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Preparation, structure and conduction properties of SeCN-containing mixed anion TTF conductors

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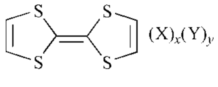
Six new mixed anion salts of tetrathiafulvalene (TTF, $C_6H_4S_4$) containing SeCN were prepared electrochemically. Their chemical compositions were found to be $(TTF)(SeCN)_x(Y)_y$, where Y was a small inorganic anion with $0.5 < x + y < 1.0$, similar to other mixed anion salts reported so far. The temperature dependence of the dc conductivity of these salts has revealed that the anions are less disordered in the crystal lattice than in SCN analogues. They behave as typical one-dimensional conductors with various degrees of anion order. It was shown that the anion disorder in position and orientation has decisive effects on the conductivity as well as on the conduction mechanism of the TTF chains.

Introduction

The nature of conduction and the composition–structural relations of low dimensional materials have been subjects of great interest in the last three decades.[1–7] 1D conductors based on TTF are regarded as prototype molecular conductors due to their simple composition, highly symmetric crystal packing and single conduction column with various kinds of instabilities. In spite of the importance of the salts as prototype organic conductors, the system is still not fully understood. However, this compound gained renewed interest recently when a new series of salts with mixed anions was found (Scheme 1). This could provide us with a wealth of chemical and physical data that would give us more insight into the structure and conductivity of 1D conductors.

The composition and conductivity of the new mixed anion salts are summarized in Table 1, together with all the other salts that have been found so far.[8] These mixed anion TTF conductors are inherently disordered in a non-stoichiometric way along the anion site in the predominant regime of the TTF lattice. This, in turn, imposes random potentials over the TTF conducting chains, leading to the variable range hopping (VRH) conduction envisioned by Mott[9,10] and evidenced by the conduction in a variety of materials with structural disorder such as amorphous semiconductors.[11]

It has been revealed that the disordered anion structure is also effective in preventing the Peierls transition of a TTF lattice from taking place. The effect of order–disorder change in the orientation of linear SCN and SeCN anions has revealed itself as the thermal hysteresis in variable temperature conduction measurements. The present work could shed light upon the conduction mechanism and its influencing factors in low dimensional semi-conductors. Here we present the preparation and properties of the mixed anion TTF conductors to discuss the effects of anion disorder on the conduction properties and band gap structures.



Scheme 1 Chemical formula of mixed anion TTF conductors. X, Y are small inorganic anions with $0.5 < x + y < 1.0$.

Experimental

Preparation

The first mixed anion TTF conductors was found during an attempted electrochemical preparation of a complex between TTF and $Ni(dmbit)_2$ (dmbit = dimercaptobenzoisotrithione†) in 1,2-dichloroethane with tetrabutylammonium perchlorate as the electrolyte.[12] This electrolysis yielded long needle-like crystals which were found to be $(TTF)(ClO_4)_{0.14}(Cl)_{0.42}$. A chloride ion that appeared seems to have derived from the 1,2-dichloroethane employed as the solvent. This solvent always brings chloride ions into the grown crystal as a partner of the mixed anions[13] (method 1, see Table 1).

The usual way of preparing mixed anion TTF salts is to use two kinds of electrolytes as the anion source in conjunction with a non-chlorinated solvent, such as acetonitrile or tetrahydrofurun. Eight kinds of small anions were used for the anions: Cl^-, Br^-, I^-, $SeCN^-$, SCN^-, NO_3^-, ClO_4^- and BF_4^-. Most of the thiocyanate-containing mixed anion TTF salts were prepared by this usual method (method 2). When an electrolyte such as potassium salt is not soluble in an organic solvent, 18-crown-6 ether is added as a phase transfer agent. All the selenocyanate-containing TTF compounds were obtained here by this modified method (method 3).

$(TTF)(SeCN)_{0.26}(Cl)_{0.43}$. 0.100 g of TTF (Tokyo Kasei Co., GR), 0.200 g of tetrabutylammonium chloride (Tokyo Kasei Co., GR), 0.104 g of potassium selenocyanate (Wako Pure Chemical Industries Co., 80%), and 0.190 g of 18-crown-6 ether (Tokyo Kasei Co., GR) were dissolved in 60 ml of acetonitrile (Junsei Chemical Co., GR) and placed in an H-shaped electrolysis cell equipped with platinum electrodes of 1 mm diameter separated by a glass frit of porosity G3. It was electrolyzed at 5 °C in a dark incubator at a constant current of 5 μA for one month. The crystals were harvested from the platinum anode, washed with a small amount of acetonitrile and stored in a refrigerator. Elemental analysis was performed on samples dried over silica gel under reduced pressure overnight. Other compounds were prepared in a similar way to that mentioned above.

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†The IUPAC name for dmbit is 2-thioxo-1,3-benzodithiole-5,6-dithiolate.

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Table 1 The prepared mixed anion TTF compounds

TTF Salt	Method[a]	Solvent[b]	DPO[c]	Conductivity σ_{RT}/S cm^{-1}			Ref.
				Range	Mean value	Standard deviation	
$(TTF)(Cl)_{0.42}(ClO_4)_{0.14}$	1	DCE	+0.56	7–27	17.5	±5.5	12
$(TTF)(Cl)_{0.60}(BF_4)_{0.02}$	1	DCE	+0.62	19–28	23	±3	13
$(TTF)(Cl)_{0.66}(SCN)_{0.09}$	1	DCE	+0.75	17–72	42	±21	13
$(TTF)(Cl)_{0.29}(Br)_{0.24}$	1	DCE	+0.53	74–105			8
$(TTF)(Cl)_{0.29}(I)_{0.21}$	1	DCE	+0.50	11–129			8
$(TTF)(Cl)_{0.28}(NO_3)_{0.59}$	1	DCE	+0.87	2.3–5.9	39	±1.3	16
$(TTF)(SCN)_{0.47}(NO_3)_{0.10}$	2	AN	+0.57	12–110	43	±30	15
$(TTF)(SCN)_{0.12}(Cl)_{0.57}$	2	AN	+0.69	5–51	3.8	±1.4	8
$(TTF)(SCN)_{0.56}(ClO_4)_{0.01}$	2	AN	+0.57	2.9–53	19	±14	16
$(TTF)(SCN)_{0.09}(Br)_{0.59}$	2	AN	+0.68	0.7–1.6	1.0	±0.4	16
$(TTF)(SCN)_{054}(BF_4)_{0.06}$	2	AN	+0.60				8
$(TTF)(SCN)_{0.21}(I)_{0.44}$	2	AN	+0.61				8
$(TTF)(SeCN)_{0.26}(Cl)_{0.43}$	3	AN	+0.57	0.06–1.17	0.56	±0.36	
$(TTF)(SeCN)_{0.22}(Br)_{0.44}$	3	AN	+0.69	0.04–1.54	0.44	±0.50	
$(TTF)(SeCN)_{0.22}(I)_{0.42}$	3	AN	+0.55	0.02–0.57	0.22	±0.17	
$(TTF)(SeCN)_{0.35}(SCN)_{0.22}$	3	AN	+0.66	0.62–2.33	1.10	±0.57	
$(TTF)(SeCN)_{0.47}(NO_3)_{0.10}$	3	AN	+0.64	1.07–11.1	3.8	±4.2	
$(TTF)(SeCN)_{0.51}(ClO_4)_{0.04}$	3	AN	+0.57	0.25–1.98	0.77	±0.56	
$(TTF)(Br)_{0.33}(ClO_4)_{0.26}$	2	AN	+0.59	0.02–0.56	0.31	±0.23	
$(TTF)(Br)_{0.46}(I)_{0.27}$	2	AN	+0.73				8
$(TTF)(I)_{0.62}(ClO_4)_{0.04}$	2	AN	+0.66				8

[a] See text. [b] DCE: 1,2-Dichloroethane, AN: Acetonitrile. [c] Degree of partial oxidation.

Structure analysis of $(TTF)(SeCN)_{0.26}(Cl)_{0.43}$

The density of the crystal was determined by floating it in an aqueous solution of zinc chloride, and measuring the density of the solution using a pycnometer. A black needle-shaped crystal of the compound having approximate dimensions of $0.37 \times 0.30 \times 0.17$ mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated MoKα radiation. The data were collected at a temperature of 300 K using the ω–2θ scan technique to a maximum 2θ value of 59.9°. The X-ray structure was determined using SHELXS 86.[14] During the least squares analysis, the Cl and C atoms of SeCN were tentatively located at the positions (0, ½, 0) and (0, ½, ¼) based on the difference Fourier to obtain reasonable convergence. The Se and N atoms in the SeCN anion could not be found in the analysis, most probably due to its orientational disorder. The occupancy factors were adjusted so that those of chloride (Cl(1) and Cl(2)) and carbon (C(11) and C(12)) are in accordance with the composition determined by the elemental analysis. Furthermore, the occupancy ratios between Cl(1) and Cl(2), and between C(11) and C(12), were refined by the least squares method.

Conductivity measurement

Conventional four-probe dc conductivity measurements were carried out in the range of 50–300 K for a single crystal or bundle of crystals along their horizontal axis using a helium-circulating refrigerator of CTI-Cryogenics, a Neocera LTC-10 temperature controller and a Keithley 236 Source Measure Unit. Crystals were mounted on an IC socket with four gold wires and were fixed by using colloidal graphite. The conductivity of each salt was examined using at least 10 well-formed crystals and sufficient strength for the measurements.

Results and discussion

Mixed anion TTF salts

Analytical results for the samples are given below. The Se content was determined by difference from the sum of the contents of other elements.

$(TTF)(SeCN)_{0.26}(Cl)_{0.43}$. Calc. C, 30.45; H, 1.63; N, 1.47; S, 51.95; Cl, 9.03; Se, 5.46; Found C, 30.20; H, 1.64; N, 1.48; S, 52.12; Cl, 9.07; Se, 5.48%.

$(TTF)(SeCN)_{0.22}(Br)_{0.44}$. Calc. C, 28.44; H, 1.54; N, 1.11; S, 48.91; Br, 13.33; Se, 6.67; Found C, 28.34; H, 1.53; N, 1.21; S, 48.91; Br, 13.34; Se, 6.67%.

$(TTF)(SeCN)_{0.22}(I)_{0.42}$. Calc. C, 26.61; H, 1.44; N, 1.10; S, 45.69; I, 18.98; Se, 6.19; Found C, 26.64; H, 1.35; N, 1.12; S, 45.76; I, 18.86; Se, 6.29%.

$(TTF)(SeCN)_{0.35}(SCN)_{0.22}$. Calc. C, 31.08; H, 1.59; N, 3.15; S, 53.30; Se, 10.89; Found C, 31.09; H, 1.51; N, 3.15; S, 53.36; Se, 10.89%.

$(TTF)(SeCN)_{0.47}(NO_3)_{0.10}$. Calc. C, 29.90; H, 1.55; N, 3.07; S, 49.35; O, 6.28; Se, 9.84; Found C, 29.78; H, 1.41; N, 2.80; S, 49.59; O, 6.40; Se, 10.02%.

$(TTF)(SeCN)_{0.51}(ClO_4)_{0.04}$. Calc. C, 29.86; H, 1.54; N, 2.73; S, 48.98; Cl, 0.95; O, 3.81; Se, 12.14; Found C, 29.88; H, 1.39; N, 2.77; S, 48.99; Cl, 0.96; O, 3.83; Se, 12.19%.

Attempts to prepare the mixed anion TTF salts with relatively big anions such as ReO_4^-, PF_6^-, or I_3^- have failed, probably because their anion size did not fit the rigid TTF lattice. The non-stoichiometric compositions of 21 compounds were identified by chemical analysis with the aid of the crystal density measurements and structural analysis listed in Table 1.

It is apparent from the table that each anion has a different degree of affinity to TTF. This degree is reflected in the anion content of the salts. Therefore, it would be appropriate to use the average content of each anion in this series of salts as an indicator of the degree of affinity to TTF. Thus the following affinity series was obtained in decreasing order of the average content of the 21 compounds in Table 1 (average content is in parentheses).

$$Cl\ (0.44) > Br\ (0.41) > I\ (0.39) > SeCN\ (0.34) > SCN\ (0.29) > NO_3\ (0.26) > ClO_4\ (0.10) > BF_4\ (0.04)$$

Table 2 Degree of partial oxidation of SeCN and SCN salts

SeCN salts	DPO	SCN salts	DPO	Ref.
$(TTF)(SeCN)_{0.26}(Cl)_{0.43}$	0.69	$(TTF)(SCN)_{0.12}(Cl)_{0.57}$	0.69	8
$(TTF)(SeCN)_{0.22}(Br)_{0.44}$	0.66	$(TTF)(SCN)_{0.09}(Br)_{0.59}$	0.68	16
$(TTF)(SeCN)_{0.22}(I)_{0.42}$	0.64	$(TTF)(SCN)_{0.21}(I)_{0.44}$	0.65	8
$(TTF)(SeCN)_{0.47}(NO_3)_{0.10}$	0.57	$(TTF)(SCN)_{0.47}(NO_3)_{0.10}$	0.57	15
$(TTF)(SeCN)_{0.51}(ClO_4)_{0.04}$	0.55	$(TTF)(SCN)_{0.56}(ClO_4)_{0.01}$	0.57	16
$(TTF)(SeCN)_{0.54}(BF_4)_{0.00}$	0.54	$(TTF)(SCN)_{0.56}(BF_4)_{0.06}$	0.60	8

The halide ions showed the largest affinity to TTF of the anions employed here. They were followed by chalcocyanate anions, which are linear in shape. The other polyatomic anions had the least affinity.

Some combinations of small anions did not give any mixed anion TTF salt but single anion TTF salts. For example, attempted preparation of $(TTF)(Cl/NO_3)$, $(TTF)(Br/NO_3)$, and $(TTF)(I/NO_3)$ from acetonitrile solution resulted in the formation of $TTF(Cl)_{0.72-0.80}$, $TTF(Br)_{0.68-0.69}$, and $(TTF)(I)_{0.67}$, respectively. In a similar way, the attempted preparations of $(TTF)(I/BF_4)$ and $(TTF)(SeCN/BF_4)$ ended in producing $(TTF)(I)_{0.67}$ and $(TTF)(SeCN)_{0.54}$, respectively. This fact also means that BF_4 ion has the least affinity to TTF among the anions employed here.

Degree of partial oxidation (DPO) of TTF in SeCN and SCN salts

The SeCN-containing salts were proved to form mixed anion TTF salts where the corresponding SCN salts had a quite close anion stoichiometry as shown in Table 2. $(TTF)(SeCN)_{0.47}(NO_3)_{0.10}$ and $(TTF)(SCN)_{0.47}(NO_3)_{0.10}$[15] had the same composition as each other while other pairs had the same or very close DPO values.

Conduction properties

$(TTF)(SeCN)_{0.26}(Cl)_{0.43}$. Reddish-black lath-shaped crystals of averaging $1.3 \times 0.1 \times 0.03$ mm^3 in size were harvested after three or four weeks of electrocrystallization in an H-shaped cell with a 1 μA constant current. The room temperature dc conductivity, which was examined for 10 samples, ranged from 0.06–1.17 S cm^{-1} with an average value of 0.56 ± 0.36 S cm^{-1}. This value is one or two orders of magnitude smaller than for the corresponding SCN analogue, $(TTF)(SCN)_{0.12}(Cl)_{0.57}$.

The temperature dependence of the four-probe dc conductivity is shown in Fig. 1 where typical thermal activation conduction was dominant down to a temperature of 50 K with an activation energy of 50 meV. Very little VRH behavior was exhibited there. This makes a sharp contrast to the behavior of the SCN analogue where a big VRH conduction is apparent. Very slight thermal hysteresis was observed in the entire region of temperature examined.

$(TTF)(SeCN)_{0.22}(Br)_{0.44}$. Black-brown shiny needles or their bundles were obtained from electro-crystallization. Their average size was $1.1 \times 0.08 \times 0.02$ mm^3 and dc electrical conductivity at 300 K was in the range of 0.04–1.54 S cm^{-1} with an average of 0.44 ± 0.50 S cm^{-1}. The temperature dependence of the sample, shown in Fig. 2, was very similar to the case of the chloride analogue $(TTF)(SeCN)_{0.26}(Cl)_{0.43}$. It had less temperature dependence of activation energy than did the thiocyanate analogue $(TTF)(SCN)_{0.09}(Br)_{0.59}$ and a very slight thermal hysteresis appeared above 100 K, but disappeared after the first thermal cycle down to 50 K.

1D VRH behavior at the low temperature region below 100 K was evidenced by a linear dependence of activation energy on inverse temperature, but this small VRH character was weakened to a normal activation conduction as the temperature went above 100 K.

$(TTF)(SeCN)_{0.22}(I)_{0.42}$. Black bundles of long wedge-shaped crystals were obtained by galvanostatic electrolysis. The average size of the bundle was $1.23 \times 0.17 \times 0.12$ mm^3. The

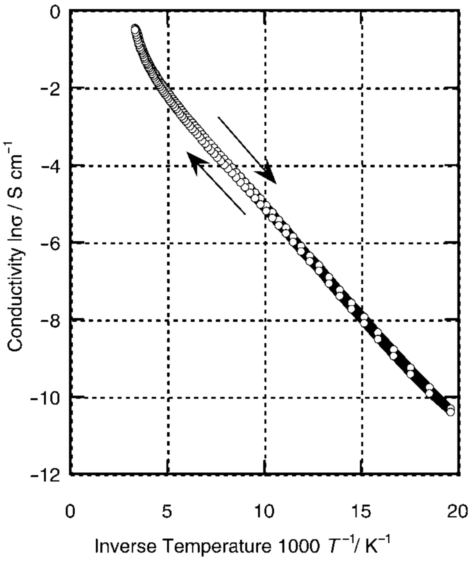

Fig. 1 The temperature dependence of dc conductivity of mixed anion TTF conductor $(TTF)(SeCN)_{0.26}(Cl)_{0.43}$. Arrows indicate the direction of temperature changes.

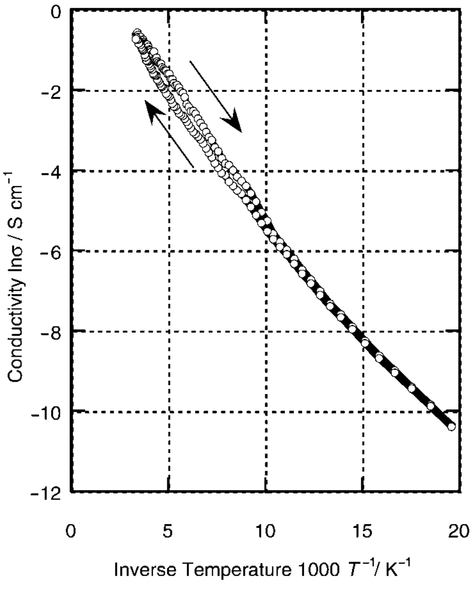

Fig. 2 The temperature dependence of dc conductivity of mixed anion TTF conductor $(TTF)(SeCN)_{0.22}(Br)_{0.44}$. Arrows indicate the direction of temperature changes.

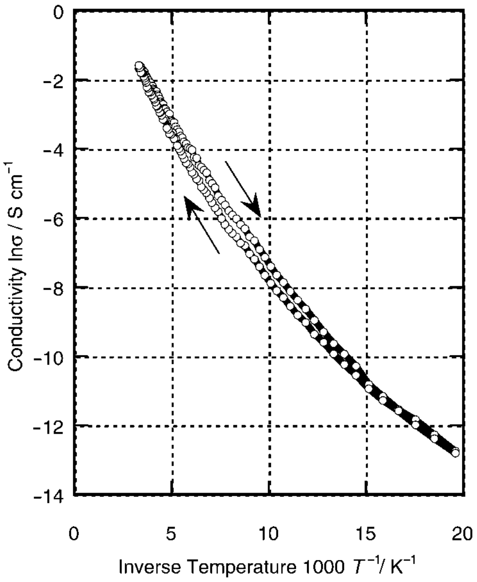

Fig. 3 The temperature dependence of dc conductivity of mixed anion TTF conductor (TTF)(SeCN)$_{0.22}$(I)$_{0.42}$. Arrows indicate the direction of temperature changes.

dc conductivity at 300 K was found to be in the range of 0.02–0.57 S cm^{-1} with an average value of 0.22 ± 0.17 S cm^{-1}. The temperature dependence shown in Fig. 3 indicates a linearly decreasing conductivity with decreasing temperature without distinct change over the entire temperature region. The VRH plot of the data showed the conduction to fit this model. This salt also showed a small degree of thermal hysteresis over a wide range from room temperature down to 65 K. This thermal hysteresis (Fig. 3) apparently disappeared and exhibited the same conduction behavior as the trace of conductivity in the warming process when it cooled down again.

(TTF)(SeCN)$_{0.35}$(SCN)$_{0.22}$. The anion content suggests that SeCN has more affinity than SCN towards TTF. The difference in affinity has also been reflected in the averaged anion content of the mixed anion salts examined so far (see Table 1). Black-brown needles of average size of 2.00 × 0.06 × 0.06 mm^3 were obtained by electrocrystallization. The conductivity at 300 K was in the range of 0.62–2.33 S cm^{-1} with an average value of 1.10 ± 0.57 S cm^{-1}. The temperature dependence of the crystal is shown in Fig. 4, which also shows that conductivity underwent a clear change in activation energy at *ca.* 134 K, below which it was dominated by a typical VRH character. Above 134 K it behaved nearly as an activation-type conductor with activation energy of 20 meV. A slight thermal hysteresis was noticed above 134 K, but it disappeared after cooling to 50 K.

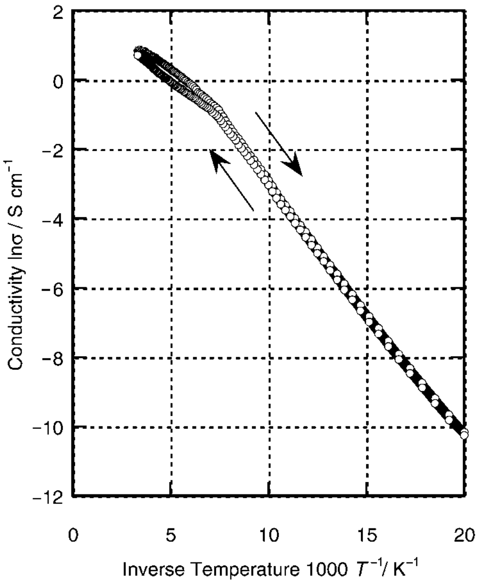

Fig. 4 The temperature dependence of dc conductivity of mixed anion TTF conductor (TTF)(SeCN)$_{0.35}$(SCN)$_{0.22}$. Arrows indicate the direction of temperature changes.

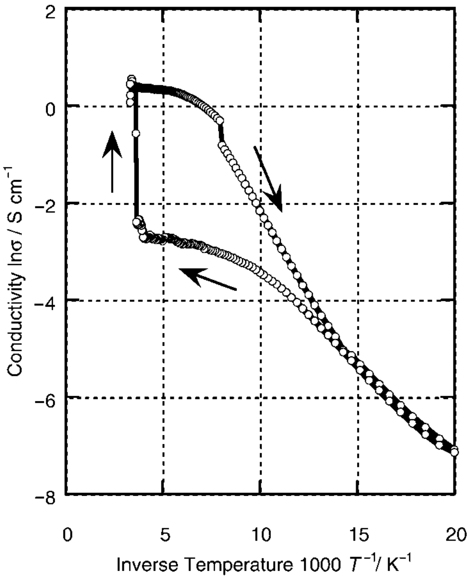

Fig. 5 The temperature dependence of dc conductivity of mixed anion TTF conductor (TTF)(SeCN)$_{0.47}$(NO$_3$)$_{0.10}$. Arrows indicate the direction of temperature changes.

(TTF)(SeCN)$_{0.47}$(NO$_3$)$_{0.10}$. Black-purple wedge-shaped shiny needles and their bundles or conglomerates were obtained. The average size of a single crystal was 1.5 × 0.06 × 0.06 mm^3. The conductivity at 300 K was in the range of 1.07–11.1 S cm^{-1} with an average value of 3.8 ± 4.2 S cm^{-1}. This value is one order of magnitude larger than those of the other SeCN-containing salts. The temperature dependence of the conductivity sometimes exhibits a large thermal hysteresis below 276 K down to 70 K, as is shown in Fig. 5. Although the extent of thermal hysteresis was dependent on the individual crystal, it had always disappeared after the first thermal cycle down to 50 K.

(TTF)(SeCN)$_{0.51}$(ClO$_4$)$_{0.04}$. Black needles of average size 0.9 × 0.04 × .03 mm^3, sometimes forming big conglomerates of 9 mm in length. Conductivity at 300 K was in the range of 0.25–1.98 S cm^{-1} with an average value of 0.77 ± 0.56 S cm^{-1}. The temperature dependence in Fig. 6. shows a small degree of VRH below 180 K. Just the same as the case of (TTF)(SeCN)$_{0.35}$(SCN)$_{0.22}$, it showed a slight thermal hysteresis over a wide temperature region. It completely disappeared when it was cooled down to 50 K.

The conduction properties of SeCN-containing mixed anion TTF salts are summarized as follows.

(1) Dc conductivity is one or two orders of magnitude lower than SCN analogues. (2) Coexistence of activation type conduction at a higher temperature region and VRH conduction at a lower region with less domination than in SCN-containing salts. (3) Thermal hysteresis appear in the first thermal cycle down to 50 K, then disappear later in the thermal cycle.

SeCN anions have larger van der Waals radii and electronegativity than SCN anions. The replacement of SCN with SeCN in the salts may promote more anion ordering in the

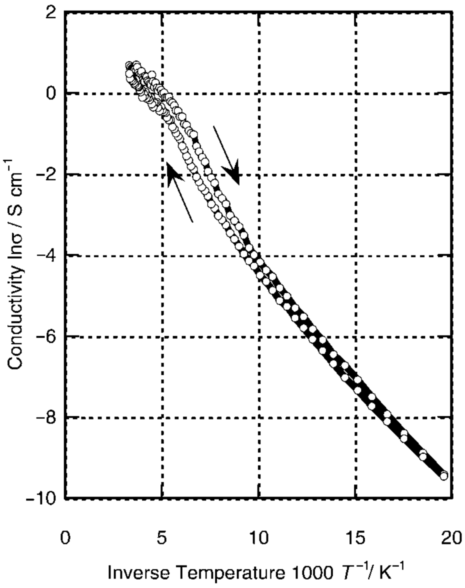

Fig. 6 The temperature dependence of dc conductivity of mixed anion TTF conductor (TTF)$(SeCN)_{0.51}(ClO_4)_{0.04}$. Arrows indicate the direction of temperature changes.

crystal lattice, reducing the VRH contribution to conductivity. As was reported in our previous paper, anion ordering, even a partial one, could restore the activation-type conduction.[15] Thus the temperature dependence of the conductivity is very sensitive to the order of lattices, not only to that of the conducting cation radical lattice but also to that of the counter anion lattice.

The temperature dependence of conductivity of Cl series and SCN series salts showed typical VRH behavior in the entire temperature region examined. In contrast, the VRH behavior of SeCN containing salts was very slight, as in the temperature dependence of (TTF)$(SeCN)_{0.26}(Cl)_{0.43}$ shown in Fig. 1.

This weak VRH character reveals the smaller degree of hopping conduction and greater contribution of thermal activation to the conductivity. At higher temperatures, most of the SeCN-containing salts behaved nearly as activation-type conductors with a slight amount of thermal hysteresis. This transition between the two conduction mechanisms was in accordance with the VRH model picture where hopping assisted conduction is more dominant at low temperatures but is eventually overwhelmed by the activation-type conduction as the temperature increases. This activation-type behavior of the disorder system should be distinguished from the intrinsic activation conduction in the ordered system.

VRH conduction of the disordered salts

The mixed anion TTF conductors summarized in Table 1 can be classified into three groups for convenience, namely, Cl^-, SCN^- and $SeCN^-$-containing groups. The room temperature conductivity of the Cl^- or SCN^- salts is in the range of 0.7–129 S cm^{-1}, which is one or two orders of magnitude smaller than those of the single anion TTF conductors studied so far.[4,5] This suppressed conductivity is due simply to the mixing in the anion lattice.

So far, most of the mixed anion TTF conductors including Cl and/or SCN have shown a temperature dependence of conductivity typical of VRH conduction except for (TTF)$(SCN)_{0.47}(NO_3)_{0.10}$. This behavior is very common to the disordered 1D system proposed by N. F. Mott decades ago.[9] According to this model, the conductivity $\sigma(T)$ of the disordered 1D system depends on the temperature obeying the following eqn. (1):

$$\sigma(T) = \sigma_0 \exp[-(T/T_0)^{1/2}] \tag{1}$$

where T is the temperature and σ_0, T_0 are constants. This VRH conduction could be induced by an impurity or disorder included in the ordered system. In the case of mixed anion conductors, the 1D VRH behavior is considered due to the existence of the 1D disordered structure included in the system. This point of view was partly evidenced to be true when the crystal structure of (TTF)$(Cl)_{0.42}(ClO_4)_{0.14}$ was analyzed and anions were found to be completely disordered, giving a uniform electron density of anions along the conducting TTF chains in the Fourier map. In the temperature dependence of (TTF)$(Cl)_{0.42}(ClO_4)_{0.14}$, the VRH conduction is clearly evidenced.[12] There is only one exception among them which does not follow the VRH model: (TTF)$(SCN)_{0.47}(NO_3)_{0.10}$, which follows Arrhenius conduction and in which anions are partially ordered in their lattice due to its nearly commensurate composition.[15]

When the SeCN ion is introduced as the mixed anion pair, the conductivity of the salt drops by another order of magnitude, as shown in Table 1. The temperature dependence of conductivity of (TTF)$(SeCN)_{0.26}(Cl)_{0.43}$, (TTF)$(SeCN)_{0.22}(Br)_{0.44}$, (TTF)$(SeCN)_{0.22}(I)_{0.42}$, (TTF)$(SeCN)_{0.35}(SCN)_{0.22}$, (TTF)$(SeCN)_{0.47}(NO_3)_{0.10}$, and (TTF)$(SeCN)_{0.51}(ClO_4)_{0.04}$ are shown in Fig. 1–Fig. 6, respectively. These results reveal that the VRH character is less apparent than those of Cl- and/or SCN-containing mixed anion TTF conductors.

Thermal hysteresis in SCN^- and $SeCN^-$ salts

So far, every SCN series conductor has shown a large thermal hysteresis below room temperature down to 130 K (SCN/NO_3, SCN/ClO_4) or 100 K (SCN/Cl).[13] This phenomenon appeared repeatedly in each thermal cycle except for one salt, (TTF)$(SCN)_{0.47}(NO_3)_{0.10}$.[15] For this sample the thermal hysteresis disappeared after experiencing the first thermal cycle down to 50 K.

Thermal hysteresis was also observed in SeCN-containing salts in the temperature dependence of conductivity below room temperature down to 120 K (SeCN/Cl, SeCN/SCN), 100 K (SeCN/Br) or 65 K (SeCN/I). However, what is distinctly different from the SCN series, is that (1) the extent of hysteresis was less than that of SCN-containing salts and (2) for no crystal examined could hysteresis be restored by warming up to 300 K after experiencing temperatures as low as 50 K.

To explain the above findings, we propose a model of transitions between two phases: the orientationally disordered quasi-stable phase, and the ordered stable phase for SCN- and SeCN-containing salts. This model includes the following hypothesis:

(1) When crystals are harvested from the electrochemical crystallization, all the chalcocyanate-containing salts are in a quasi-stable phase concerning the freedom of orientational movement due to the linear-shaped anions. (2) When a crystal is cooled down to as low as 50 K, it enters the stable phase where anions are partially ordered in orientation. (3) SCN-containing salts can transit to the quasi-stable phase again by thermal agitation at high temperatures up to 300 K. (4) However, due to the increased moment of inertia of the linear anion, SeCN-containing salts cannot be agitated to the quasi-stable phase below 300 K.

Within the temperature range examined here, SeCN-containing salts cannot transit to a quasi-stable phase. Thus the thermal hysteresis in the conductivity of Se-containing salts does not appear again after the first experience of temperatures as low as 50 K. This is the same behavior as that

Table 3 Interplanar distances of mixed anion TTF conductors

Salt	$d_{\mathrm{TTF-TTF}}$/Å	Reference
$(\mathrm{TTF})(\mathrm{Cl})_{0.42}(\mathrm{ClO_4})_{0.14}$	3.600(1)	12
$(\mathrm{TTF})(\mathrm{Cl})_{0.60}(\mathrm{BF_4})_{0.02}$	3.595(1)	13
$(\mathrm{TTF})(\mathrm{Cl})_{0.66}(\mathrm{SCN})_{0.09}$	3.608(2)	13
$(\mathrm{TTF})(\mathrm{Cl})_{0.28}(\mathrm{NO_3})_{0.59}$	3.592(2)	16
$(\mathrm{TTF})(\mathrm{SCN})_{0.47}(\mathrm{NO_3})_{0.10}$	3.623(1)	15
$(\mathrm{TTF})(\mathrm{SCN})_{0.12}(\mathrm{Cl})_{0.57}$	3.606(4)	Unpublished data
$(\mathrm{TTF})(\mathrm{SCN})_{0.56}(\mathrm{ClO_4})_{0.01}$	3.624(1)	16
$(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$	3.600(1)	This work

Table 4 Crystal data of $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$

Empirical formula	$\mathrm{S_4C_{6.26}H_4Se_{0.26}Cl_{0.43}N_{0.26}}$
Formula weight	246.88
DPO	0.69
Crystal system	Tetragonal
Space group	*P*4$_2$/*mnm*
Z	2
a/Å	11.203(1)
b/Å	11.203(1)
c/Å	3.600(1)
V/Å^3	451.9(1)
D_{obs}/g cm^{-3}	1.80
D_{calc}/g cm^{-3}	1.814
Maximum 2θ	59.9°
Number of observed reflections	857
Number of independent	400
Number of observations ($I > 1.00\sigma(I)$)	258
Number of parameters	22
R	0.082
R_{w}	0.106
Maximum peak in final diff. map	0.77 e Å^{-3}

of $(\mathrm{TTF})(\mathrm{SCN})_{0.47}(\mathrm{NO_3})_{0.10}$, where the anions were partly ordered.[15] The relationship between the disappearance of thermal hysteresis and increase in anion order is also suggested by the structural analysis of $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$, where the anions partially order giving localized electron density along the anion lattice.

Crystal structures of mixed anion salts

The crystal structure was analyzed for the seven of the currently identified 21 mixed anion TTF conductors. They were $(\mathrm{TTF})(\mathrm{Cl})_{0.42}(\mathrm{ClO_4})_{0.14}$,[12] $(\mathrm{TTF})(\mathrm{Cl})_{0.60}(\mathrm{BF_4})_{0.02}$,[13] $(\mathrm{TTF})(\mathrm{Cl})_{0.66}(\mathrm{SCN})_{0.09}$,[13] $(\mathrm{TTF})(\mathrm{Cl})_{0.28}(\mathrm{NO_3})_{0.59}$,[16] $(\mathrm{TTF})(\mathrm{SCN})_{0.47}(\mathrm{NO_3})_{0.10}$,[15] $(\mathrm{TTF})(\mathrm{SCN})_{0.12}(\mathrm{Cl})_{0.57}$, and $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$. All of them have a tetragonal lattice and space group *P*4$_2$/*mnm* and are isostructural to each other except $(\mathrm{TTF})(\mathrm{Cl})_{0.28}(\mathrm{NO_3})_{0.59}$, which has an orthorhombic lattice and space group *Pnnm*. However, the molecular packing and cell dimensions of these conductors are all quite similar. The crystal data of $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$ are summarized in Table 4.‡

In the crystal, the cation radical plane lies in the *ab*-plane and stacks equatorially to form a 1D radical stack. The values for TTF–TTF distance within a cation stacking are distributed around 3.60 Å. Table 3 lists values of $d_{\mathrm{TTF-TTF}}$ for the mixed anion TTF conductors. No direct correlation was observed between the conductivity and the interplanar distance.

In the channels between the stacks are inorganic mixed anions which are packed in a non-stoichiometric way and, in most cases, are fully disordered in a one-dimensional way along the TTF columns. A complete structural analysis has never been successful for these compounds. Most of the time, the Fourier calculations of the anion structure show uniformly distributed electron densities at (0, ½, *z*) ($0 < z < 1$) for the atomic parameters of the anions.

Table 5 Atomic coordinates, B_{eq} and occupancy factor in the unit cell of $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$

Atom	X	Y	Z	$B_{\mathrm{eq}}{}^{a}$/Å^2	Occupancy factor
Cl(1)	0.0000^b	0.5000^b	0.0000^b	3.6(2)	0.057
Cl(2)	0.0000^b	0.5000^b	0.2500^b	3.5(3)	0.051
S(1)	0.0100(3)	0.8061(3)	0.0000^b	4.61(7)	0.500
C(1)	0.0412(9)	0.9588	0.0000^b	3.3(2)	0.250
C(2)	0.158(1)	0.760(1)	0.0000^b	5.5(4)	0.500
C(11)	0.0000^b	0.5000^b	0.0000^b	3.5631	0.034
C(12)	0.0000^b	0.5000^b	0.2500^b	3.5178	0.031
H(1)	0.16(1)	0.665(10)	0.0000^b	5(2)	0.500

$^a B_{\mathrm{eq}} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$. ^{b}Fixed.

The reason for the 1D VRH conduction behavior of the mixed anion TTF conductors could be attributed to this 1D disordered structure of anions, which exerts a random Coulomb potential on the adjacent conducting TTF chains being as close as around 5.6 Å away. This reasoning is partly supported by observations of the exceptional Arrhenius conduction behavior in $(\mathrm{TTF})(\mathrm{SCN})_{0.47}(\mathrm{NO_3})_{0.10}$, where partial anion ordering was confirmed later.[15]

Structural comparison between $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$ and $(\mathrm{TTF})(\mathrm{SCN})_{0.09}(\mathrm{Cl})_{0.66}$

The crystal structure of $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$ was found to have structural data very close to those of $(\mathrm{TTF})(\mathrm{SCN})_{0.09}(\mathrm{Cl})_{0.66}$ which have appeared elsewhere.[13] Table 4 summarizes these crystal data, while Table 5 lists atomic coordinates and B_{eq} of $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$.

It would be interesting to compare the properties of the closely related crystals, $(\mathrm{TTF})(\mathrm{SCN})_{0.09}(\mathrm{Cl})_{0.66}$ and $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$. As summarized in Table 4, both compounds have close degrees of partial oxidation (0.75 and 0.69, respectively), and are isostructural concerning the radical structure. The unit cell dimensions are very close to each other and their unit cell volumes are almost the same.

The biggest difference to be pointed out is in the localization of anions along the *c*-axis. The mixed anions are fully disordered in the lattice of $(\mathrm{TTF})(\mathrm{SCN})_{0.09}(\mathrm{Cl})_{0.66}$ showing a uniform charge distribution along the anion sites in the Fourier analysis. This is reflected in the variable temperature conductivity, which is a typical VRH conduction as shown in Fig. 4 in our earlier report.[13]

Structural analysis of the salt $(\mathrm{TTF})(\mathrm{SeCN})_{0.26}(\mathrm{Cl})_{0.43}$ has shown that the electron density is localized at two sites along the anion lattice in the unit cell, (0,½,0) and (0,½, ¼) as shown in Table 5. Exclusive assignment of a Se or Cl atom to these peaks did not lead to a conversion in the least square calculations. Only a competitive assignment of the Cl atom and C atom for SeCN led to a reasonable solution. This is one piece of evidence for the development of the positional ordering along the anion lattice in the of SeCN-containing salt, still leaving a heavy orientational disorder for SeCN and compositional mixing among Cl and SeCN anions. This may explain their conduction properties where VRH conduction is less dominant than in SCN-containing salts. This is in accordance also with the activation-type conduction behavior at higher temperature region shown in Fig. 1–Fig. 6. Increased anion size and mass would help the anion ordering in the lattice positionally and/or orientationally. These features in the conduction behavior are also noticeable in the other SeCN-containing salts, suggesting they are more ordered than SCN-containing salts.

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‡CCDC reference number 162981. See http://www.rsc.org/suppdata/jm/b1/b101864g/ for crystallographic files in .cif or other electronic format.

The band structure of the disordered TTF conductors

The band structure of the disordered conductors was investigated by Mott[9] and Cohen *et al.*[17,18] It was predicted that there are continuous bands extended states with tails of localized states in the band gap, called "mobility edges". The existence of mobility edges signifies a narrowing of the band gap due to the disorder, because as randomness increases in a conductor, mobility edges move inward toward the band gap, making it narrower and narrower. This eventually reduces the electronic energy to be gained by the structural change associated with the Peierls transition and keeps the structural change from being completed.

The effect of the disorder on the Peierls[19] instability was reported in more detail in our previous article on mixed anion commensurate salts.[16]

Conclusion

Six new one-dimensional Se containing mixed anion TTF conductors were prepared electrochemically. Including the 15 other mixed anion salts, they showed that the anion affinity to TTF is, in decreasing order, halogens > chalcocyanates > other polyatomic anions. The dc conductivity, which ranges from 0.02–11.1 S cm^{-1}, is one or two orders of magnitude smaller than that of the SCN analogues.

Se-containing salts exhibited activation-type conduction at higher temperatures and were less dominated by VRH conduction at lower temperatures. The thermal hysteresis due to the orientational freedom of anion disappeared after the first thermal cycle in the variable temperature conduction measurements. A simple transition model between the disordered quasi-stable phase and the ordered stable phase was proposed to explain this phenomenon.

Crystal structure analysis of the seven compounds showed that the anion lattice was fully disordered except for $(TTF)(SeCN)_{0.26}(Cl)_{0.43}$, where anions began to localize at four sites in the unit cell, evidencing the development of anion ordering in Se-containing conductors. The conductivity of 1D mixed anion salts was very sensitive to the anion ordering.

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