precipitate of $[TTF]_{2.7}[Pt(C_2O_4)_2]\cdot 0.5MeCN$ (**1**) was filtered and dried *in vacuo*, 71% yield based on $[TTF]_3[BF_4]_2$. Similarly, $[TTF]_{2.7}[Pt(C_2O_4)Cl_2]\cdot MeCN$ (**2**) was obtained in a 48% yield by the reaction of $[TTF]_3[BF_4]_2$ with $[NBu^n_4]_2[Pt(C_2O_4)Cl_2]$ in acetonitrile. $[TSF]_{4.5}[Pt(C_2O_4)_2]$ (**4**) and $[TSF]_{3.5}[Pt(C_2O_4)Cl_2]$ (**5**) also were prepared in 29 and 20% yields, respectively, by the reaction of $[TSF]_3[BF_4]_2$ with $[NBu^n_4]_2[Pt(C_2O_4)_2]$ or $[NBu^n_4]_2[Pt(C_2O_4)Cl_2]$ in acetonitrile. Analogous reactions of $[NH_4]_2[Cu(C_2O_4)_2]$ in dimethyl sulfoxide with $[TTF]_3[BF_4]_2$ and $[TSF]_3[BF_4]_2$ in acetonitrile afforded $[TTF]_3[Cu(C_2O_4)_2]\cdot 1.5Me_2SO$ (**3**) and $[TSF]_3[Cu(C_2O_4)_2]\cdot 2Me_2SO$ (**6**) in 50 and 64% yields, respectively. Mol ratios of the $TTF^{+\cdot}$ radical cation to neutral TTF^0 in the salts obtained were determined not only by electronic absorption spectra in acetonitrile or in dimethyl sulfoxide, but also by 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 TTF and TSF salts are listed in Table I.

Physical Measurements

Powder electronic reflectance [2], ESR [2], and X-ray photoelectron spectra [13] were recorded as described elsewhere. Electrical resistivities were measured as compacted samples by the conventional two-probe method [14].

Results and Discussion

Electrical Resistivity

All the salts obtained behave as semiconductors in the temperature range measured; namely −40 to +50 °C. The resistivities (ρ) at 25 °C measured for compacted samples and activation energies (E_a)

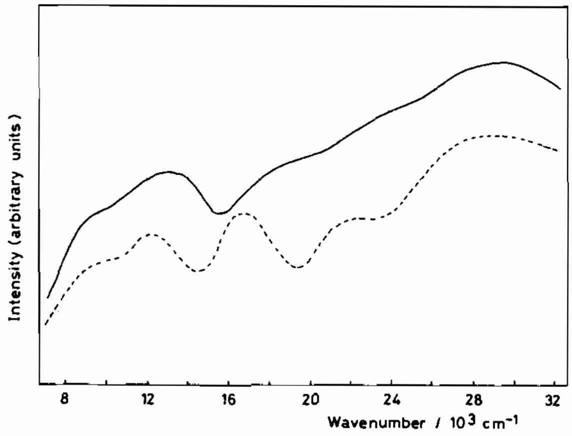

Fig. 1. Powder reflectance spectra of **1** (——) and **4** (------).

for the electrical conduction calculated from the equation $\rho = \rho_0 \exp(E_a/kT)$ are summarized in Table II, which also lists electronic reflectance and ESR spectral data of the salts. The $\rho_{25\,°C}$ values of the TTF and TSF salts are in the order of 10^2–10^4 Ω cm, suggesting a columnar structure of the TTF$^{+\cdot}$ or TSF$^{+\cdot}$ radical cation and its neutral molecule in the crystals. These values are somewhat smaller than $\rho_{25\,°C}$ for tris(oxalato)metallate anion simple salts of TTF and TSF ($1 \times (10^3$–$10^5)$ Ω cm) [2], which may be due to the fact that all the present salts contain both neutral TTF^0 or TSF^0 as well as the TTF$^{+\cdot}$ or TSF$^{+\cdot}$ radical cation. In addition, the planar metallate anions may be more favourable than the tris(oxalato)metallate anions with octahedral configurations for the stacking of the donor molecules. The TSF salts exhibit resistivities and activation energies smaller than the corresponding TTF salts. This is consistent with the observation that the charge transfer (CT) energy between the TSF$^{+\cdot}$ radical cations is smaller than that between the TTF$^{+\cdot}$ radical cations, as described below.

Configurations of the Salts

Figure 1 shows the electronic reflectance spectra of salts **1** and **4**. The two bands around 18500 and 30000 cm^{-1} observed in **1** may be ascribed to local electronic excitations of both the TTF$^{+\cdot}$ radical cation and neutral TTF^0. The bands around 13100 and 8800 cm^{-1} are reasonably assigned to CT transitions between the TTF$^{+\cdot}$ radical cations [15] and between TTF$^{+\cdot}$ and TTF^0 [16], respectively. Similar spectra were observed in salts **2** and **3**. Salt **4** exhibits the corresponding two bands; CT transitions between TSF$^{+\cdot}$ and TSF$^{+\cdot}$, and between TSF$^{+\cdot}$ and TSF^0 around 12300 and 8800 cm^{-1}, respectively. Similar spectra were observed also in salts **5** and **6** (Table II). These findings suggest the columnar structure of donor molecules which involves both the D$^{+\cdot}$/D$^{+\cdot}$ and D$^{+\cdot}$/D^0 (D = TTF and TSF) arrangements. Such a structure is compatible with considerably low resistivities of those salts, as mentioned above.

TABLE III. Binding Energies (eV) of the Pt $4f_{5/2}$ and $4f_{7/2}$ Electrons of Some Platinum(II and IV) Salts.

Salt	Pt $4f_{5/2}$	Pt $4f_{7/2}$
$[TTF]_{2.7}[Pt(C_2O_4)_2]\cdot 0.5MeCN$	74.3	70.9
$[NBu^n_4]_2[Pt(C_2O_4)_2]$	75.5	72.3
$[TTF]_{2.7}[Pt(C_2O_4)Cl_2]\cdot MeCN$	73.9	70.4
$[NBu^n_4]_2[Pt(C_2O_4)Cl_2]$	75.2	71.5
K_2PtCl_6	79.0	75.6

Table III lists the binding energies of Pt $4f_{5/2}$ and $4f_{7/2}$ electrons of two TTF salts, **1** and **2**, and related platinum(II and IV) complexes obtained from X-ray photoelectron spectra (XPS); the TSF salts, **4** and **5**, have been unsuccessful to obtain well-resolved XPS spectra. The binding energies of Pt $4f_{5/2}$ and $4f_{7/2}$ electrons in the TTF salts are smaller (1.1–1.4 eV) than those in the tetrabutylammonium salts of $[Pt^{II}(C_2O_4)_2]^{2-}$ and $[Pt^{II}(C_2O_4)Cl_2]^{2-}$ anions, and much smaller than those of $K_2Pt^{IV}Cl_6$. This result indicates that the platinum(II) moieties in the TTF salts are somewhat reduced through a transfer of some negative charges from the TTF moieties. Such a reduced species is in contrast to partially oxidized $[Pt(C_2O_4)_2]^{2-}$, which forms anion stacks exhibiting high electrical conductivities [3–5]. A similar negative charge transfer from TTF$^{+\cdot}$ and/or TTF^0 moieties to metal-containing anions has also been reported to occur for $[TTF]_3[SnCl_6]$, $[TTF]_3[SnMe_2Cl_4]$, and $[TTF][SnMe_2Cl_3]$ [17].

The TTF and TSF salts with uni- and bis(oxalato)-platinates exhibited anisotropic weak ESR signals at 77 K, though the signal of salt **2** has been isotropic, indicating that all the spins observed are ascribed to TTF$^{+\cdot}$ and TSF$^{+\cdot}$ radical cations forming dimers through a weak spin-pairing. The g values obtained (Table II) are close to those of the TTF and TSF salts with tris(oxalato)silicate, -germate, and -stannate anions reported previously [2].

The NH_4^+ and Na^+ salts of $[Cu(C_2O_4)_2]^{2-}$ are known to assume an infinite columnar structure which involves a face-to-face weak interaction among the anion moieties, and to give ESR signals at $g_\parallel = 2.31$ and $g_\perp = 2.08$ together with a weak signal around 1600 G [6, 7]. On the other hand, the powder spectrum of salt **3** exhibits signals due to the $[Cu(C_2O_4)_2]^{2-}$ anion with an extremely anisotropic mode at $g_1 = 2.321$, $g_2 = 2.112$, and $g_3 = 1.855$ (Fig. 2), in addition to a weak signal due to the TTF$^{+\cdot}$ radical cation exhibiting as a weakly interacting dimer at $g = 2.006$. The occurrence of the signal with such a low g_3 value suggests the presence of a dimeric species of $[Cu(C_2O_4)_2]^{2-}$ with a weak

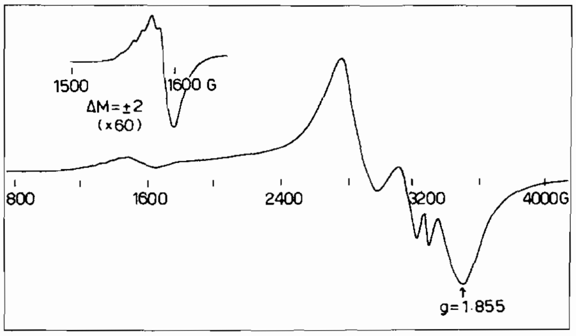

Fig. 2. The powder ESR spectrum of 3 at 77 K.

interaction between two anions rather than any polymeric ones, as was reported for $[Cu(pip)_2]_2(im)(NO_3)_3$ (pip = 2-[(2-(2-pyridyl)ethylimino)-methyl]pyridine and im = imidazolate anion) [18]. The appearance of the half band due to $\Delta M = \pm 2$ at 1600 G is compatible with the interaction between two copper(II) ions in the dimeric species. The TSF salt **6** also gave anisotropic signals due to the $[Cu(C_2O_4)_2]^{2-}$ anion (g_1 = 2.268, g_2 = 2.112, and g_3 = 1.877) and a weak signal due to the $TSF^{\cdot+}$ radical cation at g = 2.009, together with the $\Delta M = \pm 2$ resonance at 1600 G; the spectral feature is very similar to that of salt **3**.

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