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Highly Conductive 1 : 1 Radical Cation Salts of Anthra[1,9-*cd*: 4,10-*c′d′*]bis[1,2]dichalcogenoles

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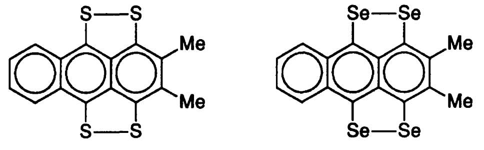
Various radical cation salts of 2,3-dimethyl-tetrathioanthracene (DMTTA) and -tetraselenoanthracene (DMTSA) with NO_3^-, BF_4^-, ClO_4^-, PF_6^-, AsF_6^-, and Br^- counter anions were prepared by an electrocrystallization technique. It has been found that these salts have either 1 : 1 or 2 : 1 stoichiometry depending on the volumes of the anions, but all are electrically conductive regardless of the stoichiometries. In particular, the NO_3 and BF_4 salts of DMTSA, in spite of 1 : 1 stoichiometry, recorded unusually high room temperature conductivities of 440 and 450 $S\,cm^{-1}$, respectively, and had metallic behaviors down to around 200 K. In addition, the other salts were semiconductors with very low activation energies. X-Ray crystallographic analyses showed that the crystal structures of all the salts consist of one-dimensional stacking columns of the donor molecules, but the two metallic salts have more favorable uniform stacking columns in which there are not only effective π electronic interactions but also strong heteroatomic interactions. Furthermore, solid electronic spectra indicated that these 1 : 1 radical cation salts have the advantage of marked reduction of on-site Coulombic repulsion in the donor molecules, which serves to suppress a Mott transition.

Polyacenes bearing peri-dichalcogen bridges are known as a prototype of superior electron donors, but have the disadvantage of low solubilities in common solvents, accordingly having a great difficulty in forming good crystals of their charge-transfer complexes.[1] We recently reported the syntheses and properties of methyl derivatives of anthra[1,9-*cd*: 4,10-*c′d′*]bis-[1,2]dithiole with a common name, tetrathioanthracene (abbreviated as TTA), and its selenium isologue (TSA).[2] The introduced methyl groups serve to enhance not only the donor strengths but also the solubilities, allowing ready formation of conductive charge-transfer complexes with various electron acceptors. Some of these complexes showed high electrical conductivities, which were induced by strong heteroatomic interactions.

Electrocrystallization is the best method for obtaining good single crystals of radical cation salts, and a number of organic metals involving organic superconductors of tetrathiafulvalene derivatives have been prepared by this technique.[3] However, little has been known about conductive salts based on peri-dichalcogen bridged arenes.[4] It has been expected that the good solubilities and strong heteroatomic interactions of the methyl derivatives of TTA and TSA also might facilitate the formation of their radical cation salts by electrocrystallization. In this paper we report the preparation of the radical cation salts of 2,3-dimethyltetrathioanthracene (DMTTA) and 2,3-dimethyltetraselenoanthracene (DMTSA) with various counter anions and their unusual electrical behaviors, crystal structures, and electronic spectra (Chart 1).



DMTTA **DMTSA**

Chart 1.

Experimental

General. The preparations of DMTTA and DMTSA were reported in our previous paper.[2] 1,1,2-Trichloroethane was distilled from CaH_2 under a nitrogen atmosphere. Bu_4NNO_3 (Aldrich) and Bu_4NBF_4 (Nacalai Tesque) were commercially available and used without purification. Bu_4NClO_4 and Bu_4NPF_6 were used after triple recrystallization of the commercial materials (Tokyo Kasei) from ethanol. Bu_4NBr (Tokyo Kasei) was used after recrystallization from benzene–hexane. Bu_4NAsF_6 was synthesized according to the reported procedure[4] and used after double recrystallization from ethyl acetate–hexane. Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrometer with a KBr tablet. Conductivity measurements were done with a Fuso multi-Channel 4-Terminal Conductometer HECS 994.

Typical Procedure of Electrocrystallization. Into a 50-ml H-shaped glass cell with a fine frit dividing the anolyte and catholyte compartments and equipped with platinum wire electrodes was placed 30 ml of 1,1,2-trichloroethane containing Bu_4NBF_4. After the solution was degassed by nitrogen stream, DMTSA (5 mg) was added into the anolyte compartment and electrolyzed under a constant current of 2 μA. Black lustrous needles of DMTSA•BF_4 gradually grew on the anode electrode during several days. The crystals were collected by filtration, washed with cold dichloromethane, and dried in vacuo.

Crystal Structural Analyses. X-Ray diffraction data were collected with a Rigaku automated four-circle diffractometer with Cu $K\alpha$ radiation monochromatized by a graphite plate. Independent reflections within $2\theta=126°$

($|F_o| \geq 1.0\sigma(F_o)$) were used for the usual analyses.[5)] The structures were solved by a direct method combined with the Monte-Carlo method for the selection of the initial set of phase,[6)] and refined by a full-matrix least squares method.[7)] Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[8)] The anisotropic temperature factors were used for the refinement and hydrogen atoms were not included in the refinement.[9)] Tables of final atomic parameters, structure factors, and anisotropic thermal parameters are deposited as Document No. 67012 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Various radical cation salts of DMTTA and DMTSA were prepared as black needle-shaped single crystals by use of electrochemical oxidations under a constant current of 2 μA in 1,1,2-trichloroethane containing tetrabutylammonium nitrate, tetrafluoroborate, perchlorate, hexafluorophosphate, bromide, or hexafluoroarsenate. The analytical data and properties of these salts are summarized in Table 1. The ratios of the donor molecule to the counter anion were measured on the basis of C, H, N elemental analyses to be either 1 : 1 or 2 : 1. These stoichiometries were also confirmed by X-ray crystallographic analyses as described later. The different stoichiometries apparently depend on the volumes of the counter anions. Thus the smaller NO_3^-, BF_4^-, ClO_4^-, and Br^- anions form the 1 : 1 salts, but the larger AsF_6^- anion forms the 2 : 1 salts. The PF_6^- anion is on the borderline and takes 2 : 1 with DMTTA and 1 : 1 with DMTSA.

Simple 1 : 1 radical cation salts with closed shell anion species are generally known to be Mott insulators, which need a cost of large Coulombic energy in transferring an unpaired electron on the donor molecule to a neighbouring site. These 1 : 1 salts, however, had high electrical conductivities, as shown in Table 1. In particular, the NO_3 and BF_4 salts of DMTSA showed markedly high conductivities of 440 and 450 $S\,cm^{-1}$, respectively, along the long crystal axis at room temperature and metallic behavior down to 230 and 180 K, respectively (Fig. 1).[10)] The other 1 : 1 salts behaved as semiconductors with conductivities ranging from 10^{-1} to 40 $S\,cm^{-1}$ except 3.2×10^{-3} $S\,cm^{-1}$ for the powdered DMTTA·Br sample, but the activation energies are very low below 0.1 eV. Table 1 also demonstrates that the 2 : 1 salts have conductivities of the order of 10^{-1} $S\,cm^{-1}$ somewhat lower than those of the 1 : 1 salts. This observation is rather unusual for organic conductors, since the 2 : 1 salts generally form a mixed valence state for the assembly of the donor molecules, in which an unpaired electron can transfer to a neighboring site with no Coulombic energy. In addition, a comparison between the DMTTA salts and the DMTSA salts with the same counter anion indicates that the latter salts are more conductive at room temperature.

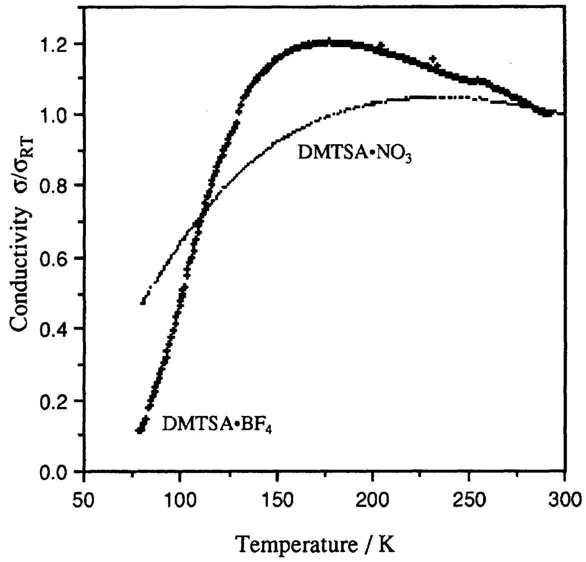


Fig. 1. Temperature dependence of the electrical conductivities of DMTSA·NO_3 salt and DMTSA·BF_4 salt.

To analyze these unusual results, all the radical cation salts except the DMTTA·Br and DMTSA·AsF_6 salts offering only microcrystals were examined by X-ray crystallographic analyses. The crystal data and final *R* values are listed in Tables 2, 3, and 4. These crystal structures are mainly classified into three types. The first one (Type I) comprises those of the NO_3^- and BF_4^- salts of DMTTA and DMTSA, which are orthorhombic with similar unit-cell parameters. In a more detailed comparison, both NO_3^- salts have the *Cmc*2₁ space group, while the BF_4^- salts have *Cmcm* space group. However, these salts are essentially isostructural, because the distinct space groups arise from restriction of point groups to which the anion parts belong. Though the large thermal parameters of O and F atoms of the anion parts suggest an orientational disorder, the normal thermal parameters of central N and B atoms indicate no positional disorder. Figures 2 and 3 shows the crystal structure of DMTSA·NO_3 as a representative of Type I. In accord with the result of the elemental analysis, the crystal composition comprises one donor and one inorganic anion. The geometry of the DMTSA molecule carrying a positive charge is somewhat different from that of neutral DMTSA. The most different point is the bond length (2.321 Å) of the Se–Se bridges, which is somewhat shorter than the neutral one (2.336 Å).[2)] The donor molecules stack uniformly along the *c* axis, and the stacking direction coincides with the long crystal axis, along which the high conduction is observed. As Fig. 4a shows an overlapping view perpendicular to the molecular plane, the two methyl groups are alternately arranged in the opposite directions in order to avoid their mutual steric repulsion. The donor columns are surrounded by the anion columns in the *a* and *b* directions and isolated from one another, indicating that this salt is a one-dimensional conductor (Fig. 3). The molec-

Table 1. Physical and Spectral Properties of Radical Cation Salts of DMTTA and DMTSA

Radical Salt$^{a)}$	D : A	Appearance	D_p	Found (Calcd)$^{b)}$/%			$\sigma^{c)}$	E_{act}	$\lambda_{max}{}^{d)}$
			°C	C	H	N	S cm^{-1}	eV	×10^3 cm^{-1}
DMTTA·NO$_3$	1 : 1	Black needles	239	48.80 (48.96	2.69 2.57	2.55 3.57)	4.4	0.065	5.2, 9.7, 17.5, 22.7
DMTTA·BF$_4$	1 : 1	Black needles	253	46.90 (46.05	2.89 2.42	0 0)	7.0	0.063	5.2, 9.8, 17.2, 22.5
DMTTA·ClO$_4$	1 : 1	Black needles	285	45.24 (44.70	2.38 2.34	0 0)	5.0×10^{-1}	0.072	5.1, 10.0, 17.6, 23.1
DMTTA·PF$_6$	2 : 1	Black needles	249	46.17 (46.84	2.33 2.41	0 0)	1.2×10^{-1}	0.072	3.3, 10.5, 17.5, 20.7, 23.8
DMTTA·AsF$_6$	2 : 1	Black needles	276	45.32 (45.22	2.37 2.37	0 0)	1.9×10^{-1}	0.079	3.5, 10.5, 17.5, 20.7, 23.8
DMTTA·Br	1 : 1	Black microcrystals	229	46.17 (46.82	2.33 2.46	0 0)	3.2×10^{-3} $^{e)}$	0.106	5.5, 11.7, 16.5, 22.5
DMTSA·NO$_3$	1 : 1	Black needles	>300	33.46 (33.13	1.72 1.74	1.62 2.41)	4.4×10^2	Metallic (down to 220 K)	4.6, 9.5, 16.6, 23.0
DMTSA·BF$_4$	1 : 1	Black needles	253	31.70 (31.77	1.63 1.67	0 0)	4.5×10^2	Metallic (down to 180 K)	4.5, 9.5, 16.6, 23.0
DMTSA·ClO$_4$	1 : 1	Black needles	285	32.06 (31.12	1.89 1.63	0 0)	4.0×10	0.020	4.6, 9.1, 16.5, 23.8
DMTSA·PF$_6$	1 : 1	Black needles	249	28.98 (29.04	1.52 1.51	0 0)	6.5×10^{-1}	0.092	4.8, 9.4, 16.5, 23.8
DMTSA·AsF$_6$	2 : 1	Black crystals	274	31.04 (31.37	1.58 1.65	0 0)	1.0×10^{-1} $^{e)}$	0.117	3.5, 10.1, 16.9, 20.7, 23.5

a) Obtained from 1,1,2-trichloroethane. b) Calculated from stoichiometry indicated for each salt. c) Measured on a single crystal along the long crystal axis with a four-probe method unless otherwise stated. d) Measured with a KBr disk method. e) Measured on a compressed pellet with a four-probe method.

Table 2. Crystal Data of Radical Cation Salts of Type I

	DMTTA·NO$_3$	DMTTA·BF$_4$	DMTSA·NO$_3$	DMTSA·BF$_4$
Formula	$C_{16}H_{10}S_4N_1O_3$	$C_{16}H_{10}S_4B_1F_4$	$C_{16}H_{10}Se_4N_1O_3$	$C_{16}H_{10}Se_4B_1F_4$
Formula wt	392.50	417.32	580.08	604.90
Cryst system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Cmc2_1$	$Cmcm$	$Cmc2_1$	$Cmcm$
a/Å	13.787(1)	13.922(1)	14.036(2)	14.214(1)
b/Å	16.331(1)	16.454(1)	16.585(2)	16.620(1)
c/Å	6.677(1)	6.7087(6)	6.737(1)	6.770(1)
V/Å^3	1503.2(4)	1536.8(2)	1568.3(3)	1599.3(2)
Z	4	4	4	4
No. of data	650	648	656	705
R	0.081	0.075	0.041	0.048

ular planes lie perpendicular to the c axis, so that the interstack distance is $c/2$, that is, 3.37 Å, indicating the presence of a strong π-electronic interaction (Table 5). In addition, the shortest nonbonded Se–Se distance between the stacks is 3.67 Å, which is much shorter than the van der Waals contact distance (3.80 Å).[11] The DMTSA·BF$_4$ salt has completely the same situation with the close interstack distance of 3.39 Å and nonbonded Se–Se distance of 3.69 Å. On the other hand, the two DMTTA salts, on the whole, have strong structural resemblances with the slightly shorter interstack distances of 3.34—3.35 Å. However, the shortest nonbonded S–S distances of 3.69—3.72 Å are rather longer than the van der Waals contact distance (3.60 Å).[11]

The second type contains the other 1 : 1 salts, DMTTA·ClO$_4$, DMTSA·ClO$_4$, and DMTSA·PF$_6$, which belong to the monoclinic space group. Figures 5 and 6 show the crystal structures of DMTTA·ClO$_4$ as a representative of Type II. Unlike the above Type I with uniformly stacked columns, the donor molecules stack at alternate spaces of 3.29 and 3.44 Å, with sliding along the c-axis. The shortest nonbonded S–S distances in the two spaces are 3.37 and 3.75 Å, respectively. As shown in Fig. 4b, the perpendicular overlap between closely paired molecules is quite similar to that of Type I. On the other hand, the overlap between molecules in adjacent pairs is greater because of less steric hindrance of the methyl groups in the more separate space. The ClO_4^- anions in which the oxygen atoms show an orientational disorder also surround the donor molecules,

Table 3. Crystal Data of Radical Cation Salts of Type II

	DMTTA·ClO$_4$	DMSTA·ClO$_4$	DMTSA·PF$_6$
Formula	$C_{16}H_{10}S_4Cl_1O_4$	$C_{16}H_{10}Se_4Cl_1O_4$	$C_{16}H_{10}Se_4P_1F_6$
Formula wt	429.94	617.52	663.06
Cryst system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/c$	$P2_1/c$
a/Å	19.804(2)	7.166(1)	7.262(6)
b/Å	11.798(1)	11.837(1)	12.220(1)
c/Å	7.023(1)	20.203(2)	20.611(2)
β/°	94.72(1)	93.81(1)	95.65(8)
V/Å^3	1635.4(3)	1709.9(3)	1820(3)
Z	4	4	4
No. of data	2224	1685	1980
R	0.091	0.081	0.080

Table 4. Crystal Data of Radical Cation Salts of Type III

	(DMTTA)$_2$·PF$_6$	(DMTTA)$_2$·AsF$_6$
Formula	$C_{32}H_{20}S_8P_1F_6$	$C_{32}H_{20}S_8As_1F_6$
Formula wt	805.96	849.94
Cryst system	Orthorhombic	Orthorhombic
Space group	$Pnmn$	$Pnmn$
a/Å	14.987(1)	15.180(2)
b/Å	14.247(1)	14.275(1)
c/Å	7.219(1)	7.211(1)
V/Å^3	1541.4(3)	1546.7(3)
Z	2	2
No. of data	1046	1002
R	0.059	0.057

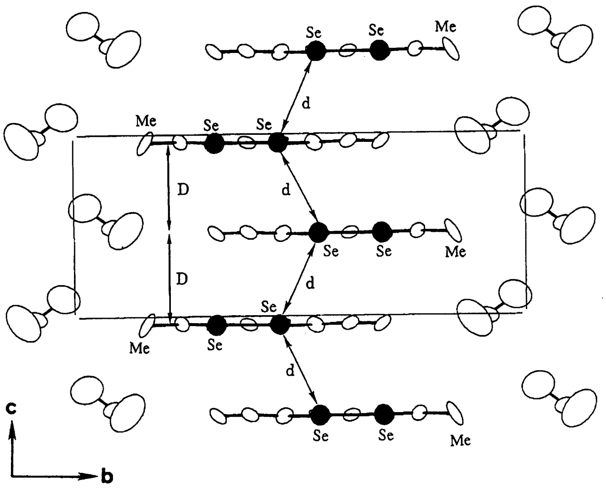


Fig. 2. Crystal structure of DMTSA·NO$_3$ salt projected along the a axis (D=3.37 Å, d=3.67 Å).

but are no longer located by their transverse and longitudinal sides. This strong distortion of the donor stacks as well as the anion sites is probably ascribable to the increasing volume of the counter anion.

Of the third type is the crystal structures of 2:1 DMTTA·PF$_6$ and DMTTA·AsF$_6$ salts, which are orthorhombic with the *Pnnn* space group, and that of DMTTA·PF$_6$ is shown in Fig. 7. The donor molecules like those of Type II alternately stack with spaces 3.39 and 3.55 Å, and the shortest nonbonded S–S distances are 3.65 and 3.69 Å. The overlap modes of the paired donors are the same as those of Type II (Fig. 4c). In this case, the PF_6^- anions are located by the side of and at an equal distance from the paired donors. The bonded S–S length (2.083 Å) is just in the middle of those of neutral DMTTA (2.102 Å) and the 1:1 salts (2.066—2.077 Å), supporting a half formal charge on the donor molecules.[12] Another 2:1 salt, DMTSA·AsF$_6$, with a similar conductivity presumably has the same structural feature.

The detailed crystal structural analyses provide the following possible explanation for the unusual conductivities in these systems. The high conductivities observed in the salts of DMTSA with BF$_4$ and NO$_3$ can be ascribed to wide conduction bands arising from not only effective π-electronic interactions, but also strong heteroatomic interactions among the stacking molecules. The band widths are presumably greater than on-site Coulombic energy to suppress a Mott transition and then induce the metallic conduction at room temperature. Since their electronic structures are one-dimensional, the observed metal-insulator transitions at the low temperatures may be ascribed to a Peierls transition.

On the other hand, the other 1:1 salts do not form such wide conduction bands, because their crystal structures, though the close interstack distances are observed, demonstrate the nonbonded X–X distances longer than van der Waals contact distance (Table 5). Thus these systems have a small energy gap between valence and conduction states and the electrical conductivities are semiconductive with thermal activation-type of temperature dependence.

The 2:1 salts have much weaker π-electronic as well as heteroatomic interactions among the stacking molecules. In particular, one of the interstack distances is beyond 3.5 Å. Thus the conductivities in these systems may arise from thermal hopping, which is responsible for their smaller conductivities as compared to the above 1:1 salts.

The electronic absorption spectra of the radical

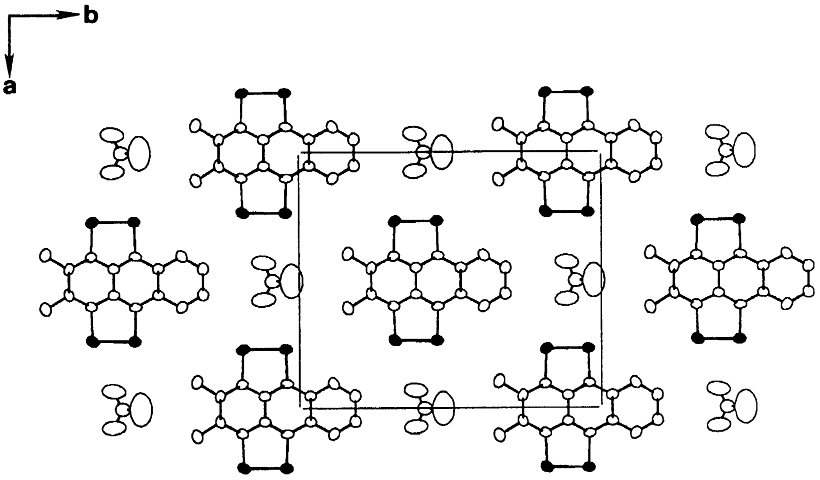


Fig. 3. Crystal structure of DMTSA·NO$_3$ salt projected along the *c* axis.

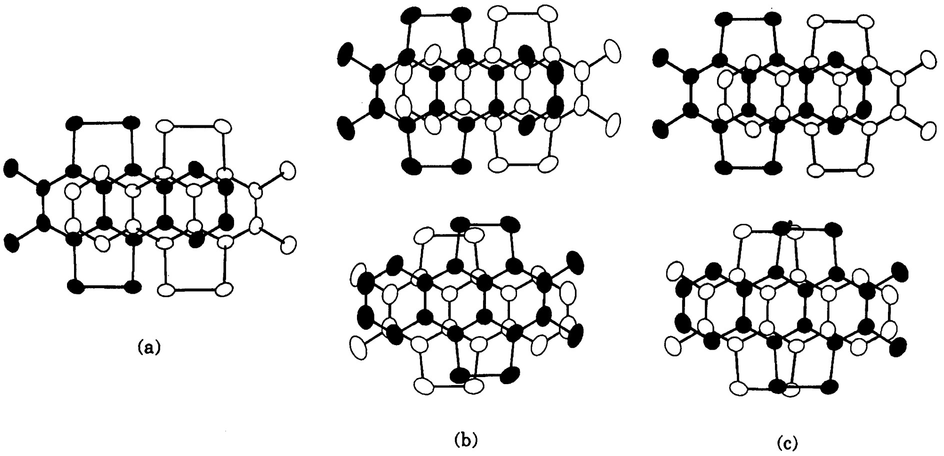


Fig. 4. Overlapping modes of the donor molecules of radical cation salts viewed perpendicular to the molecular planes; (a) DMTSA·NO$_3$; (b) DMTTA·ClO$_4$; (c) DMTTA·PF$_6$.

Table 5. Bonded and Nonbonded Heteroatomic Distances and Interstack Distances of Radical Cation Salts

Salt	Formal charge	Bonded X–X distance/Å	Nonbonded X–X distance/Å	Interstack distance/Å
DMTTA·NO$_3$	1	2.070	3.69	3.34
DMTTA·BF$_4$	1	2.077	3.72	3.35
DMTTA·ClO$_4$	1	2.066	3.37, 3.75	3.29, 3.44
DMTTA·PF$_6$	1/2	2.083	3.65, 3.69	3.39, 3.55
DMTTA·AsF$_6$	1/2	2.085	3.66, 3.69	3.39, 3.56
DMTSA·NO$_3$	1	2.321	3.67	3.37
DMTSA·BF$_4$	1	2.325	3.69	3.39
DMTSA·ClO$_4$	1	2.319	3.32, 3.88	3.32, 3.49
DMTSA·PF$_6$	1	2.319	3.42, 3.95	3.33, 3.42

cation salts taken on a compressed pellet with KBr give some information on their electronic states. As summarized in Table 1, the absorption maxima completely depend on the crystal types, though the absorptions of the selenium complexes are shifted to smaller wavenumbers as compared with the corresponding sulfur ones. The spectral shapes of the representative salts of Types I—III are illustrated in Fig. 8. The 1 : 1 simple salts of Types I and II generally have characteristic absorption bands at around 5, 10, 17, and 23×10^3 cm^{-1}, and make no apparent spectral difference between the types. On the other hand, the spectra of the 2 : 1 salts of Type

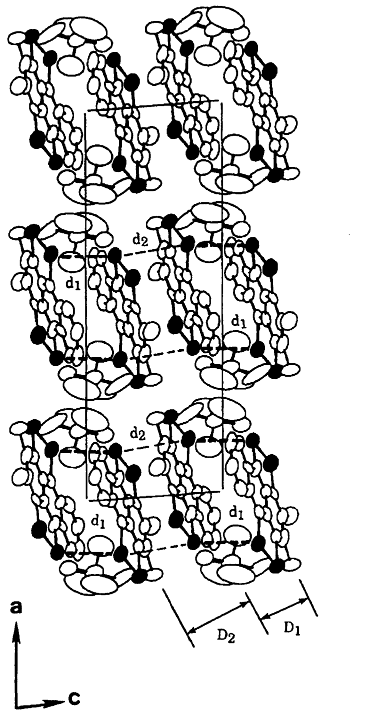


Fig. 5. Crystal structure of DMTTA·ClO$_4$ salt projected along the *b* axis ($D_1=3.29$ Å $D_2=3.44$ Å $d_1=3.37$ Å $d_2=3.75$ Å).

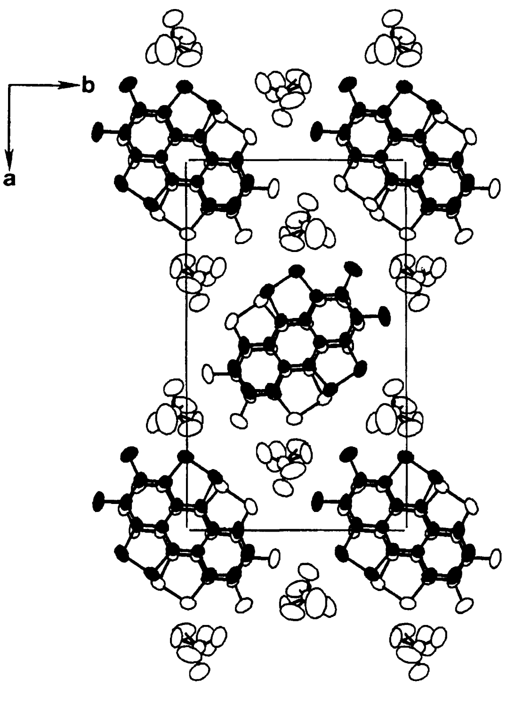


Fig. 6. Crystal structure of DMTTA·ClO$_4$ salt projected along the *c* axis.

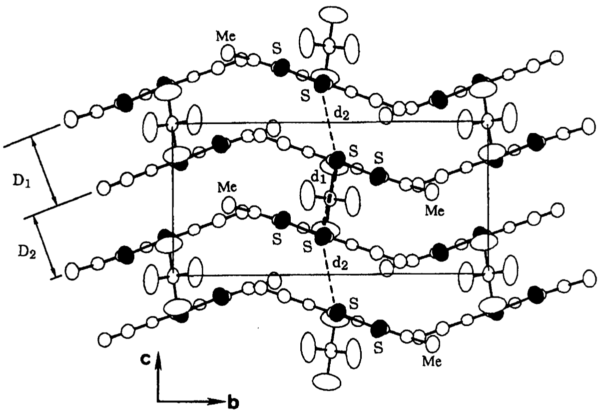


Fig. 7. Crystal structure of DMTTA·PF$_6$ salt projected along the *a* axis ($D_1=3.55$ Å $D_2=3.39$ Å $d_1=3.65$ Å $d_2=3.69$ Å).

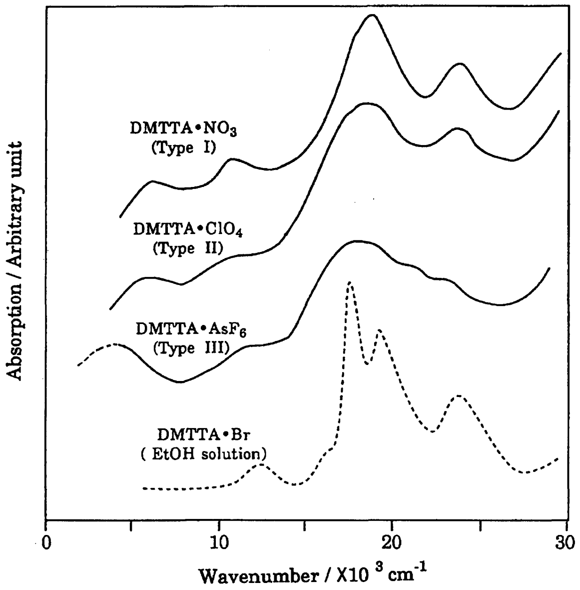


Fig. 8. Electronic absorption spectra measured with a KBr disk.

III show a broad absorption band in the infrared region around 3.5×10^3 cm^{-1} together with bands at 10, 17, 20, and 23×10^3 cm^{-1}. The common three bands (10, 17, and 23×10^3 cm^{-1}) are ascribable to intramolecular transitions of the radical cation species, because the corresponding absorption are also observed in the solution spectrum of DMTTA·Br. The 20×10^3 cm^{-1} band of the 2:1 salts is based on the intramolecular transition of the neutral species. The remaining 3.5×10^3 cm^{-1} band is assigned to an electron transition from the neutral to cationic stacked molecules, and occurs with the very low energy because of not accompanying Coulombic repulsion.[13] In this regard, we infer that the 5×10^3 cm^{-1} band of the 1:1 salt corresponds to an electron transition between the cationic molecules in the solid. However, this type of transition is usually observed at around 10×10^3 cm^{-1} for the radical cation salts of tetrathiafulvalene (TTF).[13] Thus this lower energy transition indicates the occurrence of marked reduction of Coulombic repulsion in the dication state of DMTTA and DMTSA. The half-wave oxidation potentials of DMTTA are 0.32 and 0.73 V vs. Ag/AgCl in benzonitrile, and those of DMTSA are 0.31 and 0.72 V, being almost comparable to those of TTF (0.34 and 0.72 V); DMTTA and DMTSA as a single component have the same degree of on-site Coulombic repulsion as that of TTF. This suggests that the origin of the small on-site Coulombic repulsion in the DMTTA and DMTSA salts should be present in the crystal structures and ascribable to an electrostatic interaction with the neighboring counter anions as a possibility. It is believed that the cationic charge of DMTTA and DMTSA is mainly distributed over the two dichalcogen-containing heterocyclic moieties owing to the formation of an aromatic sextet, as supporting by shortening of the Se–Se bonds, and furthermore is electrostatically stabilized by the closely located anions. This electrostatic interaction can be supported by extremely short nonbonded distances of the chalcogen atoms of the donor molecules and the fluorine or oxygen atoms of the counter anions; S–F for DMTTA$\cdot$BF$_4$, 2.95 Å; S–O for DMTTA$\cdot$NO$_3$, 2.90 Å; Se–F for DMTSA$\cdot$BF$_4$, 2.99 Å; Se–O for DMTSA$\cdot$NO$_3$, 2.97 Å. As a result, this electrostatic interaction causes much charge separation to the opposite sides, leading to reduction of on-site Coulombic repulsion, that is, suppression of Mott-type insulation.

It is thus concluded that these 1 : 1 radical cation salts DMTSA$\cdot$NO$_3$ and DMTSA$\cdot$BF$_4$ are one-dimensional conductors, which consist of uniform donor stacking columns with effective π-electronic and strong nonbonded Se–Se interactions. In addition, there are marked reduction of on-site Coulombic repulsion of the DMTSA molecule in their crystal structures. They accordingly have, in spite of 1 : 1 stoichiometry, unusually high room-temperature conductivities with metallic behavior down to around 200 K.

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