

## Effect of positional disorder of anions on the conduction mechanism of the one-dimensional conductors $(\text{TTF})(\text{BF}_4)_{0.02}(\text{Cl})_{0.60}$ and $(\text{TTF})(\text{SCN})_{0.09}(\text{Cl})_{0.66}$

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Following  $(\text{TTF})(\text{ClO}_4)_{0.14\pm 0.02}(\text{Cl})_{0.42\pm 0.08}$ , two more quasi-one-dimensional tetrathiafulvalenium conductors with mixed inorganic anions of nonstoichiometric composition,  $(\text{TTF})(\text{BF}_4)_{0.02}(\text{Cl})_{0.60}$  and  $(\text{TTF})(\text{SCN})_{0.09}(\text{Cl})_{0.66}$ , were obtained by electrochemical crystallization. They were found to have a tetragonal lattice with  $a=b=11.213(2)$  Å,  $c=3.600(1)$  Å,  $Z=2$  for the former and with  $a=b=11.186(2)$  Å,  $c=3.608(2)$  Å,  $Z=2$  for the latter. Analysis of the crystal structures assuming the space group  $P4_2/mnm$  revealed that both compounds were isostructural to the first one, where TTF radicals formed stable segregated eclipsed stacks along the elongated  $c$  axis but the anion sublattices were fully disordered in the channels between the TTF stacks. The room-temperature conductivity along the stacks was 18–28 S/cm (with an average value of  $23\pm 3$  S/cm) for the former and 17–72 S/cm (with an average value of  $42\pm 21$  S/cm) for the latter. The tetrafluoroborate/chloride salt showed a sharp metal-insulator transition at  $251\pm 2$  K, but the thiocyanate/chloride salt showed structured transition accompanied by a thermal hysteresis in the range of 250–117 K. Below the transition temperature, the compounds behaved as one-dimensional variable-range-hopping conductors down to low temperature. This suggests that this conduction behavior results from the positional disorder of the mixed anion sublattice. The nonstoichiometric salts of TTF,  $(\text{TTF})(\text{BF}_4)_{0.46}$ , and  $\text{TTF}(\text{SCN})_{0.47}$  were also obtained in polycrystalline form and were found to have conductivities of  $8\times 10^{-3}$  S/cm for the tetrafluoroborate/chloride salt and  $5\times 10^{-2}$  S/cm for the thiocyanate/chloride salt. These low powder conductivities suggest condensed Peierls structures.

### INTRODUCTION

The nature of the conduction and the composition-structural relations of the tetrathiafulvalene- (TTF)-based low-dimensional single-chain conductors is a subject of great interest.<sup>1–5</sup> These conductors are regarded as prototype molecular conductors with a simplified composition and various degrees of structural instability. However, further research on quasi-one-dimensional (Q1D) compounds is needed to understand in more detail and in a systematic way the physicochemical characteristics associated with the low dimensionality.<sup>6</sup> Recently, a compound of 1D conductor type based on a TTF salt with mixed nonstoichiometric inorganic anions,  $(\text{TTF})(\text{ClO}_4)_{0.14\pm 0.02}(\text{Cl})_{0.42\pm 0.08}$  [hereafter referred to as (1)] was described where 1D variable-range-hopping (VRH) conduction occurs.<sup>7</sup> In this paper, we report on two further TTF conductors, the tetrafluoroborate analogue  $(\text{TTF})(\text{BF}_4)_{0.02}(\text{Cl})_{0.60}$  (2) and the thiocyanate analogue  $(\text{TTF})(\text{SCN})_{0.09}(\text{Cl})_{0.66}$  (3) along with preliminary results for the salts  $(\text{TTF})(\text{BF}_4)_{0.46}$  (4) and  $(\text{TTF})(\text{SCN})_{0.47}$  (5) which were obtained in the same preparation.

### EXPERIMENT

#### Preparation of $(\text{TTF})(\text{BF}_4)_{0.02}(\text{Cl})_{0.60}$ (2) and $(\text{TTF})(\text{BF}_4)_{0.46}$ (4)

0.1 g of TTF (Tokyo Kasei, GR) and 0.45 g of tetrabutyl ammonium tetrafluoroborate (Nacalai Tesque, SPR) were dissolved in 65 ml of 1,2-dichloroethane (Nacalai

Tesque, liquid chromatography grade) and placed in an  $H$ -shaped cell equipped with airtight caps and platinum rod electrodes of 1 mm diameter separated into two compartments by a glass frit of medium porosity. The solution was electrolyzed galvanostatically at ca.  $4\ \mu\text{A}$  for several weeks. Within the first week, a layer of black polycrystalline deposit covered the anode; later, very fine long needles began to grow. After more than one month, the crystals (2) and polycrystalline produce (4) were harvested separately, washed with 1,2-dichloroethane and air dried. The crystals obtained were black-purple and had rectangular cross sections, 0.05–0.09 mm wide and 4–8 mm long. The products were stored in sample tubes at room temperature. Analytical results for the samples of each compound are given below.

	$(\text{TTF})(\text{BF}_4)_{0.02}(\text{Cl})_{0.60}$ (2) (needle crystal)				
Calc.	C, 31.70	H, 1.77	F, 0.67	Cl, 9.36%	
Found	C, 31.47	H, 2.15	F, 0.62	Cl, 9.26%	
	$(\text{TTF})(\text{BF}_4)_{0.46}$ (4) (polycrystalline solid)				
Calc.	C, 29.50	H, 1.65	F, 14.31%		
Found	C, 29.45	H, 1.62	F, 13.53%		

#### Preparation of $(\text{TTF})(\text{SCN})_{0.09}(\text{Cl})_{0.66}$ (3) and $(\text{TTF})(\text{SCN})_{0.47}$ (5)

These were prepared in the same way as (2) and (4) except that tetrabutyl ammonium thiocyanate (Nacalai Tesque, SPR) was substituted for  $\text{BF}_4$ .

After one month of electrolysis, the crystals (3) and

polycrystalline product (5) were harvested separately. The needle crystals obtained were black and had rectangular cross sections 0.09–0.23 mm wide and 3–7 mm long. The products were stored in sample tubes at room temperature. Analytical results for the samples are given below.

	(TTF)(SCN) <sub>0.09</sub> (Cl) <sub>0.66</sub> (3) (needle crystal)			
Calc.	C, 31.40	H, 1.73	N, 0.54	S, 56.29
Found	C, 31.02	H, 1.82	N, 0.56	S, 56.61
	(TTF)(SCN) <sub>0.47</sub> (5) (polycrystalline solid)			
Calc.	C, 33.54	H, 1.74	N, 2.84	S, 61.86%
Found	C, 33.08	H, 1.60	N, 2.58	S, 62.78%

In all cases the chlorine content was determined by difference instead of by titration.

#### Structural analysis for (TTF)(BF<sub>4</sub>)<sub>0.02</sub>(Cl)<sub>0.60</sub> (2) (*M* = 227.35)

The density of the crystals were determined by flotation in an aqueous solution of zinc bromide. Crystals of dimensions 0.05 × 0.05 × 0.46 mm<sup>3</sup> were used. The reflection data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu *K*α radiation using the  $\omega/\theta$  scan technique ( $2\theta \leq 130^\circ$ ). Empirical corrections based on  $\Psi$  scans were made for absorptions (transmission factors  $T_{\min} = 0.9226$ ,  $T_{\max} = 0.9981$ ). The x-ray structure was determined using MULTAN78.<sup>8</sup>

Fourier calculations based on the atomic parameters of the TTF radical showed the anion was located at (0, 0.5, 0–1.0). With the exception of the anion structure, the structure was determined from the 193 ( $|F_o| \geq 3\sigma|F_c|$ ) independent reflections with  $R = 6.6\%$  [ $\omega = 1/F(\sigma)^2$ ] for the tetrafluoroborate/chloride salt (2). The crystal data are shown in Table I along with those of perchlorate/chloride salt (1).

#### Structural analysis for (TTF)(SCN)<sub>0.09</sub>(Cl)<sub>0.66</sub> (3) (*M* = 232.96)

The density and crystal structure have been determined similarly as in the case of the tetrafluoroborate/chloride salt (2) and the final *R* factor

is 7.9% [ $\omega = 1/F(\sigma)^2$ ]. The crystal data are shown in Table I.

#### Conductivity measurements

Conventional four-probe dc conductivity measurements at various temperatures were carried out for single crystals. The two-probe method was applied to pressed pellets for powdered samples. The conduction properties have been examined using more than 10 well-formed single crystals with rectangular cross sections and of sufficient strength for the measurements. The results are summarized in Table II. Details of the measurements were given in our previous report.<sup>7</sup>

## RESULTS AND DISCUSSION

#### Preparation of crystals

The chloride ion in the anion sublattice of the mixed-anion compounds is incorporated through the decomposition of the solvent 1,2-dichloroethane during the electrolysis. This is thought to occur since both of the chloride-free TTF salts form early in the electrolysis procedure due to the insufficient chloride concentration in the solution. The growth of the TTF mixed-anion salts was found to be light insensitive.

#### Crystal structure

The systematic absence of  $0kl$  with  $k + l = 2n + 1$  and of  $h0l$  with  $h + l = 2n + 1$  indicated that the space group was  $P4_2/mnm$ ,  $P4_2nm$ , or  $P4n2$ . The first space group was assumed for the structural analysis, considering the  $D_{2h}$  symmetry of the TTF radical. The x-ray photographs revealed neither additional weak satellite-type reflection indicating the existence of lattice superstructure nor a diffuse scattering line.

A complete structural analysis could not be obtained for (TTF)(BF<sub>4</sub>)<sub>0.02</sub>(Cl)<sub>0.60</sub> and (TTF)(SCN)<sub>0.09</sub>(Cl)<sub>0.66</sub> due to the disordered structure of the inorganic anions, as in (TTF)(ClO<sub>4</sub>)<sub>0.14</sub>(Cl)<sub>0.42</sub>. Fourier calculations showed uniformly distributed electron densities at  $(0, \frac{1}{2}, z)$  ( $0 \leq z < 1$ ) for the atomic parameters of the anions, indicating posi-

TABLE I. Crystal data for the TTF conductors with mixed-anion composition.

	(TTF)(ClO <sub>4</sub> ) <sub>0.14±0.02</sub> (Cl) <sub>0.42±0.08</sub>	(TTF)(BF <sub>4</sub> ) <sub>0.02</sub> (Cl) <sub>0.60</sub>	(TTF)(SCN) <sub>0.09</sub> (Cl) <sub>0.66</sub>
<i>M</i>	233.15	227.35	232.96
Space group	$P4_2/mnm$	$P4_2/mnm$	$P4_2/mnm$
Crystal lattice	Tetragonal	Tetragonal	Tetragonal
Unit cell			
<i>a</i> = <i>b</i>	11.213(2) Å	11.201(1) Å	11.186(7) Å
<i>c</i>	3.600(1) Å	3.595(1) Å	3.608(2) Å
<i>Z</i>	2	2	2
<i>V</i>	452.59(3) Å <sup>3</sup>	451.05(7) Å <sup>3</sup>	451.52(39) Å <sup>3</sup>
Density (g/cm <sup>3</sup> )			
<i>D<sub>m</sub></i>	1.701(2)	1.636(3)	1.716(5)
<i>D<sub>calc</sub></i>	1.704	1.674	1.714
Formal Charge $\delta^+$	0.56	0.62	0.75

TABLE II. Room-temperature (RT) conductivity and metal-insulator (MI) transition temperatures for the TTF conductors with mixed-anion composition.

	(TTF)(ClO <sub>4</sub> ) <sub>0.14±0.02</sub> (Cl) <sub>0.42±0.08</sub>	(TTF)(BF <sub>4</sub> ) <sub>0.02</sub> (Cl) <sub>0.60</sub>	(TTF)(SCN) <sub>0.09</sub> (Cl) <sub>0.66</sub>
$\sigma_{RT}$ (21–24 °C) (S/cm)	7–27 17.5±5.5	18–28 23±3	17–72 42±21
$T_{MI}$ (K)	253±4	251±2	226±2, 137±1 (during the cooling process) 202 K, 152K (during the heating process)

tional disorder along the crystal *c* axis. Therefore only the chloride anion was considered to have a large anisotropic temperature factor in the structural analysis. Figure 1 shows the *c*-axis projection of the unit cell structure common to these salts and Table III contains the positional parameters for the TTF radicals and chloride ions in the cell.

The TTF cation radical formed a stable sublattice and stacked in an eclipsed column. The molecular plane lay in the *ab* plane and the sulfur atomic orbitals of the TTF overlapped face to face with those of the adjacent radicals in the stack. They had a similar mean interplanar spacing of 3.595–3.608 Å, although the formal charge on the radical varies from +0.56 to +0.75. This is very unlike the case of platinum chain compounds, such as tetracyano- and/or bisoxalato-platinate complexes, where the average Pt-Pt distances are related empirically to the degree of oxidation of the Pt atom.

The interplanar separation is less than twice the van der Waals radius of a sulfur atom, 3.70 Å, and short

enough to make adjacent sulfur orbitals overlap each other. Thus the 3*p* orbitals of peripheral sulfur atoms partially overlap between adjacent TTF radicals in a stack, providing a conduction path through the stack for electrons and holes. Two TTF radicals in the unit cell were staggered with respect to the molecular long axis with one unit being located 0.5*c* above the other. This style of radical packing in the crystal has commonly been seen in the 1D TTF salts found so far and seems to ensure the formation of extended band states. Inorganic anions were packed on a nonstoichiometric, disordered way in the channels between the TTF stacks.

The size of the channel formed between TTF stacks was approximately a tube of diameter of 3.07 Å—significantly smaller than the estimated size of the anions, but still large enough for the anions to move freely in the channel along the *c* direction. The estimated ionic sizes of tetrafluoroborate (4.04 Å) and thiocyanate ions (3.70×4.59 Å<sup>2</sup>) exceed that of bromide (3.92 Å), yet they yielded fully disordered sublattices once combined with nonstoichiometric amounts of chloride ion (3.60 Å). This is contrary to the proposed criterion for anion size for 1D conductors which is based on TTF radical salts ei-

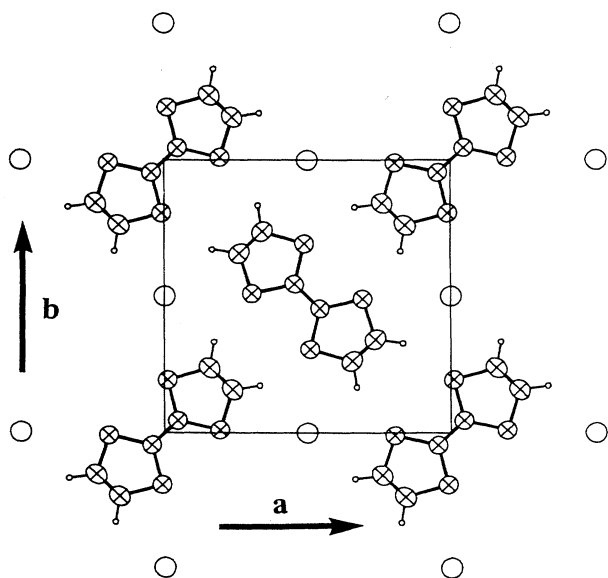


FIG. 1. Projection of the TTF radical arrangement on the *ac* plane. The central radical lies at position *c*/2 above or below the surrounding TTF radicals. The positions of the mixed anions disordered along the *c* axis are denoted by circles.

TABLE III. Fractional atomic coordinates and thermal parameters.

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	$B_{eqv}^a$ (Å <sup>2</sup> )
TTF(BF <sub>4</sub> ) <sub>0.02</sub> (Cl) <sub>0.60</sub>				
S(1)	−0.1939(2)	0.0098(2)	0.5000 <sup>b</sup>	5.6(1)
C(1)	−0.0450(14)	0.0450 <sup>b</sup>	0.5000 <sup>b</sup>	4.7(2)
C(2)	−0.2381(7)	0.1575(7)	0.5000 <sup>b</sup>	6.2(1)
H[C(2)]	−0.334 <sup>b</sup>	0.172 <sup>b</sup>	0.5000 <sup>b</sup>	8.5 <sup>c</sup>
Cl	0.0 <sup>b</sup>	0.5 <sup>b</sup>	(0–1.0) <sup>d</sup>	20.9 <sup>c</sup>
TTF(SCN) <sub>0.09</sub> (Cl) <sub>0.66</sub>				
S(1)	−0.1942(3)	0.0097(3)	0.5000 <sup>b</sup>	4.7(1)
C(1)	−0.0450(20)	0.0450 <sup>b</sup>	0.5000 <sup>b</sup>	3.8(4)
C(2)	−0.2395(12)	0.1582(12)	0.5000 <sup>b</sup>	5.4(3)
H[C(2)]	−0.334 <sup>b</sup>	0.173 <sup>b</sup>	0.5000 <sup>b</sup>	8.5 <sup>c</sup>
Cl	0.0 <sup>b</sup>	0.5 <sup>b</sup>	(0–1.0) <sup>d</sup>	19.5 <sup>c</sup>

$$^a B_{eqv} = 4(a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + 2ab B_{12} \cos \gamma + 2bc B_{23} \cos \alpha + 2ca B_{13} \cos \beta) / 3.$$

<sup>b</sup>Fixed.

<sup>c</sup>Isotropic temperature factor (Å<sup>2</sup>).

<sup>d</sup>Disordered along the *c* axis.

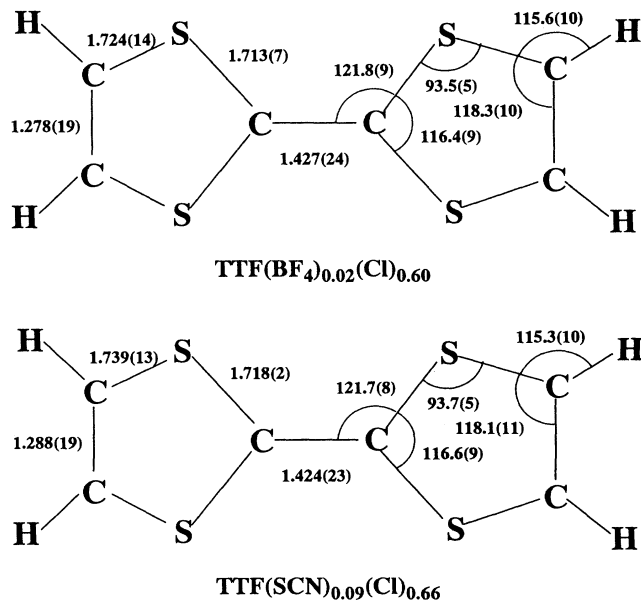


FIG. 2. Molecular geometry (Å and deg) of the TTF radical cations.

ther with a single disordered anion ( $\leq 3.60$  Å) or as part of a modulated superlattice ( $\geq 3.92$  Å).<sup>9</sup>

#### Molecular geometry

The molecular geometry of the TTF radical in each salt is shown in Fig. 2, and the main bond length is compared with those of the neutral and cationic perchlorate TTF species in order of degree of oxidation in Table IV. No relationship is apparent between the bond length and the degree of oxidation of the TTF radicals, contrary to our expectation, whereas, in the case of the perchlorate/chloride salt (1), the central bond length was approximately proportional to the degree of oxidation.<sup>7</sup>

#### Conduction properties

##### 1. Tetrafluoroborate/chloride salt (2)

The room-temperature conductivity of single crystals of (2) was in the 18–28 S/cm range with an average value

of  $23 \pm 3$  S/cm and it was 17–72 S/cm with an average value of  $42 \pm 2$  S/cm for (3). These conductivity values are comparable with the reported value of (1), 7–27 S/cm with an average value of  $18 \pm 6$  S/cm. They are all 1.5 orders of magnitude lower than the conductivity of other TTF conductors with a single inorganic ordered anion (300–900 S/cm), although the TTF stacks of the latter have very similar interplanar separation (3.607–3.631 Å) to the present salts. The decrease of conductivity can be attributed to the disorder and the additional complexation of the anion sublattice.

The temperature dependence of the conductivity is illustrated in Fig. 3 where natural logarithmic conductivity is plotted versus inverse temperature from 60 to 300 K. The two compounds have quite different behavior. The electrical conductivity of (2) is quite reproducible and is very similar to that of the perchlorate/chloride salt (1), showing the typical temperature dependence of Q1D conductors with a distinct metal-insulator transition temperature at  $251 \pm 2$  K. This is close to the transition temperature  $253 \pm 4$  K in the perchlorate/chloride salt (1), which is clearly indicated by the derivative of the logarithmic plot of conductivity versus inverse temperature. To our knowledge, these are the highest metal-insulator temperatures found for this series of TTF compounds, suggesting a relatively large interchain interaction between the conducting TTF stacks.

##### 2. Thiocyanate/chloride salt (3)

The thiocyanate/chloride salt (3) showed a structured transition accompanied by thermal hysteresis in the range of 250–117 K [Figs. 3(b) and 3(c)]. There were two transitions, at 136 and 225 K during cooling and at 152 and 202 K during heating. This reproducible thermal behavior of the thiocyanate/chloride salt is illustrated in Fig. 4 where the transition is shown at two temperatures during cooling and heating. Previous results on TTF thiocyanate single-anion salts have shown a large thermal hysteresis in the range of 300–130 K.<sup>10</sup> This may suggest that the conduction behavior results from the extra freedom of local displacement or orientation of the rodshaped thiocyanate ion, which is loosely trapped in the channel. This is different from the other two salts with tetrahedral anions, even though they all have chloride ion as the common partner. A conduction study

TABLE IV. Averaged bond length (Å) of the TTF molecule and salts with formal charge  $\delta$ .

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	$\delta$	Ref.
TTF	1.349(3)	1.757(2)	1.730(2)	1.314(3)	0.0	29
TTF(ClO <sub>4</sub> ) <sub>x</sub> (Cl) <sub>y</sub>	1.381(15)	1.723(4)	1.713(8)	1.326(11)	+0.56	7
TTF(BF <sub>4</sub> ) <sub>x</sub> (Cl) <sub>y</sub>	1.427(24)	1.713(7)	1.724(14)	1.278(19)	+0.62	This work
TTF(SCN) <sub>x</sub> (Cl) <sub>y</sub>	1.424(23)	1.718(2)	1.739(13)	1.288(19)	+0.75	This work
TTF(ClO <sub>4</sub> )	1.404(14)	1.713(9)	1.725(12)	1.306(17)	+1.0	30

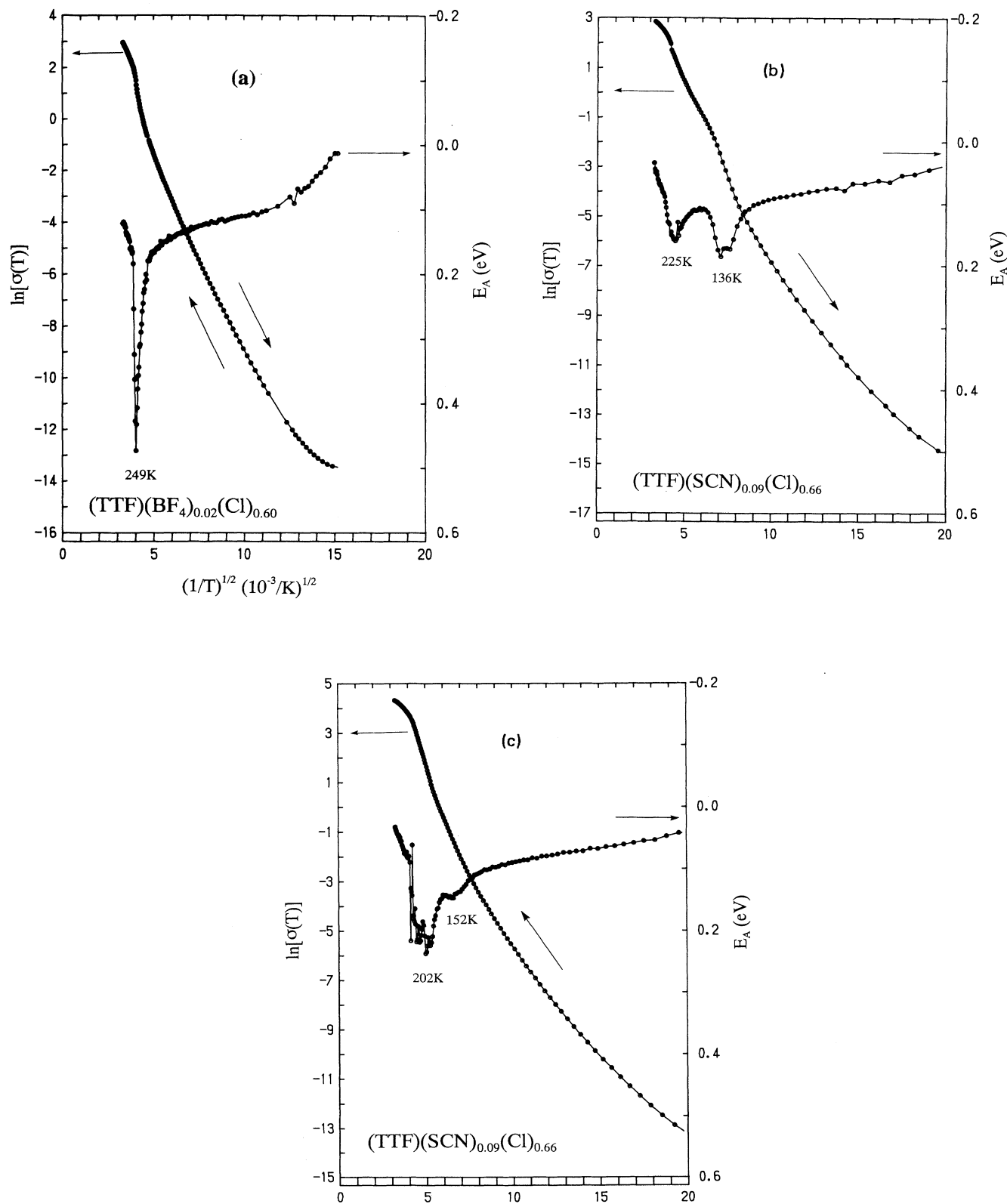


FIG. 3. Temperature dependence of the four-probe dc conductivity  $\sigma(T)$  and its activation energy  $E_A$  plotted versus inverse temperature of (a)  $(TTF)(BF_4)_{0.02}(Cl)_{0.60}$ , (b)  $(TTF)(SCN)_{0.09}(Cl)_{0.66}$  during the cooling process, and (c)  $(TTF)(SCN)_{0.09}(Cl)_{0.66}$  during the heating process. The arrows ( $\rightleftharpoons$ ) indicate the direction of the thermal process.  $E_A$  is defined as  $E_A = -k_B[\partial(\ln\sigma(T))/\partial(T^{-1})]$  where  $k_B$  is Boltzmann's constant.

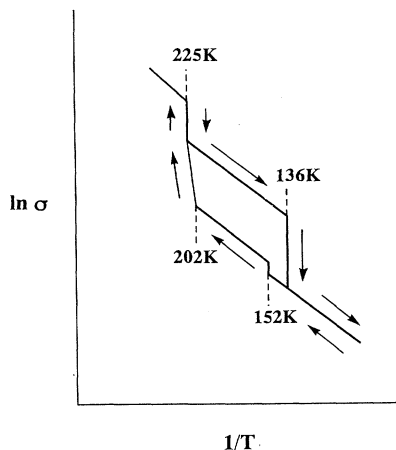


FIG. 4. An example of the thermal hysteresis in the conductivity of  $(\text{TTF})(\text{SCN})_{0.09}(\text{Cl})_{0.66}$ . The arrows ( $\rightleftharpoons$ ) indicate the direction of the thermal process.

performed over a longer duration suggested that the relaxation time for the transition is much longer than 1 h. Our recent conduction data for the thiocyanate/nitrate mixed-anion TTF salt,  $(\text{TTF})(\text{SCN})_{0.47}(\text{NO}_3)_{0.10}$ ,<sup>11</sup> also showed a similar thermal behavior over a broader temperature range.

The structural phase transition of chloride salts,  $\text{TTF}(\text{Cl})_x$  ( $x = 0.67$  and  $0.70$ ) was extensively studied by Williams and co-workers.<sup>12</sup> According to their results, the metal-insulator transition of  $\text{TTF}(\text{Cl})_{0.67}$  takes place at around 250 K. Below this temperature the TTF sublattice undergoes a phase transition from tetragonal to monoclinic symmetry by slippage along the  $c$  axis. This transition was assigned to be the order-disorder transition of the chloride sublattice.<sup>12</sup> The close coincidence of the metal-insulator transition temperatures of  $(\text{TTF})(\text{ClO}_4)_{0.14 \pm 0.02}(\text{Cl})_{0.42 \pm 0.08}$  (1) and  $(\text{TTF})(\text{BF}_4)_{0.02}(\text{Cl})_{0.60}$  (2) to that of  $\text{TTF}(\text{Cl})_{0.67}$  suggests the dominant role of the chloride ion in determining the phase transition behavior of these mixed-anion TTF salts.

We confirmed that the conductivity in both these compounds deviates from the Arrhenius law and obeys instead a  $T^{-1/2}$  temperature dependence as is illustrated in Fig. 5. This applicability of the 1D VRH model to the dc conduction of these compounds is of great interest. It suggests that the conduction electrons or holes transfer from one localized state to the nearest adjacent localized state within the TTF stack.<sup>13,14</sup> To date, the VRH model has been successfully applied to the conduction data of amorphous silicon and to 1D conductors with disordered structure.

The temperature dependence of the conductivity in Mott's variable-range-hopping model is derived as

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/n}], \quad (1)$$

where  $\sigma_0$  is the conductivity at  $T_0$  and  $n$  is an integer representing the  $(n-1)$  dimensionality of the conduction. Assuming this model for the conduction of 1D TTF

conductors with mixed anions,  $T_0$  values were estimated using Eq. (1) (see Table V). It is interesting to note that the perchlorate/chloride and tetrafluoroborate/chloride salts have similar  $T_0$  values to the one reported for  $\text{KCP}(\text{Br})$ ,<sup>15</sup> the prototype of 1D metal chain conductors. The thiocyanate/chloride salt, however, has smaller values for both heating and cooling than the other conductors. This difference probably reflects the difference in the geometrical shape of the anions in the sublattice.

#### The origin of the hopping conduction

The applicability of the 1D VRH conduction model to several compounds implies the existence of an intrinsic origin of the localization of the electronic states resulting in the hopping conduction. If the hopping conduction had an extrinsic origin such as impurities or lattice defects, the conduction properties would change in a random manner depending upon the degree of the localization effects from one sample to another even in the same batch preparation.

There have been arguments about the origin of the hopping conduction of the low-dimensional conductors. Bloch, Weisman, and Varma suggested that electronic conduction in disordered 1D systems can occur only by phonon-assisted hopping, which explains the deviation of the available conduction data from the Arrhenius law.<sup>14,15</sup> On the other hand, Garito and Heeger have claimed that the deviation is due to impurities or lattice imperfection.<sup>16</sup> Coleman *et al.* showed that the conduction of extremely pure NMP-TCNQ (where NMP is N-methylphenazinium and TCNQ is tetracyanoquinodimethane) has a  $T^{-1}$  dependence.<sup>17</sup>

However, careful examination of their conduction data reveals that the deviation from the Arrhenius law is unchanged by purification and can be superimposed upon the data of Shchegolev *et al.*<sup>18</sup> after accounting for the room-temperature conductivity and activation-energy differences. Thus the deviation from  $T^{-1}$  dependence most likely results from structural instability, such as the NMP sublattice orientational disorder in this case.

The next question is what form of the structural instability is required to induce the localization of the electronic states of conducting chains, leading to hopping conduction. In Table VI, the structural and conduction properties of the anion sublattice of known TTF halides and pseudohalides are summarized in order of degree of instability and conductivity. The halide sublattices are well ordered in the iodide<sup>19</sup> and bromide<sup>20</sup> non-stoichiometric salts of TTF. Both are accompanied by periodically modulated superstructures and their logarithmic conductivities appear to show a linear dependence on  $T^{-1}$ .<sup>21</sup> The chloride,<sup>3,12</sup> thiocyanate,<sup>22</sup> and selenocyanate<sup>22</sup> salts, however, exhibit diffuse scattering due to anion lattice instability. The conduction data for the TTF chloride deviate from the Arrhenius law in the same way as do those for the present mixed-anion TTF conductors, while the conductivity of the thiocyanate and selenocyanate salts is linearly dependent on  $T^{-1}$  below the metal-insulator transition temperature.<sup>22</sup> The salts with superstructure and/or diffuse scattering have the highest conductivity among the TTF-based conductors.

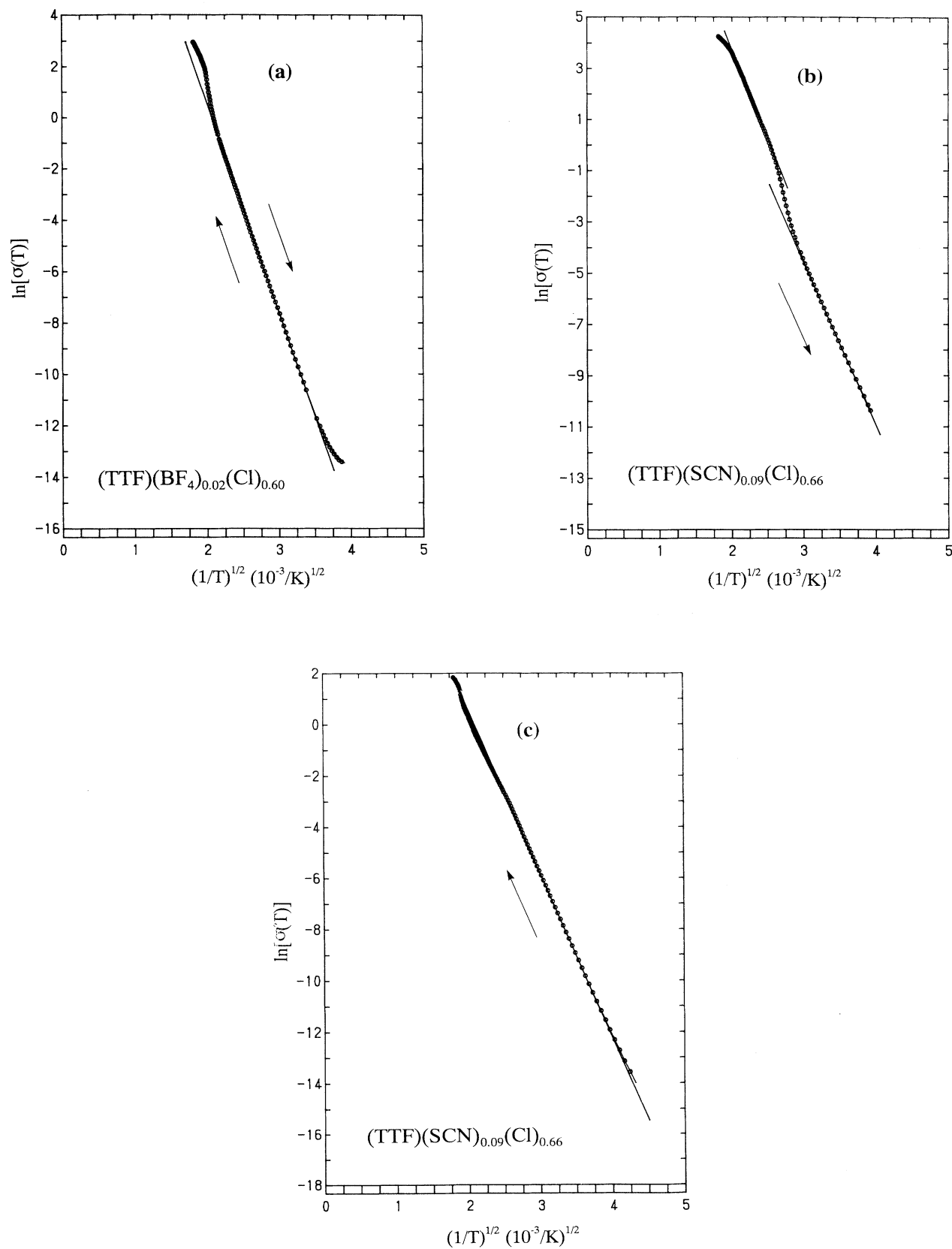


FIG. 5. Conductivity of the conductors plotted versus  $T^{-1/2}$ . The straight line is a visual fit to the data. (a)  $(TTF)(BF_4)_{0.02}(Cl)_{0.60}$ , (b)  $(TTF)(SCN)_{0.09}(Cl)_{0.66}$  during cooling, and (c)  $(TTF)(SCN)_{0.09}(Cl)_{0.66}$  during heating.

TABLE V. Values of  $T_0$  obtained from regressing Eq. (1) onto the conduction data.

TTF conductors	$T_0$ (K)
TTF(ClO <sub>4</sub> ) <sub>0.14</sub> (Cl) <sub>0.42</sub>	$6.37 \times 10^4$
TTF(BF <sub>4</sub> ) <sub>0.02</sub> (Cl) <sub>0.60</sub>	$6.66 \times 10^4$
TTF(SCN) <sub>0.09</sub> (Cl) <sub>0.66</sub>	$4.40 \times 10^4$ (↓), <sup>a</sup> $4.01 \times 10^4$ (↑) <sup>a</sup>
K <sub>2</sub> Pt(CN) <sub>4</sub> Br <sub>0.32</sub> ·3H <sub>2</sub> O	$5.79 \times 10^4$ <sup>b</sup>

<sup>a</sup>Arrows indicate the direction of the thermal process.

<sup>b</sup>Reference 15.

When the anion sublattice is fully disordered and shows neither superstructure nor diffuse scattering, such as in the case of other thiocyanates<sup>11,23</sup> and our mixed-anion TTF conductors, the conductivity again has a  $T^{-1/2}$  temperature dependence and all can be regarded as 1D VRH conductors. Upon complete disordering of the anion sublattices, the room-temperature conductivity is reduced to  $\frac{1}{3}$ – $\frac{1}{5}$  of those of the highly conducting TTF conductors. Further complexation of the disordered anion sublattice by allowing mixed-anion composition, as in the present compounds, leads to a reduction of conductivity by one order of magnitude compared with those of the single-anion TTF conductors. Thus this extra randomness in the anion sublattice strongly affects the conductivity.

Therefore it is likely that the positional instability of the anion sublattice induces Coulomb potential fluctuations on the atomic scale. This gives rise to random po-

tentials over the TTF lattices, which result in the breakdown of the extended electronic state to the localized gap state with randomly distributed "traps" in the mobility gap within the equally spaced lattice structure.<sup>24,25</sup> This eventually leads to 1D VRH conduction as Bloch, Weisman, and Varma have suggested.<sup>15</sup> The degree of randomness of the potential depends on the degree of positional and/or compositional disorder of the anion sublattice. Thus the structural instability of the anion sublattice producing a diffuse scattering may define the critical borderline dividing Arrhenius conduction for ordered systems and Mott 1D VRH conduction for disordered systems. However, the perturbation created by full positional disorder and compositional modification by anion mixing is small enough to yield isostructural crystals, yet large enough to cause decreasing conductivity and hopping conduction in the incommensurate 1D conductors, in spite of the equally spaced TTF chain structure.

#### Commensurate Peierls structure

The nonstoichiometric TTF conductors of (TTF)(BF<sub>4</sub>)<sub>0.46</sub> (4) and TTF(SCN)<sub>0.47</sub> (5) are classified together with (TTF)(ClO<sub>4</sub>)<sub>0.62±0.02</sub> (6) into the commensurate group of salts (see Table VI). These radical salts have a very low powder conductivity [e.g.,  $7 \times 10^{-4}$  S/cm for (6),  $8 \times 10^{-3}$  S/cm for (4), and  $5 \times 10^{-2}$  S/cm for (5)]. Owing to the nonstoichiometric composition, these salts are expected to be members of the group highly conducting TTF compounds (e.g., 85–900 S/cm conductivity). Some of the TTF and TSeF (where TSeF is tetraselenaful-

TABLE VI. Structural and conduction properties of the TTF-based conductors.

Conductors	Ref.	Composition	Structure	Conductivity (S/cm)	MI transition temperature (K)
(TTF)I <sub>0.71</sub>	19	Incommensurate	Periodically modulated superstructure	300–900	250±5, 210
(TTF)Br <sub>0.71-0.76</sub>	20	Single anion			180
(TTF)(Cl) <sub>0.77-0.80</sub>	3				
(TTF)(Cl) <sub>0.67</sub>	12		Structure with diffuse line	300–900	250
(TTF)(SCN) <sub>0.58</sub>	22				169±1
(TTF)(SeCN) <sub>0.58</sub>	22				173±5
(TTF)(SCN) <sub>0.57</sub>	10		Fully disordered structure	85–310	169
(TTF)(SCN) <sub>0.66</sub>	23				
(TTF)(ClO <sub>4</sub> ) <sub>0.14</sub> (Cl) <sub>0.42</sub>	7	Incommensurate		7–44	253±4
(TTF)(BF <sub>4</sub> ) <sub>0.02</sub> (Cl) <sub>0.60</sub>	This work	Mixed anions		18–28	251±2
(TTF)(SCN) <sub>0.09</sub> (Cl) <sub>0.66</sub>	This work			17–72	226±2, 137±1
(TTF)(Br) <sub>0.24</sub> (Cl) <sub>0.29</sub>				74–105	229±5
(TTF)(I) <sub>0.21</sub> (Cl) <sub>0.29</sub>				11–129	242±8
(TTF)(NO <sub>3</sub> ) <sub>0.59</sub> (Cl) <sub>0.28</sub>				0.6–1	271±6
(TTF)(SCN) <sub>0.47</sub> (NO <sub>3</sub> ) <sub>0.10</sub>	11			12–110	269±6
(TTF)(ClO <sub>4</sub> ) <sub>0.67</sub>	26	Commensurate	Static Peierls structure	10 <sup>-4</sup>	
(TTF)(BF <sub>4</sub> ) <sub>0.67</sub>	26,28			10 <sup>-4</sup>	
(TTF)(ClO <sub>4</sub> ) <sub>0.62</sub>	7			$7 \times 10^{-4}$	
(TTF)(BF <sub>4</sub> ) <sub>0.46</sub>	This work			$8 \times 10^{-3}$	
(TTF)(SCN) <sub>0.47</sub>	This work			$5 \times 10^{-2}$	



valene) radical salts with nonstoichiometric composition were, contrary to our expectation, found to be very poor electrical conductors.<sup>26</sup>

As we have reported previously,<sup>7</sup> there are several linear-chain metal complex compounds with nonstoichiometric composition having low conductivity.<sup>27</sup> They all belong to the family of bis(oxalato)platinate complexes with condensed commensurate Peierls instability. They have a simple nonintegral oxidation number (e.g.,  $\frac{4}{5}$  or  $\frac{5}{6}$ ) and very poor conductivity at room temperature (e.g.,  $10^{-2}$ – $10^{-5}$  S/m). These facts strongly suggest that  $(\text{TTF})_3(\text{ClO}_4)_2$ ,  $(\text{TTF})_3(\text{BF}_4)_2$ ,  $(\text{TSeF})_3(\text{ClO}_4)_2$ , and  $(\text{TSeF})_3(\text{BF}_4)_2$  all have a  $\frac{2}{3}$ , nonintegral oxidation state with the cation radical stacks having a commensurate Peierls structure with three-fold periodicity where no equally spaced stacking is realized. Actually, Legros *et al.*<sup>28</sup> have reported the crystal structure of  $(\text{TTF})_3(\text{BF}_4)_2$ , where one neutral TTF molecule and two TTF cation radicals coexist in a repeating unit. The TTF salts with a single anion studied in this work most likely belong to this class of compounds. Their conductivity lies in the range of  $5 \times 10^{-2}$ – $10^{-4}$  S/cm, which spans the conductivity spectrum between the highly conducting incommensurate radical salts and the insulating integral-oxidation-state salts. We are currently investigating other mixed-anion TTF conductors based on iodide/chloride, bromide/chloride, nitrate/chloride, and thiocyanate/nitrate salts.

## CONCLUSIONS

The TTF-based conductors with mixed nonstoichiometric anion compositions  $(\text{TTF})(\text{BF}_4)_{0.02}(\text{Cl})_{0.60}$  and  $(\text{TTF})(\text{SCN})_{0.09}(\text{Cl})_{0.66}$  were crystallized electrochemically. They were found to have fully disordered anion sublattices and a tetragonal lattice with space group  $P4_2/mnm$ , isostructural to  $(\text{TTF})(\text{ClO}_4)_{0.14 \pm 0.02}(\text{Cl})_{0.42 \pm 0.08}$ . It was confirmed that anion mixing reduces the conductivity by one order of magnitude compared to that in single-anion TTF conductors, reflecting the effect of additional complexity in the disordered sublattice. The compounds exhibited a  $T^{-1/2}$  temperature dependence below the metal-insulator transition temperature, suggesting that conduction occurs via a 1D variable-range-hopping mechanism. The origin of the hopping conduction was attributed to the instability of the anion sublattices rather than to inclusion of impurities. It was found that anion sublattice instability of the order of diffuse scattering can induce such hopping conduction. The perturbation created by the positional disorder in the mixed-anion sublattice is small enough to yield isostructural crystals yet large enough to cause decreasing conductivity and hopping conduction in the equally spaced TTF chains.

Other nonstoichiometric salts,  $(\text{TTF})(\text{BF}_4)_{0.46}$ ,  $(\text{TTF})(\text{SCN})_{0.47}$ , and  $(\text{TTF})(\text{ClO}_4)_{0.62 \pm 0.02}$ , were classified as commensurate salts and supposed to have a condensed Peierls structure.

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