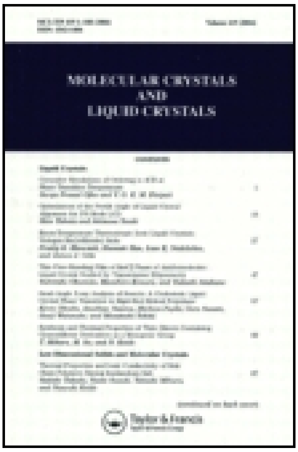

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Structures and Properties of Radical Cation Salts of Novel Tetraselenafulvalene Derivatives (BPT-TSF, EDT-PT-TSF, and BEST-TSF) with MX 4 (M = Fe, Ga, X = Cl, Br)-Type Anions

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Structures and Properties of Radical Cation Salts of Novel Tetraselenafulvalene Derivatives (BPT-TSF, EDT-PT-TSF, and BEST-TSF) with MX_4($M = Fe, Ga$, $X = Cl, Br$)-Type Anions

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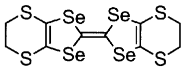
Abstract Using three different BETS variants (BPT-TSF **2**, EDT-PT-TSF **3**, and BEST-TSF **4**), six new radical cation salts of $D_2 \cdot MX_4$-type are prepared. The κ–type salts with $FeCl_4^-$ anion obtained from the donors **2** and **3** are isostructural with the corresponding BETS salts. From the donor **3**, a radical salt with β–type donor packing is obtained with $GaCl_4^-$ anion. All these salts from donors **2** and **3** are metallic down to low temperature. On the other hand, the donor **4** possessing selenium atoms in outer heterocycles gives two λ–type salts. They are highly conductive at room temperature, but not metallic at low temperature range.

Keywords electron donor; electrocrystallization; radical cation salt; molecular conductor, X-ray crystallographic analysis

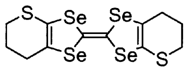
INTRODUCTION

In the last two decades, numbers of electron donors and thus obtained conductive radical cation salts have been developed [1]. Only a limited number of electron donors, however, are capable of forming superconducting radical cation salts, and among them, bis(ethylendithio)tetraselenafulvalene (BETS **1**) is a very important electron donor, because BETS gives about 70 metallic salts, more than 10% of which undergo a superconducting transition at low temperature [2]. Furthermore, an unprecedented antiferromagnetic molecular superconductor, κ–$(BETS)_2 \cdot FeBr_4$, has been recently reported [3].

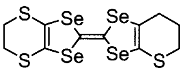
We have recently established a facile synthetic procedure of heterocycle-fused TSF derivatives [4], which is applicable to the synthesis of bis(propylenedithio)-TSF (BPT-TSF **2**) [5], ethylenedithio-propylenethio-TSF (EDT-PT-TSF **3**) [6], and bis(ethyleneselenothio)-TSF (BEST-TSF **4**) [7]. These new TSF derivatives can be regarded as BETS variants with modified outer heterocycles. Since a number of superconductors and stable metals are found from $(BETS)_2 \cdot MX_4$ (M = Fe, Ga, X = Cl, Br) type radical cation salts, we have synthesized analogous radical salts of the BETS variants. In this paper, synthesis, conductive properties and crystal structures of $D_2 \cdot MX_4$ (Donor = BPT-TSF **2**, EDT-PT-TSF **3**, and BEST-TSF **4**) salts are described.



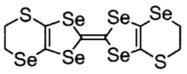
BETS **1**



BPT-TSF **2**



EDT-PT-TSF **3**



BEST-TSF **4**

RESULTS AND DISCUSSION

Crystal growth

Electrocrystallization of electron donors, **2**, **3**, and **4** was carried out in chlorobenzene or THF containing an appropriate tetraethylammonium salt at room temperature or 50 ℃ with a constant current of 0.3−1.0 μA. Crystals of radical cation salts were grown in two weeks.

X-ray structure analysis

From three BETS variants (**2**-**4**), six $D_2 \cdot MX_4$-type radical cation salts were obtained and characterized by X-ray crystallographic analysis as summarized in TABLE 1. It turned out that three salts, $\mathbf{2}_2 \cdot FeCl_4$, $\mathbf{2}_2 \cdot FeBr_4$, and $\mathbf{3}_2 \cdot FeCl_4$, have κ–type structures, and two salts, $\mathbf{4}_2 \cdot FeCl_4$ and $\mathbf{4}_2 \cdot GaCl_4$, λ–type structures, which are isostructural with the corresponding κ– and λ–BETS salts, respectively [8]. The crystal structures of $\mathbf{2}_2 \cdot FeCl_4$, and $\mathbf{4}_2 \cdot GaCl_4$ are depicted as κ–type and λ–type representatives in FIG. 1.

On the other hand, $\mathbf{3}_2 \cdot GaCl_4$ has a different crystal structure from the BETS counterpart and is classified as the β–type as shown in FIG. 2. Its band structure and Fermi surface calculated on the basis of the extend Hückel tight-binding approximation [9] suggest that the salt has a two dimensional electronic structure (FIG. 3.).

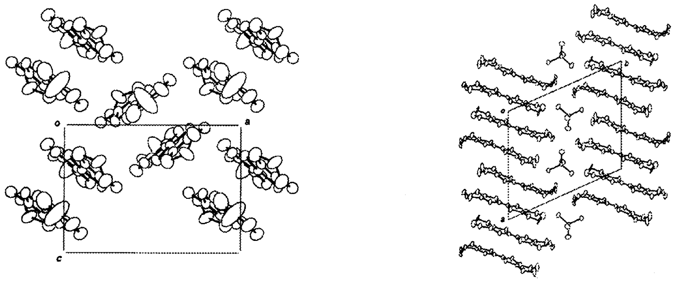


FIG. 1. Crystal structures of $\mathbf{2}_2 \cdot FeCl_4$ (left) and $\mathbf{4}_2 \cdot GaCl_4$ (right)

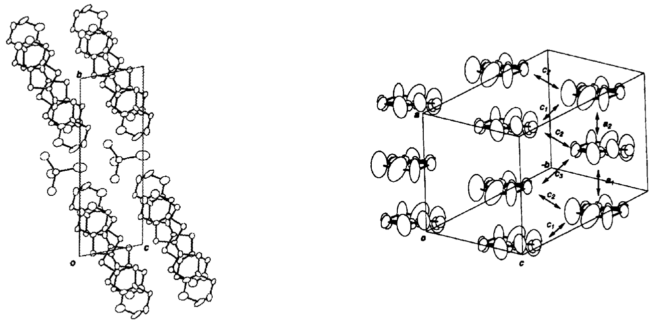


FIG. 2. Crystal structure of $\mathbf{3}_2 \cdot GaCl_4$: a-axis projection (left) and a side view of the donor sheet (right). Calculated overlap integrals are $a_1 = 20.75$, $a_2 = 9.95$, $c_1 = 4.45$, $c_2 = -1.64$ and $c_3 = 2.79$ (x 10^{-3}).

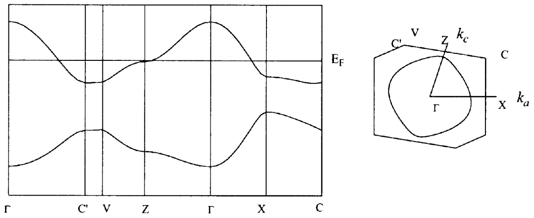


FIG. 3 Band structure and Fermi surface of β–$\mathbf{3}_2 \cdot GaCl_4$

Conductivity

Conductive properties of these salts are listed in TABLE 2, and temperature dependent resistivities of representative salts (κ–$\mathbf{3}_2 \cdot FeCl_4$, β–$\mathbf{3}_2 \cdot GaCl_4$ and λ–$\mathbf{4}_2 \cdot GaCl_4$) are depicted in FIG. 4. All the salts are highly conductive at room temperature like the BETS counterparts. The κ–type and β–type salts are metallic down to 4.2 K, but these salts are less temperature dependent:

resistivity of κ–$(BETS)_2 \cdot FeCl_4$ around 4 K is smaller by more than three orders of magnitude than that at room temperature, while the minimum resistivity of κ–$\mathbf{3}_2 \cdot FeCl_4$ at 4.2 K is about one tenth of that at room temperature. This would be a consequence of disordering of the donor orientation in the crystal structure due to the lower symmetry of the present donors.

Although room temperature conductivities of the λ–type salts are comparable to those of the corresponding BETS salts, conducting behaviors at low temperature are rather different from the metallic ones of the latter. As seen in FIG. 4 for λ–$\mathbf{4}_2 \cdot GaCl_4$, its resistivity curve is almost flat around room temperature, and then it behaves as a semiconductor below 100 K. This indicates that introduction of large selenium atoms into the outer heterocycles is undesirable modification for the synthesis of molecular metals.

TABLE 1 Crystal data for radical cation salts of **2**–**4**.

	κ–$\mathbf{2}_2$•$FeCl_4$	κ–$\mathbf{2}_2$•$FeBr_4$	κ–$\mathbf{3}_2$•$FeCl_4$	β–$\mathbf{3}_2$•$GaCl_4$	λ–$\mathbf{4}_2$•$FeCl_4$	λ–$\mathbf{4}_2$•$GaCl_4$
chemical formula	$C_{24}H_{24}S_4Se_8FeCl_4$	$C_{24}H_{24}S_4Se_8FeBr_4$	$C_{22}H_{20}S_6Se_8FeCl_4$	$C_{22}H_{20}S_6Se_8GaCl_4$	$C_{20}H_{16}S_4Se_{12}FeCl_4$	$C_{20}H_{16}S_4Se_{12}GaCl_4$
formula weight	1270.03	1447.84	1306.10	1319.98	1529.77	1543.64
crystal system	*orthorhombic*	*orthorhombic*	*orthorhombic*	*triclinic*	*triclinic*	*triclinic*
a/Å	11.731(4)	11.848(3)	11.727(3)	7.857(2)	16.287(4)	16.250(2)
b/Å	35.41(2)	36.096(4)	35.642(9)	18.068(7)	18.701(4)	18.732(2)
c/Å	8.609(3)	8.643(3)	8.555(2)	6.701(2)	6.682(1)	6.6775(6)
α/°				100.09(3)	98.01(2)	98.02(1)
β/°				102.25(3)	97.11(2)	97.15(1)
γ/°				93.18(3)	112.31(1)	112.39(1)
V/Å^3	3576(2)	3696(1)	3575(1)	910.9(6)	1829.5(7)	1825.6(4)
space group	*Pnma* (no. 62)	*Pnma* (no. 62)	*Pnma* (no. 62)	*P*–1 (no. 2)	*P*–1 (no. 2)	*P*–1 (no. 2)
Z	4	4	4	1	2	2
D_{calc} /gcm^{-3}	2.359	2.602	2.427	2.406	2.777	2.808
No. of data (I >3.0σ (I))	2464	852	2312	1973	2034	3296
R^a, Rw^b	0.067, 0.055	0.050, 0.066	0.053, 0.054	0.062, 0.067	0.060, 0.060	0.066, 0.068

[a] $R = \Sigma(|Fo| - |Fc|)/\Sigma|Fo|$. [b] $Rw = \{\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2\}^{1/2}$.

TABLE 2 Radical cation salts of **2**, **3**, and **4**.

Salt	Appearance	σ/S cm$^{-1\,a}$	Remarks
κ–$\mathbf{2}_2 \cdot FeCl_4$	black plates	99	metallic (4.2 K)
κ–$\mathbf{2}_2 \cdot FeBr_4$	black plates	10	metallic
κ–$\mathbf{3}_2 \cdot FeCl_4$	black plates	86	metallic (4.2 K)
β–$\mathbf{3}_2 \cdot GaCl_4$	black plates	50	metallic (4.2 K)
λ–$\mathbf{4}_2 \cdot FeCl_4$	black needles	29	semiconductive
λ–$\mathbf{4}_2 \cdot GaCl_4$	black needles	24	semiconductive

[a] Measured on a single crystal with a four-probe method.

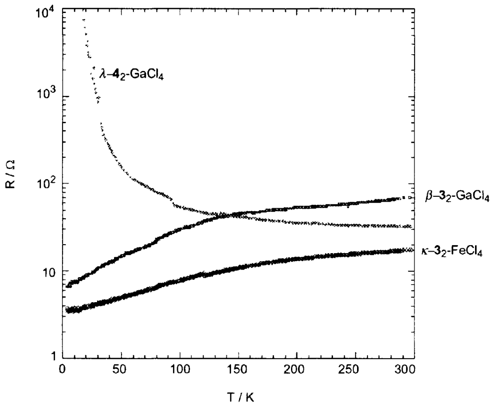


FIG. 4. Temperature dependence of resistivities of κ–$\mathbf{3}_2 \cdot FeCl_4$, β–$\mathbf{3}_2 \cdot GaCl_4$ and λ–$\mathbf{4}_2 \cdot GaCl_4$.

CONCLUSION

From three BETS variants (**2**, **3**, and **4**), we have obtained six $D_2 \cdot MX_4$-type radical cation salts. They are structurally characterized as κ– or λ–type, except for **3**·$GaCl_4$ with β–type donor packing. Although all the salts from donors **2** and **3** are metallic down to low temperature, two salts derived form **4** possessing selenium atoms in outer heterocycles behave as semiconductors at low temperature.

These results indicated that modification on the outer ring of BETS is influential in the conductive properties of the resulting radical cation salts, even though the crystal structures are not essentially influenced.

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