

Novel Conductive Radical Cation Salts Based on Methylene-diselenotetraselenafulvalene (MDSe-TSF): A Sign of Superconductivity in κ -(MDSe-TSF)₂Br Below 4 K

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Seven conductive radical cation salts based on MDSe-TSF (methylene-diselenotetraselenafulvalene) have been synthesized by electrocrystallization in the presence of Cl⁻, Br⁻, I₃⁻, I₂Br⁻, PF₆⁻, ClO₄⁻, and Cu(NCS)₂⁻ counter anions. The crystal appearances of these salts fairly depend on the anions employed. X-ray crystallographic analyses have revealed that the PF₆ and ClO₄ salts in the shape of brown thin plates adopt the θ -type structures characterized by the herringbone arrangement of donor stacks, whereas the Cl and Br salts in the shape of black thick plates favor the κ -type structures with the orthogonal arrangement of donor dimers. Regardless of different crystal appearances or crystal packing patterns, all these salts show high conductivity ($> 10^2$ S cm⁻¹) at room temperature and retain metallic properties down to 4.2 K. Of them, the Br salt shows a weak but distinct diamagnetic shielding signal below 4 K in the dc magnetization measurement under zero-field-cooled (ZFC) condition, suggesting a sign of superconductivity. The band calculations of both PF₆ and Br salts demonstrate closed Fermi surfaces indicative of two-dimensional molecular conductors. © 2002 Elsevier Science (USA)

Key Words: radical cation salt; organic superconductor; magnetic susceptibility; X-ray structure analysis; selenium-containing electron donor.

1. INTRODUCTION

The development of novel molecular superconductors has been one of the major topics in the solid state science in the last two decades since the first molecular-based superconductor, (TMTSF)₂PF₆ was discovered (1). Although more than 100 molecular superconductors have been already found principally among radical cation salts, the number of organic electron donors capable of producing the superconductors is still limited. Most of such

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electron donors are of tetrathiafulvalene (TTF) type, and especially, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is the most excellent donor that has afforded about a half of organic superconductors (2). In addition, it is worth noting that BEDT-TTF analogues with different chalcogen atoms, bis(ethylenedithio)tetraselenafulvalene (BETS) (3) and bis(ethylenedioxy)tetrathiafulvalene (BO) (4) can also form many unique organic superconductors. In this regard, we have recently been focusing on the selenium variants of heterocycle-fused TTFs in an effort to develop new superconductors. Papavassiliou and coworkers in 1988 reported that methylenedithiotetrathiafulvalene (MDT-TTF) is an electron donor capable of producing a κ -type superconducting salt with an AuI₂ ion (5). In the course of selenium substitution of MDT-TTF, we recently found that methylenedithiotetraselenafulvalene (MDT-TSF) can give a series of superconductors with AuI₂, I₃, I₂Br, and IBr₂ counter anions with high room temperature conductivities (6–8). In particular, the AuI₂ salt ($T_c = 4.5$ K) is remarkable for an extraordinarily high conductivity of 2000 S cm⁻¹ (6). This successful result of MDT-TSF has prompted us to study another selenium variant, methylene-diselenotetraselenafulvalene (MDSe-TSF), in which all the chalcogen atoms are completely replaced by selenium. In this paper, we would like to report the synthesis, structures, and conductive properties of novel radical cation salts of MDSe-TSF with versatile counter anions of monoatomic, linear, tetrahedral, octahedral, and polymeric types.

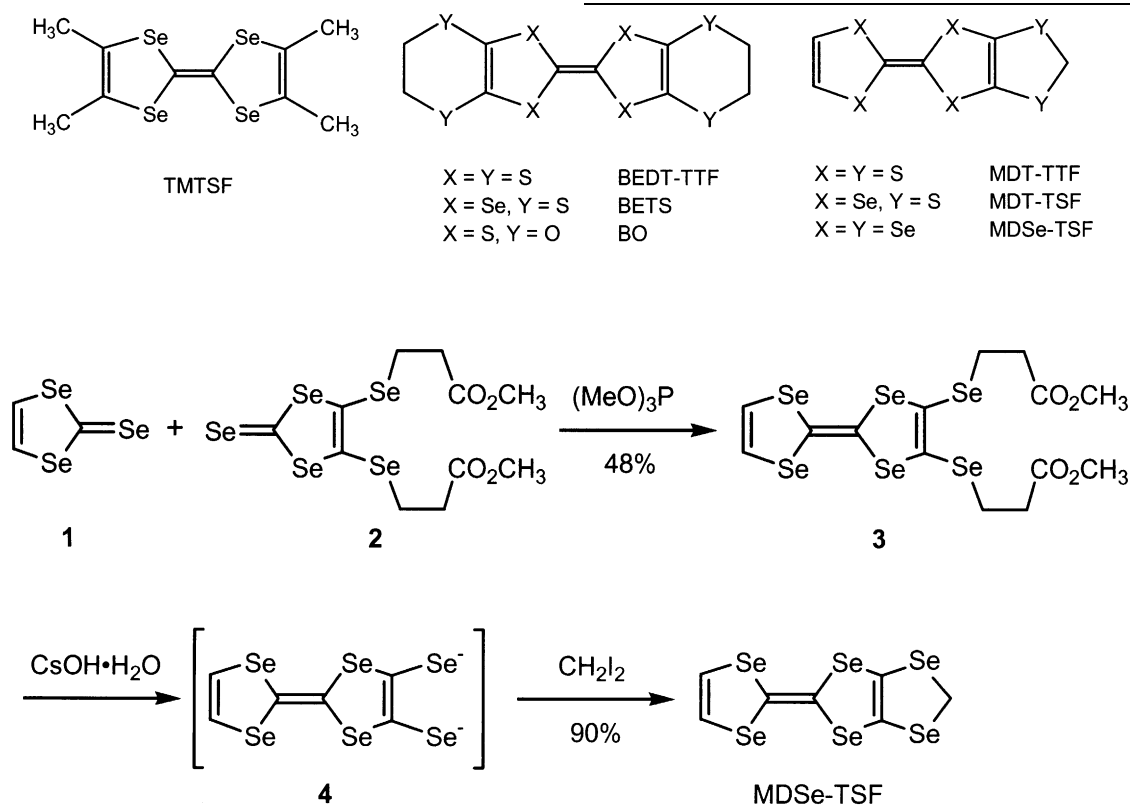
2. EXPERIMENTAL

2.1. Synthesis of MDSe-TSF

It was previously difficult to synthesize such selenocycle-fused TSF derivatives as MDSe-TSF, but we have recently established an effective synthetic method for this type of TSF derivatives (9). Scheme 1 outlines the synthetic route

of MDSe-TSF, which takes advantage of an ingenious protocol using deprotection/realkylation of 2,3-bis(2-methoxycarbonylethylseleno)tetraselenafulvelene (**3**). Only a drawback of this method is that the preparation of the starting 1,3-diselenole-2-selone (**1**) and its derivative (**2**) must use toxic carbon diselenide (10).

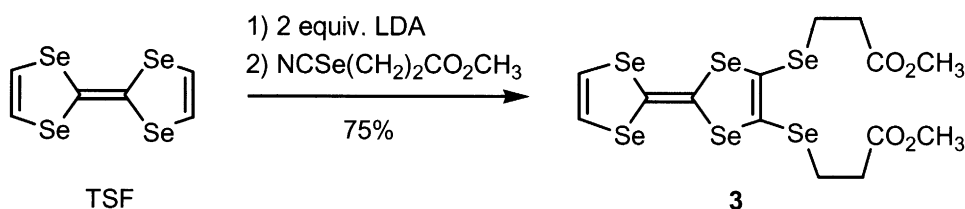
out use of carbon diselenide (11). On detailed examination, it has turned out that the reaction as shown in Scheme 2 is completely successful; TSF was treated with 2 equivalents of lithium diisopropylamide (LDA) at -78°C in THF for 30 min to generate the 2,3-dilithio-TSF, which was then reacted with methyl 3-selenocyanatopropionate at room



Scheme 1. Reported synthesis of MDSe-TSF.

In order to avoid this, we have searched for an alternative route that is generally acceptable. One potential method is to obtain the key intermediate (**3**) by direct difunctionalization of TSF, which is now accessible with-

temperature for 1 h to give **3** as red plates in 75% yield. It is worth noting that the 2,3-dithiation is very regioselective, forming no other difunctionalized products (**12**) (Scheme 2).



Scheme 2. Alternative synthesis of the intermediate **3**.

2.2. Preparation of Radical Cation Salts

The radical cation salts of MDSe-TSF were synthesized with a standard electrocrystallization technique using a 20 mL H-shaped glass cell with a glass frit. The donor (3–5 mg) was placed in the anode compartment of the cell, and 20–80 mg of an appropriate tetrabutylammonium salt [(C₄H₉)₄N]X, (X = Cl, Br, I₃, I₂Br, ClO₄, PF₆) or [(C₆H₅)₄P]Br was placed in the cathode compartment. For the synthesis of the Cu(NCS)₂ salt, a mixture of KSCN (50 mg), CuSCN (40 mg), and 18-crown-6-ether (80 mg) was used according to a synthetic protocol for the Cu(NCS)₂ salt of BEDT-TTF (13). Chlorobenzene containing 5–10% of ethanol (approx. 18 mL) was added, and the resulting solution was degassed with a dry nitrogen stream. Anode and cathode electrodes made of 1 mm platinum wires were set to the cell, and a constant direct current of 0.1–0.5 μA was applied. Within 2 weeks, crystals of the radical cation salts grew on the anode electrode and around the glass frit. The crystals were collected by filtration, washed with dichloromethane, and dried in vacuo. The properties of thus obtained radical cation salts of MDSe-TSF with Cl[−], Br[−], I₃[−], I₂Br[−], ClO₄[−], PF₆[−], and Cu(NCS)₂[−] anions are summarized in Table 1.

2.3. Conductivity and Magnetization Measurements

Electrical conductivity was measured on a single crystal with a conventional four-probe method using a FUSO HECS-994 system. In the sample setting, gold electrodes (20 μm diameter) were attached directly to the crystal with gold paste. DC magnetization experiments were carried out with a Quantum Design MPMS-5 SQUID magnetometer using randomly oriented polycrystalline samples in a gelatin capsule.

2.4. Crystal Structure Determination

A Rigaku AFC 7R diffractometer (four-circle) or a Rigaku RAPID-S area detector (IP) with graphite-mono-

chromated MoK α radiation ($\lambda = 0.7107 \text{ \AA}$) was used, and the reflection data for all the crystals were collected at room temperature. The structures were solved by the direct method (SIR 92 or SHELXS 86 (14)) or the Patterson method. Hydrogen atoms were located by calculation and not refined. All non-hydrogen atoms were refined by a full matrix least-squares technique (SHELXL) with anisotropic temperature factors (15), except the fluorine atoms of (MDSe-TSF)₂PF₆. Structure solution and refinement were carried out using the teXsan program package (16). Summary of crystal data and structural refinement results are given in Table 2. The Supporting Information data for MDSe-TSF (neutral), (MDSe-TSF)₂Cl, (MDSe-TSF)₂Br, (MDSe-TSF)₂ClO₄, and (MDSe-TSF)₂PF₆ (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 185039–185043. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: deposit@chemcrs.cam.ac.uk).

3. RESULTS AND DISCUSSION

3.1. Crystal Appearances and Electrical Conductivities of MDSe-TSF Salts

Depending on the counter anions employed, the crystals of radical cation salts of MDSe-TSF have different shapes and colors. Of them, the salts with linear I₃[−] and I₂Br[−] anions have thin needle shapes in golden olive color, and apparently look like the appearance of the superconducting (MDT-TSF)X (X = I₃, I₂Br and IBr₂) (8). In addition, these salts show very high conductivities of several hundred S cm^{−1} at room temperature, which are almost comparable to those of the corresponding MDT-TSF salts (Table 1). However, the MDSe-TSF salts unlike the MDT-TSF salts are simple metallic conductors with a monotonous increase in conductivity down to liquid helium temperature as shown in Fig. 1, and no sign of superconducting transition is observed.

The other salts crystallize in two kinds of plate shapes. The salts with tetrahedral ClO₄[−] and octahedral PF₆[−] anions appear in brown-colored thin plates, whereas the salts with monoatomic Cl[−] and Br[−] anions and with polymeric Cu(NCS)₂[−] anion appear in black-colored thick plates. As discussed below, X-ray crystallographic analyses have revealed that these two kinds of salts have quite different crystal structures: the former salts adopt the θ -type structures, whereas the latter salts favor the κ -type structures, though the structure of the Cu(NCS)₂ salt remains unsolved. Regardless of different crystal structures, all these plate-shaped crystals also show high conductivities ($> 10^2 \text{ S cm}^{-1}$ at room temperature) with

TABLE 1
Conductive Radical Cation Salts of MDSe-TSF

Anion	Color	Shape	Structure	D:A ^a	$\sigma_{\text{rt}}/\text{S cm}^{-1}$
I ₃ [−]	Golden olive	Thin needle	—	Nearly 2:1 ^b	200–400
I ₂ Br [−]	Golden olive	Thin needle	—	^c	300–900
ClO ₄ [−]	Brown	Thin plate	θ	2:1	100–400
PF ₆ [−]	Brown	Thin plate	θ	2:1	100–250
Cl [−]	Black	Thick plate	κ	2:1	1000–1200
Br [−]	Black	Thick plate	κ	2:1	200–1000
Cu(NCS) ₂ [−]	Black	Thick plate	—	^c	300–1600

^a Determined by X-ray crystallographic analysis unless otherwise stated.

^b Estimated on the basis of EDS.

^c Not determined.

TABLE 2
Crystallographic Data for Neutral MDSe-TSF and its Radical Cation Salts

	MDSe-TSF (neutral)	(MDSe-TSF) ₂ Cl	(MDSe-TSF) ₂ Br	(MDSe-TSF) ₂ ClO ₄	(MDSe-TSF) ₂ PF ₆
Chemical formula	C ₇ H ₄ Se ₆	C ₁₄ H ₈ Se ₁₂ Cl	C ₁₄ H ₈ Se ₁₂ Br	C ₁₄ H ₈ Se ₁₂ ClO ₄	C ₁₄ H ₈ Se ₁₂ PF ₆
Formula weight	561.87	1159.19	1203.64	1223.19	1268.70
Crystal dimensions (mm ³)	0.45 × 0.25 × 0.05	0.40 × 0.20 × 0.12	0.30 × 0.20 × 0.10	0.38 × 0.35 × 0.02	0.23 × 0.10 × 0.01
Instruments	Rigaku AFC7R	Rigaku AFC7R	Rigaku RAPID-S	Rigaku AFC7R	Rigaku AFC7R
Type of data collection	ω	$\omega-2\theta$	IP	$\omega-2\theta$	ω
Crystal system	<i>Monoclinic</i>	<i>Monoclinic</i>	<i>Monoclinic</i>	<i>Orthorhombic</i>	<i>Orthorhombic</i>
Space group	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 222 ₁ (No. 20)	<i>Pccn</i> (No. 56)
Unit-cell dimensions	<i>a</i> 20.207(3) Å <i>b</i> 13.381(1) Å <i>c</i> 8.603(3) Å β 100.87(2) Å	23.494(2) Å 11.220(2) Å 8.918(2) Å 99.68(1) Å	23.954(3) Å 11.1716(6) Å 8.9576(8) Å 99.298(3) Å	4.178(3) Å 31.385(4) Å 10.650(3) Å	4.189 (4) Å 10.719(4) Å 31.915(4) Å
Volume (Å ³)	2284.4(9)	2317.5(5)	2365.5(4)	1396.4(9)	1433(1)
<i>Z</i>	8	4	4	2	2
<i>D</i> _{calc} (g cm ⁻³)	3.267	3.322	3.379	2.909	2.940
Absorption coefficient (cm ⁻¹)	191.75	190.18	202.13	158.00	153.84
Reflections collected	5255	2664	2694	973	1658
No. of data	3586 [<i>I</i> > 2.0σ(<i>I</i>)]	2044 [<i>I</i> > 2.0σ(<i>I</i>)]	2392 [<i>I</i> > 2.0σ(<i>I</i>)]	663 [<i>I</i> > 2.0σ(<i>I</i>)]	553 [<i>I</i> > 2.0σ(<i>I</i>)]
<i>R</i> ^a / <i>wR</i> ^b	0.065/0.202	0.033/0.137	0.044/0.149	0.049/0.170	0.062/0.228
Solution	Direct method (SIR92)	Direct method (SIR92)	Direct method (SIR92)	Direct method (SHELXS86)	Patterson method (DIRDIF94 PATTY)
Refinement	Full-matrix LS (SHELXL)	Full-matrix LS (SHELXL)	Full-matrix LS (SHELXL)	Full-matrix LS (SHELXL)	Full-matrix LS (SHELXL)

$$^a R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}$$

$$^b wR = \left\{ \frac{\sum (|F_o|^2 - |F_c|^2)^2}{\sum \omega(F_o^2)^2} \right\}^{1/2}$$

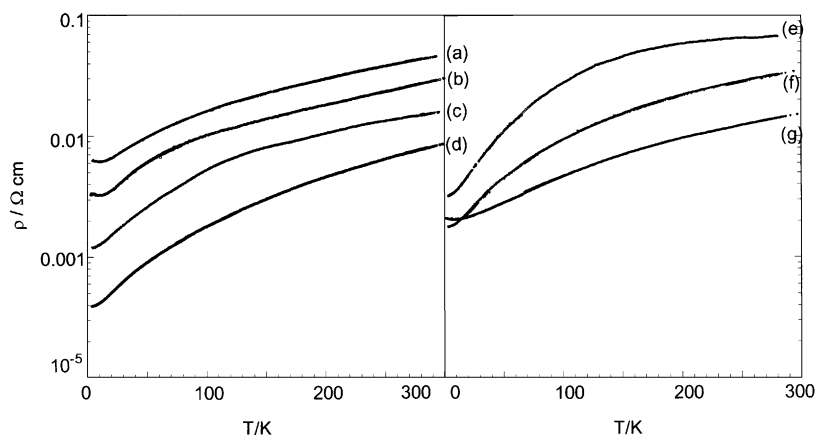


FIG. 1. Temperature dependence of electrical resistivity of MDSe-TSF salts; counter anions are: (a) I_3^- , (b) Br^- , (c) I_2Br^- , (d) Cl^- , (e) PF_6^- , (f) ClO_4^- , and (g) $Cu(NCS)_2^-$.

similar metallic behavior at low temperature (see also Fig. 1). The stoichiometry of donor and counter ion for either kind of salts is 2:1, indicating the electronic structure of mixed valence in the donor layer.

3.2. Crystal Structures and Band Calculation

The crystal of neutral MDSe-TSF belongs to the monoclinic crystal system, and the crystal structure is

close-packed by donor pairs loosely stacked in an *anti*-parallel (head-to-tail) manner (Fig. 2). There are neither marked π - π nor non-bonded Se-Se interactions among the neighboring molecules. As depicted in Fig. 3a, the molecular structure of the donor is markedly folded in two parts at the central selenium atoms, and the dihedral angle between the two parts is ca. 30° .

In contrast to that of neutral MDSe-TSF, the crystals of the ClO_4^- and PF_6^- salts belong to the orthorhombic crystal

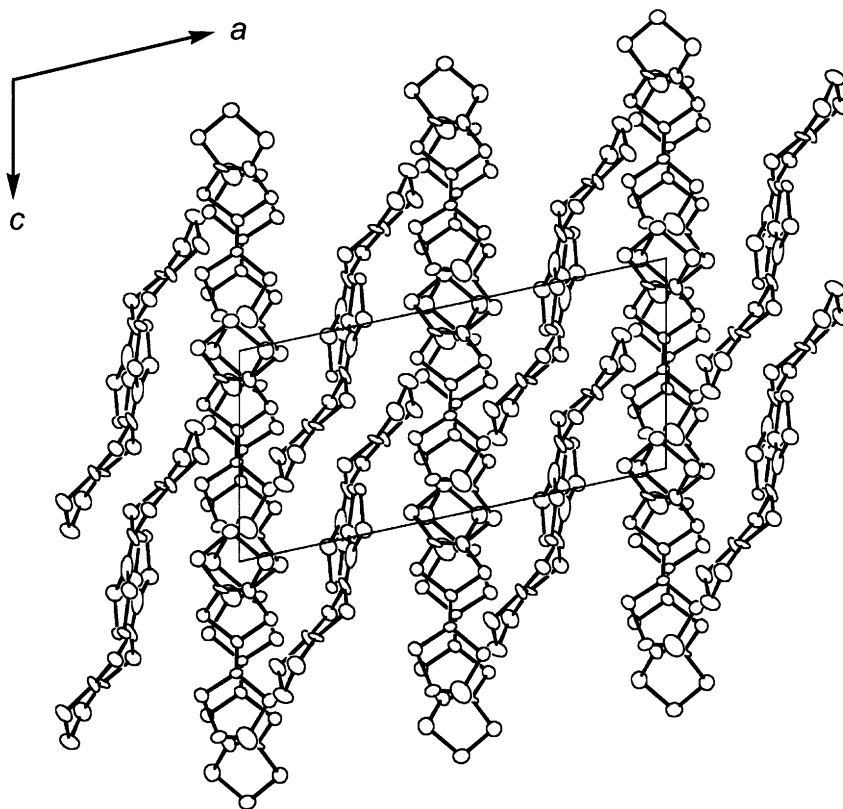


FIG. 2. Crystal structure of MDSe-TSF (neutral); *b*-axis projection.

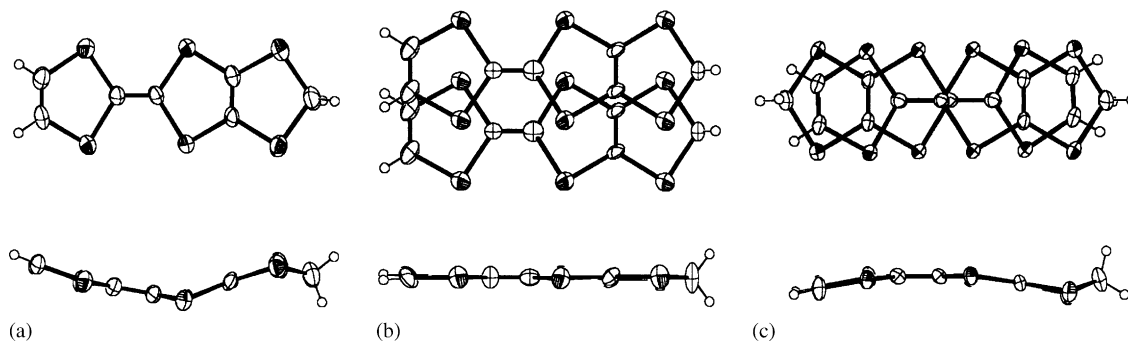


FIG. 3. Molecular structures of MDSe-TSF: (a) neutral, (b) θ -PF₆ salt, (c) κ -Br salt.

system, and as represented by Fig. 4 for the PF₆ salt, the crystal structures are characterized by uniformly stacked donor columns along the short a -axis direction and referred to as the so-called θ -type. On the edge-on projection of the donor, a herringbone arrangement of donor stacks is observed, and the dihedral angle between the neighboring stacks is 125.0° for the ClO₄ salt and 125.7° for the PF₆ salt. It is remarkable that, although these dihedral angles are considerably large as compared to those of metallic θ -BEDT-TTF salts ($104 \leq \theta \leq 116$) (17) and θ -BETS salts ($\theta \leq 105^\circ$) (18), the present salts keep stable metallic phases down to 4.2 K, suggesting the presence of strong intermolecular interactions. The donor molecules are nearly planar differently from the neutral ones, and are closely stacked in the head-to-head and ring-over-atom overlap manner (Fig. 3b). The distance between the stacked molecules is ca. 3.6 Å, indicating a sequence of π - π electronic interactions along the donor column. In addition, there are effective side-by-side interactions between the neighboring donor columns through Se-Se multi-

contacts. A calculated overlap integral (p) in the side-by-side direction is much larger than that (a) of the stacking interaction (see Fig. 4 caption). It is thus concluded that these salts are two-dimensional conductors with effective conduction paths not only along the column direction but also along the side direction. In accordance with this, the band structure of the PF₆ salt calculated from the crystal structural data according to the method of Mori *et al.* (19) demonstrates a closed Fermi surface, as shown in Fig. 5, typical of θ -type two-dimensional organic conductors (20).

The crystals of the Cl and Br salts belong to monoclinic $C2/c$ space group and are isostructural to each other. As represented by Fig. 6 for the Br salt, the crystal structures adopt κ -type with the mutually orthogonal arrangement of donor dimers. In the orthogonal donor dimer, the two donors are slightly bent and stacked in the head-to-tail and ring-over-bond manner, in contrast to that of the θ -ClO₄ and PF₆ salts (Fig. 3c). Apparently the structures are rather reminiscent of that of neutral MDSe-TTF. However, the stacked distance is much closer with 3.4 Å, and there are many marked nonbonded interactions among the neighboring molecules, as indicated by large overlap integrals c_1 , c_2 , p , and q (see Fig. 6 caption). The calculated band

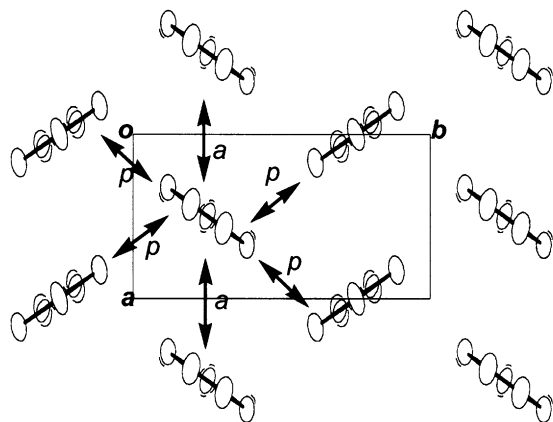


FIG. 4. Crystal structure of θ -(MDSe-TSF)₂PF₆: Donor arrangement in the conducting layer and calculated overlap integrals: $a = 5.93$, $p = -17.5 (\times 10^{-3})$.

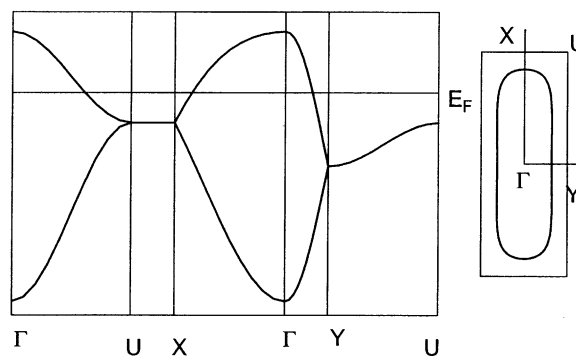


FIG. 5. Calculated band structure and Fermi surface of θ -(MDSe-TSF)₂PF₆.

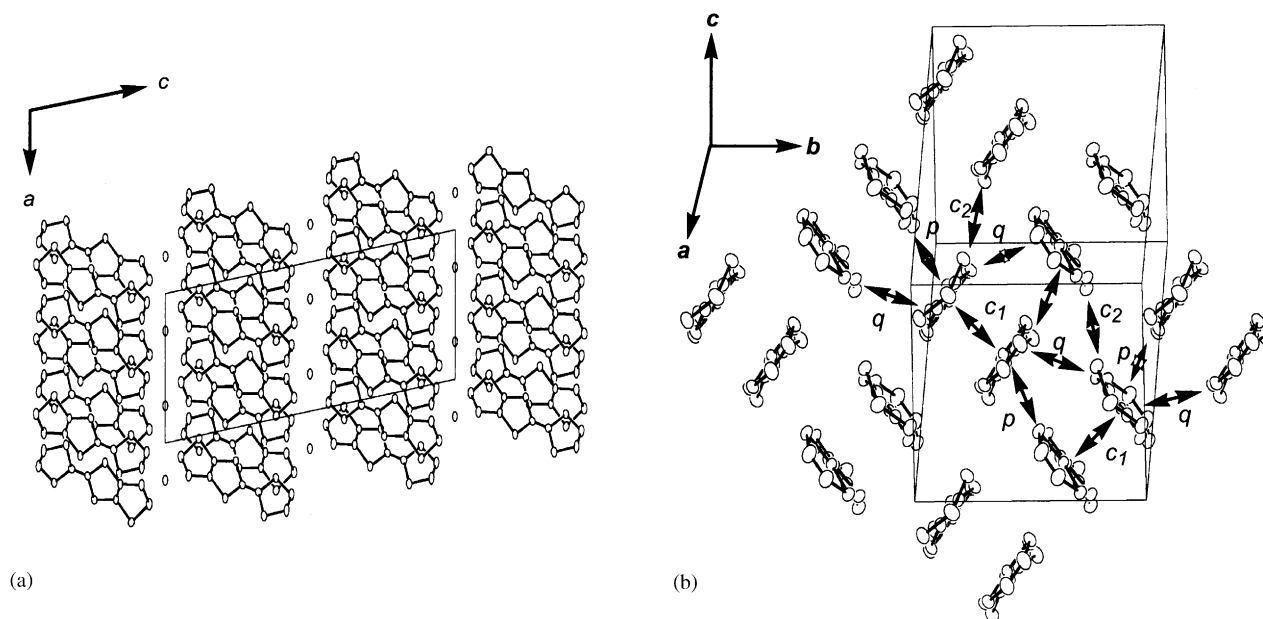


FIG. 6. Crystal structure of κ -(MDSe-TSF)₂Br: (a) b -axis projection, (b) donor arrangement in the conducting layer and calculated overlap integrals: $c_1 = 34.5$, $c_2 = 5.74$, $p = 23.4$, $q = -6.57 (\times 10^{-3})$.

structure and Fermi surface shown in Fig. 7 are typical of the κ -type two-dimensional conductors.

3.3. Magnetic Susceptibility of κ -(MDSe-TSF)₂Br

As all the MDSe-TSF salts show high conductivity ($> 10^2 \text{ S cm}^{-1}$) at room temperature and retain metallic properties down to 4.2 K, we have examined a possibility of superconductivity by use of a SQUID magnetometer cooled down to 1.8 K. In screening of magnetic susceptibility, only the κ -Br salt displayed a diamagnetic shielding signal below 4 K. Figure 8 shows temperature dependence of the zero-field-cooled (ZFC) and the field-cooled (FC) dc magnetization for the Br salt at applied magnetic field of 5 Oe. Judging from the separation between the observed

ZFC and FC magnetization, the T_c of the Br salt is estimated to be about 4.0 K. Based on the ZFC susceptibility at 1.8 K, it is calculated that the diamagnetic shielding effect for the Br salt is only ca. 0.5–4.0% (typically 1%) of that expected for a bulk superconductor. This small superconducting fraction of the Br salt involved

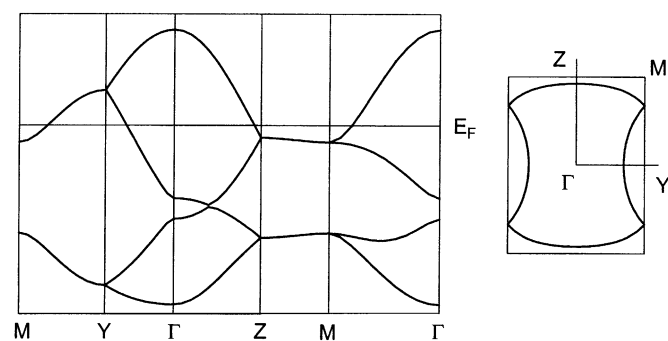


FIG. 7. Calculated band structure and Fermi surface of κ -(MDSe-TSF)₂Br.

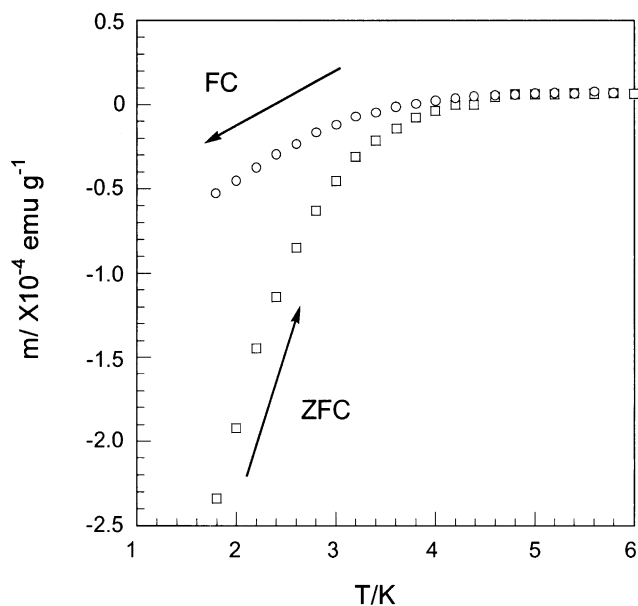


FIG. 8. Temperature dependence of magnetization at applied field of 5 Oe for κ -(MDSe-TSF)₂Br.

experimental difficulty in confirming zero resistance. At the moment, the reason for a partial manifestation of superconductivity in the Br salt is not clear. However, since this Meissner–Ochsenfeld effect was reproduced by using more than six batches of the crystals obtained from different electrocrystallization, we believe that the κ -Br salt of MDSe-TSF is a new superconductor.

4. CONCLUSION

We have discovered that MDSe-TSF is a useful electron donor molecule for producing two-dimensionally conducting radical cation salts with versatile counter anions of monoatomic, linear, tetrahedral, octahedral, and polymeric types. Regardless of different crystal structures, all these salts show high conductivity ($> 10^2 \text{ S cm}^{-1}$) at room temperature and retain metallic down to 4.2 K. Of them, only the Br salt shows a sign of partial superconductivity below 4.0 K, in contrast to the formation of many superconducting salts from MDT-TSF. Obviously the MDSe-TSF salts tend to strongly stabilize metallic phases, being presumably ascribable to enhanced intermolecular interactions of MDSe-TSF due to increasing selenium atoms as compared to MDT-TSF.

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REFERENCES

1. D. Jérôme, A. Mazaud, M. Ribault, and K. Bechgaard, *J. Phys. Lett. (Paris)* **41**, L95–L98 (1980).
2. For comprehensive reviews, see: J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M.-H. Whangbo, in “Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties, and Theory” (J. M. Williams, Ed.), Prentice-Hall, Englewood Cliff, NJ, 1992; T. Ishiguro, K. Yamaji, and G. Saito, “Organic Superconductors,” 2nd ed. Springer, Berlin, 1998.
3. H. Kobayashi, A. Kobayashi, and P. Cassoux, *Chem. Soc. Rev.* **29**, 325–333 (2000) and references cited therein
4. M. A. Beno, H. H. Wang, A. M. Kini, K. D. Carlson, U. Geiser, W. K. Kwok, J. E. Thompson, J. M. Williams, J. Ren, and M.-H. Whangbo, *Inorg. Chem.* **29**, 1599–1601 (1990); S. Kahlich, D. Schweitzer, I. Heinen, S. E. Lan, B. Nuber, H. J. Keller, K. Winzer, and H. W. Helberg, *Solid State Commun.* **80**, 191–195 (1991).
5. G. C. Papavassiliou, G. A. Mousdis, J. S. Zambounis, A. Terzis, A. Hountas, B. Hilti, C. W. Mayer, and J. Pfeiffer, *Synth. Met.* **27**, B379–B383 (1988); A. M. Kini, M. A. Beno, D. Son, H. H. Wang, K. D. Carlson, L. C. Porter, U. Welp, B. A. Vogt, J. M. Williams, D. Jung, M. Evain, M.-H. Whangbo, D. L. Overmyer, and J. E. Schirber, *Solid State Commun.* **69**, 503–507 (1989).
6. K. Takimiya, Y. Kataoka, Y. Aso, T. Otsubo, H. Fukuoka, and S. Yamanaka, *Angew. Chem., Int. Ed.* **40**, 1122–1125 (2001).
7. T. Kawamoto, T. Mori, K. Takimiya, Y. Kataoka, Y. Aso, and T. Otsubo, *Phys. Rev. B* **65**, art. no. 140508 (2002).
8. K. Takimiya, M. Kodani, Y. Kataoka, Y. Aso, T. Otsubo, T. Kawamoto, and T. Mori, unpublished results.
9. M. Kodani, K. Takimiya, Y. Aso, T. Otsubo, T. Nakayashiki, and Y. Misaki, *Synthesis* 1614–1618 (2001).
10. K. Takimiya, A. Morikami, and T. Otsubo, *Synlett* 319–321 (1997).
11. I. Johansen, K. Lerstrup, L. Henriksen, and K. Bechgaard, *J. Chem. Soc., Chem. Commun.* 89–90 (1984); Y. A. Jackson, C. L. White, M. V. Lakshimikantham, and M. P. Cava, *Tetrahedron Lett.* **28**, 5635–5636 (1987).
12. K. Takimiya, Y. Kataoka, A. Morikami, Y. Aso, and T. Otsubo, *Synth. Met.* **120**, 875–876 (2001).
13. H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, *Chem. Lett.* 55–58 (1988).
14. G. M. Schldric, SHELXS86; in “Crystallographic Computing 3” (G. M. Schldric, C. Kruger and R. Goddard, Eds), pp. 175–189. Oxford University Press, Oxford.
15. G. M. Schldric, “SHELXL (SHELX97): Programs for the Refinement of Crystal Structures.” University of Göttingen, Germany, 1997.
16. “teXsan, Single Crystal Structure Analysis Software. Version 1.11.” Molecular Structure Corporation, Rigaku Corporation, (2000).
17. H. Mori, S. Tanaka, and T. Mori, *Phys. Rev. B* **57**, 12023–12029 (1998).
18. H. Mori, N. Sakurai, S. Tanaka, H. Moriyama, T. Mori, H. Kobayashi, and A. Kobayashi, *Chem. Mater.* **12**, 2984–2987 (2000).
19. T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.* **57**, 627–633 (1984). The atomic orbital parameters used in the calculation are described in Ref. (7).
20. T. Mori, H. Mori, and S. Tanaka, *Bull. Chem. Soc. Jpn.* **72**, 179–197 (1999).