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Crystal Structure and Conductivity of Chiral Radical Ion Salts (Me$_2$ET)$_2$X

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Radical ion salts of both chiral (*R*,*R*) and racemic organic donor, (Me$_2$ET)$_2$X (Me$_2$ET=*trans*-dimethylbis(ethylenedithio)tetrathiafulvalene, X=PF$_6$, ClO$_4$, and ReO$_4$) were electrochemically prepared and their crystal structures were analyzed. The donor molecules are stacked in a twist-type column to reduce steric repulsion caused by methyl groups. The anions are contained in the cavities formed both by methylated and unsubstituted ethylene groups of the donor molecules, and their orientation is fixed through hydrogen bonds to methine and methylene protons. The structural difference between chiral and racemic salts is discussed. In spite of the difference in the crystal structure, their conductivity is almost identical, reflecting similarity of side-by-side S–S contacts between the donor molecules.

The crystal structures of radical ion salts of bis(ethylenedithio)tetrathiafulvalene (ET) are diverse and the polymorphic crystals are often obtained even from a single batch of electrocrystallization.[1,2] While the polymorphism of ET salts enables to investigate physical properties dependent on the crystal structure, the situation makes the crystal structure of ET salts difficult to predict or control. We introduced methyl groups on ET as a molecular jig for regulating the arrangement of donors in crystals. Donor ability of the methylated ET derivatives was found to be practically the same as ET.[3] On the contrary, X-ray structure analysis of the neutral methylated ETs revealed that the packing of the donor molecules is substantially affected by both the orientation and the effective volume of the methyl groups. In this paper, we report synthesis of chiral and racemic radical ion salts of *trans*-dimethyl-ET(Me$_2$ET, **1**) along with the characteristics of their crystal structures. Conducitivity of the chiral and racemic salts is also discussed based on the crystal structures.

Experimental

Preparation of optically pure (5*R*,6*R*)-2-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]-dithiin-2-ylidene)-5,6-dihydro-5,6-dimethyl-1,3-dithiolo[4,5-*b*][1,4]-dithiin ($\mathbf{1}_R$, (*R*,*R*)-Me$_2$ET) and racemic Me$_2$ET (a mixture of $\mathbf{1}_R$ and $\mathbf{1}_S$) was described previously.[3] The radical salts $(\mathbf{1})_2$X (X=PF$_6$, ClO$_4$, and ReO$_4$) were grown as black plates (typical size 0.50×0.30×0.20 mm) by galvanostatic oxidation (1—5 μA) of **1** (12 mmol dm^{-3}) in the presence of *n*-Bu$_4$NX (X=PF$_6$, ClO$_4$, or ReO$_4$, 64 mmol dm^{-3}) in 35 ml of anhydrous THF. A cylindrical platinum plate (diameter 30 mm, height 10 mm, thickness 0.1 mm) was used as an anode.[4]

The X-ray diffraction data were collected using a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated MoK_α radiation (λ=0.71073 Å), for the region of $2\theta<55°$ at ambient temperature. Absorbance correction was applied for ReO$_4$ salt using a Gaussian integration method.[5] The diffraction data for the other crystals were used with no absorbance correction. The structures were solved by a direct method (SAPI-85[6]) for PF$_6$ and ClO$_4$ salts, and by a Patterson method (SHELXS 86[7]) for ReO$_4$ salt. Structures were refined for all non-hydrogen atoms with anisotropic temperature factors by a block-diagonal least-sqares method (UNICS-III[8]). In the case of ($\mathbf{1}_R$) ($\mathbf{1}_S$)PF$_6$, the occupation ratios of the disordered pairs (C(5A) and C(5B), C(11A) and C(11B)) were also refined and converged to 0.5:0.5. The coordinates of hydrogen atoms were recalculated after an each refinement cycle with the isotropic temperature factor of 4.0 Å^2. The lattice parameters of the crystals are summarized in Table 1. The crystal data are as follows. ($\mathbf{1}_R$)($\mathbf{1}_S$)PF$_6$: chemical formula C$_{24}$H$_{24}$S$_{16}$PF$_6$, M=970.47, Z=2, D_c=1.73 g cm^{-3}, μ(Mo $K\alpha$)=9.84 cm^{-1}, ω-2θ scan, scan width $\Delta\omega=(1.30+0.15\tan\theta)°$, 2080 independent $|F_o|>3\sigma|F_o|$ reflections used, $w=0.15|F_o|(|F_o|<30.0)$, $1.00|F_o|(30.0\leqq|F_o|<60.0)$ and $2000.0/|F_o|^2(60.0\leqq|F_o|)$, final R=0.089 and R_w=0.076. ($\mathbf{1}_R$)$_2$PF$_6$: chemical formula C$_{24}$H$_{24}$S$_{16}$PF$_6$, M=970.47, Z=2, D_c=1.73 g cm^{-3}, μ(Mo $K\alpha$)=9.88 cm^{-1}, ω–2θ scan, scan with $\Delta\omega=(1.20+0.16\tan\theta)°$, 1715 independent $|F_o|>3\sigma|F_o|$ reflections used, $w=0.50|F_o|$ $(|F_o|<15.0)$, $1.00|F_o|$ $(15.0\leqq|F_o|<40.0)$ and $1600.0/|F_o|^2$ $(40.0\leqq|F_o|)$, final R=0.060 and R_w=0.067. ($\mathbf{1}_R$)$_2$ClO$_4$: chemical formula C$_{24}$H$_{24}$S$_{16}$ClO$_4$, M=924.96, Z=2, D_c=1.69 g cm^{-3}, μ(Mo $K\alpha$)=10.20 cm^{-1}, ω scan, scan width $\Delta\omega=(0.80+0.14\tan\theta)°$, 2033 independent $|F_o|>3\sigma|F_o|$ reflections used, $w=1.00|F_o|$ $(|F_o|<30.0)$ and $900.0/|F_o|^2$ $(30.0\leqq|F_o|)$, final R=0.051 and R_w=0.064. ($\mathbf{1}_R$)$_2$ReO$_4$: chemical formula C$_{24}$H$_{24}$S$_{16}$ReO$_4$, M=1075.72, Z=2, D_c=1.94 g cm^{-3}, μ(Mo $K\alpha$)=42.53 cm^{-1}, ω-2θ scan, scan width $\Delta\omega=(1.50+0.15\tan\theta)°$, 2163 independent $|F_o|>3\sigma|F_o|$ reflections used, $w=0.50|F_o|$ $(|F_o|<15.0)$, $1.00|F_o|$ $(15.0\leqq|F_o|<30.0)$ and $900.0/|F_o|^2$ $(30.0\leqq|F_o|)$, final R=0.042 and R_w=0.051. The atomic parameters and equivalent isotropic temperature factors for these crystals are summarized in Tables 2, 3, 4, and 5.[9] The crystal structure illustrations were drawn using ORTEP II.[10]

Electrical conductivities were measured along the *b* axis (a long axis of the crystal) with a DC four-probe method in the temperature range of 77—300 K.

Results and Disscussion

Racemic Me$_2$ET (mixture of $\mathbf{1}_R$ and $\mathbf{1}_S$) forms hexa-

Table 1. Crystal Data of $(Me_2ET)_2X$ Radical Salts

	$(\mathbf{1}_R)_2PF_6$	$(\mathbf{1}_R)(\mathbf{1}_S)PF_6$	$(\mathbf{1}_R)_2ClO_4$	$(\mathbf{1}_R)_2ReO_4$
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P222_1$	$P2/c$	$P222_1$	$P222_1$
a/Å	8.275(4)	8.386(4)	8.244(2)	8.449(4)
b/Å	6.870(3)	6.856(3)	6.864(1)	6.773(2)
c/Å	32.678(20)	32.580(15)	32.235(8)	32.153(20)
α/°	90.00(0)	90.00(0)	90.00(0)	90.00(0)
β/°	90.00(0)	95.55(4)	90.00(0)	90.00(0)
γ/°	90.00(0)	90.00(0)	90.00(0)	90.00(0)
V/Å^3	1857.7(17)	1864.6(15)	1819.6(6)	1839.7(12)

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors of $(\mathbf{1}_R)$ $(\mathbf{1}_S)PF_6$

Atom	x	y	z	B_{eq}[a]/Å^2	Atom	x	y	z	B_{eq}[a]/Å^2
Me_2ET					Methin and methyl carbons of ring A (population 0.5)				
S(1)	3551(4)	4994(4)	2006(1)	3.4(1)	C(4)[b]	4930(27)	7679(19)	878(4)	9.4(7)
S(2)	3033(4)	9153(4)	2171(1)	3.9(1)	C(5A)	5586(25)	9554(32)	1017(6)	3.6(6)
S(3)	5131(4)	5689(4)	1249(1)	4.2(1)	C(11A)	5427(43)	7041(34)	463(7)	7.0(10)
S(4)	4653(5)	10564(4)	1464(1)	4.6(1)	C(12)[b]	5057(21)	11091(19)	674(4)	7.2(5)
S(5)	1964(4)	3824(4)	2827(1)	3.9(1)					
S(6)	1415(4)	7967(4)	3000(1)	3.4(1)	Methin and methyl carbons of ring B (population 0.5)				
S(7)	511(5)	2302(5)	3541(1)	6.2(1)	C(4)[b]	4930(27)	7679(19)	878(4)	9.4(7)
S(8)	−38(4)	7263(4)	3775(1)	4.3(1)	C(5B)	4605(28)	9500(29)	960(5)	3.5(6)
C(1)	2861(14)	6742(16)	2330(3)	3.6(3)	C(11B)	4975(38)	6609(37)	472(5)	5.6(8)
C(2)	4286(12)	6698(16)	1672(3)	3.1(3)	C(12)[b]	5057(21)	11091(19)	674(4)	7.2(5)
C(3)	4088(13)	8607(15)	1752(3)	3.0(3)					
C(6)	2148(12)	6227(16)	2675(3)	3.1(3)	PF_6^-				
C(7)	1003(13)	4328(16)	3265(3)	3.5(3)	P(1)[c]	10000(0)	0(0)	5000(0)	5.1(2)
C(8)	736(13)	6237(18)	3345(3)	3.4(3)	F(1)	10940(14)	626(17)	5416(3)	11.1(4)
C(9)	−576(17)	3368(19)	3920(3)	5.4(4)	F(2)	8726(14)	741(28)	5254(4)	16.2(7)
C(10)	102(19)	5167(19)	4116(3)	5.7(4)	F(3)	9147(17)	1993(16)	4942(3)	13.5(6)

a) $B_{eq}=(4/3)\cdot(B_{11}\boldsymbol{a}\cdot\boldsymbol{a}+B_{12}\boldsymbol{a}\cdot\boldsymbol{b}+B_{13}\boldsymbol{a}\cdot\boldsymbol{c}+\cdots)$. b) No disorder was observed on C(4) and C(12). c) Multiplicity 0.5.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors of $(\mathbf{1}_R)_2PF_6$

Atom	x	y	z	B_{eq}[a]/Å^2	Atom	x	y	z	B_{eq}[a]/Å^2
Me_2ET $\mathbf{1}_R$					C(7)	728(12)	4452(13)	3260(2)	3.4(2)
S(1)	3717(3)	5055(4)	2002(1)	3.6(1)	C(8)	485(12)	6327(15)	3349(3)	3.6(2)
S(2)	3175(4)	9204(4)	2164(1)	4.0(1)	C(9)	−1096(17)	3430(17)	3932(3)	5.4(3)
S(3)	5497(4)	5734(3)	1228(1)	4.1(1)	C(10)	−427(16)	5240(17)	4114(3)	5.3(3)
S(4)	5013(4)	10615(3)	1457(1)	4.6(1)	C(11)	5823(16)	6970(16)	462(3)	5.0(3)
S(5)	1872(4)	3918(4)	2825(1)	4.2(1)	C(12)	5996(18)	11161(14)	683(3)	5.4(3)
S(6)	1265(3)	8031(3)	3002(1)	3.7(1)					
S(7)	152(5)	2399(4)	3538(1)	5.8(1)	PF_6^- (multiplicity 0.5)				
S(8)	−467(4)	7329(4)	3775(1)	4.4(1)	P(1)	9064(6)	0(0)	5000(0)	5.1(1)
C(1)	2937(12)	6805(13)	2326(3)	3.3(2)	F(1)	8272(18)	−390(25)	4582(4)	7.6(5)
C(2)	4564(11)	6711(13)	1664(2)	2.9(2)	F(2)	9989(27)	104(36)	5403(4)	12.2(8)
C(3)	4342(13)	8598(13)	1733(3)	3.4(2)	F(3)	8181(27)	−1811(34)	5132(6)	13.0(9)
C(4)	5191(13)	7678(13)	862(3)	3.8(2)	F(4)	9751(31)	1847(27)	4896(5)	13.6(9)
C(5)	5998(13)	9531(13)	1009(3)	3.6(2)	F(5)	7557(32)	1237(64)	5104(16)	27.2(24)
C(6)	2113(11)	6332(13)	2678(2)	2.9(2)	F(6)	10452(25)	−1340(53)	4873(10)	20.0(16)

a) $B_{eq}=(4/3)\cdot(B_{11}\boldsymbol{a}\cdot\boldsymbol{a}+B_{12}\boldsymbol{a}\cdot\boldsymbol{b}+B_{13}\boldsymbol{a}\cdot\boldsymbol{c}+\cdots)$.

fluorophosphates with a 2:1 donor/anion stoichiometry. Space group of the salt is centrosymmetric ($P2/c$), and the salt contains antipodes in a 1:1 ratio. The donor molecules are stacked along the a axis with their long axes tilted by about 60°, and their methyl groups exist as an equatorial orientation (Fig. 1a). The interplane distances are 3.596(7) Å for the pair 1 (I(x, y, z) – II($-x$, y, $0.5-z$)) and 3.504(7) Å for the pair 2 (I(x, y, z)

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors of $(\mathbf{1}_R)_2ClO_4$

Atom	x	y	z	B_{eq}[a)]/Å^2	Atom	x	y	z	B_{eq}[a)]/Å^2
Me_2ET $\mathbf{1}_R$					C(5)	5960(8)	9634(9)	1006(2)	3.7(2)
S(1)	3646(2)	5140(2)	2012(1)	3.61(4)	C(6)	2075(8)	6424(9)	2704(2)	3.3(1)
S(2)	3125(2)	9295(2)	2181(1)	3.98(4)	C(7)	720(8)	4516(9)	3300(2)	3.6(1)
S(3)	5425(3)	5814(2)	1229(1)	4.08(4)	C(8)	447(8)	6416(9)	3386(2)	3.4(1)
S(4)	4956(3)	10706(2)	1459(1)	4.68(5)	C(9)	−1113(12)	3534(12)	3977(2)	5.6(2)
S(5)	1828(3)	4003(2)	2852(1)	4.16(4)	C(10)	−403(13)	5347(12)	4167(2)	5.8(2)
S(6)	1237(2)	8122(2)	3034(1)	3.70(4)	C(11)	5762(13)	7053(11)	444(2)	5.8(2)
S(7)	145(3)	2483(3)	3581(1)	5.59(6)	C(12)	5984(12)	11229(11)	681(2)	5.4(2)
S(8)	−434(3)	7425(3)	3829(1)	4.39(5)					
C(1)	2888(8)	6894(8)	2343(2)	3.2(1)	ClO_4^-				
C(2)	4499(8)	6809(9)	1666(2)	3.3(1)	Cl(1)[b)]	9000(5)	0(0)	5000(0)	7.1(1)
C(3)	4280(8)	8703(9)	1743(2)	3.3(1)	O(1)	8201(15)	381(16)	4665(3)	14.3(4)
C(4)	5114(9)	7778(9)	864(2)	3.8(2)	O(2)	10074(19)	−1607(25)	4918(5)	21.6(7)

a) $B_{eq}=(4/3)\cdot(B_{11}\boldsymbol{a}\cdot\boldsymbol{a}+B_{12}\boldsymbol{a}\cdot\boldsymbol{b}+B_{13}\boldsymbol{a}\cdot\boldsymbol{c}+\cdots)$. b) Multiplicity 0.5.

Table 5. atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Faactors of $(\mathbf{1}_R)_2ReO_4$

Atom	x	y	z	B_{eq}[a)]/Å^2	Atom	x	y	z	B_{eq}[a)]/Å^2
Me_2ET $\mathbf{1}_R$					C(5)	4996(10)	561(11)	945(2)	3.4(2)
S(1)	3744(2)	5034(3)	2008(1)	3.21(3)	C(6)	2077(8)	3807(10)	2683(2)	2.8(1)
S(2)	3143(3)	850(3)	2179(1)	3.56(4)	C(7)	699(10)	5719(12)	3269(2)	3.8(2)
S(3)	5655(3)	4354(3)	1260(1)	3.82(4)	C(8)	395(8)	3796(11)	3354(2)	3.0(2)
S(4)	5065(3)	−577(3)	1464(1)	3.88(4)	C(9)	−1232(12)	6743(14)	3920(3)	4.7(2)
S(5)	1833(3)	6245(3)	2835(1)	3.70(4)	C(10)	−692(12)	4841(14)	4123(2)	5.1(2)
S(6)	1184(2)	2072(3)	3006(1)	3.43(4)	C(11)	6179(15)	3202(15)	479(3)	5.7(3)
S(7)	159(4)	7756(3)	3565(1)	6.92(8)	C(12)	5423(14)	−1049(14)	636(3)	5.3(3)
S(8)	−583(3)	2762(3)	3780(1)	3.89(4)					
C(1)	2903(9)	3275(10)	2339(2)	3.1(2)	ReO_4^-				
C(2)	4630(8)	3318(10)	1677(2)	2.8(1)	Re(1)[b)]	9422(1)	0(0)	5000(0)	5.20(1)
C(3)	4366(9)	1408(10)	1758(2)	3.0(1)	O(1)	8302(14)	769(18)	4604(3)	9.4(3)
C(4)	6140(10)	2274(12)	916(2)	3.7(2)	O(2)	10642(14)	−1771(28)	4806(5)	13.7(6)

a) $B_{eq}=(4/3)\cdot(B_{11}\boldsymbol{a}\cdot\boldsymbol{a}+B_{12}\boldsymbol{a}\cdot\boldsymbol{b}+B_{13}\boldsymbol{a}\cdot\boldsymbol{c}+\cdots)$. b) Multiplicity 0.5.

- II′($1-x$, y, $0.5-z$)),[11)] showing a slight dimerization of the donor stacking. Viewed along the normal direction to the molecular plane, the donors are stacked head-to-tail with their long axes being twisted alternately by 30° (Fig. 1b). There are two types of molecular overlapping in the column (Figs. 2a and 2b). While the unsubstituted dihydrodithiin ring is located over the 1,3-dithiole ring of the counterpart molecule in the case of pair 1, the methylated ring overlaps in the pair 2. No short intermolecular sulfur–sulfur contacts (S–S distance < 3.7 Å) are observed within the column because of the twist-type stacking. The features of donor stacking may be resulted from the steric hindrance caused by the methyl groups. Along the direction of the c axis, the donor columns are arranged with the methyl groups facing each other (Figs. 1a and 1b).

There are short intermolecular S–S contacts in a one-dimensional manner between the neighboring donors along the b axis (Fig. 3 and Table 6), and this direction may be the predominant conduction path. Similar donor stacking has been reported for $(ET)_2ClO_4$(dioxane),[1)] where the solvent molecule fills the space which is occupied by the methyl groups in the case of Me_2ET salt.[1)]

Table 6. Lengths of Short Intermolecular Sulfur–Sulfur Contacts

	Lengths/Å[a)]			
Compound	S(4)–S(1′)	S(4)–S(3′)	S(6)–S(7′)	S(8)–S(7′)
$(\mathbf{1}_R)(\mathbf{1}_S)PF_6$	3.676(5)	3.613(5)	3.574(6)	3.576(6)
$(\mathbf{1}_R)_2PF_6$	3.687(4)	3.613(5)	3.590(5)	3.601(5)
$(\mathbf{1}_R)_2ClO_4$	3.689(3)	3.604(3)	3.588(3)	3.594(3)
$(\mathbf{1}_R)_2ReO_4$	3.627(3)	3.531(3)	3.539(4)	3.516(4)

a) S(a)–S(b′) means the distance between (x_a, y_a, z_a)–(x_b, $1+y_b$, z_b).

The PF_6 anion is located in a "cavity", ranging along the b axis (Fig. 1b). When the local environment around the counter anion is watched closely, the anion is surrounded by the methyl groups above and below, and by the unsubsitiuted ethylene moieties on both sides (Fig. 4a). The methylated ethylenedithio bridge is disordered in the ratio of 1:1 (ring A and B). The conformation of methylated dihydrodithiin ring is a sofa form for ring A and a boat form for ring B, while the unsubstituted ring exists as a sofa form.

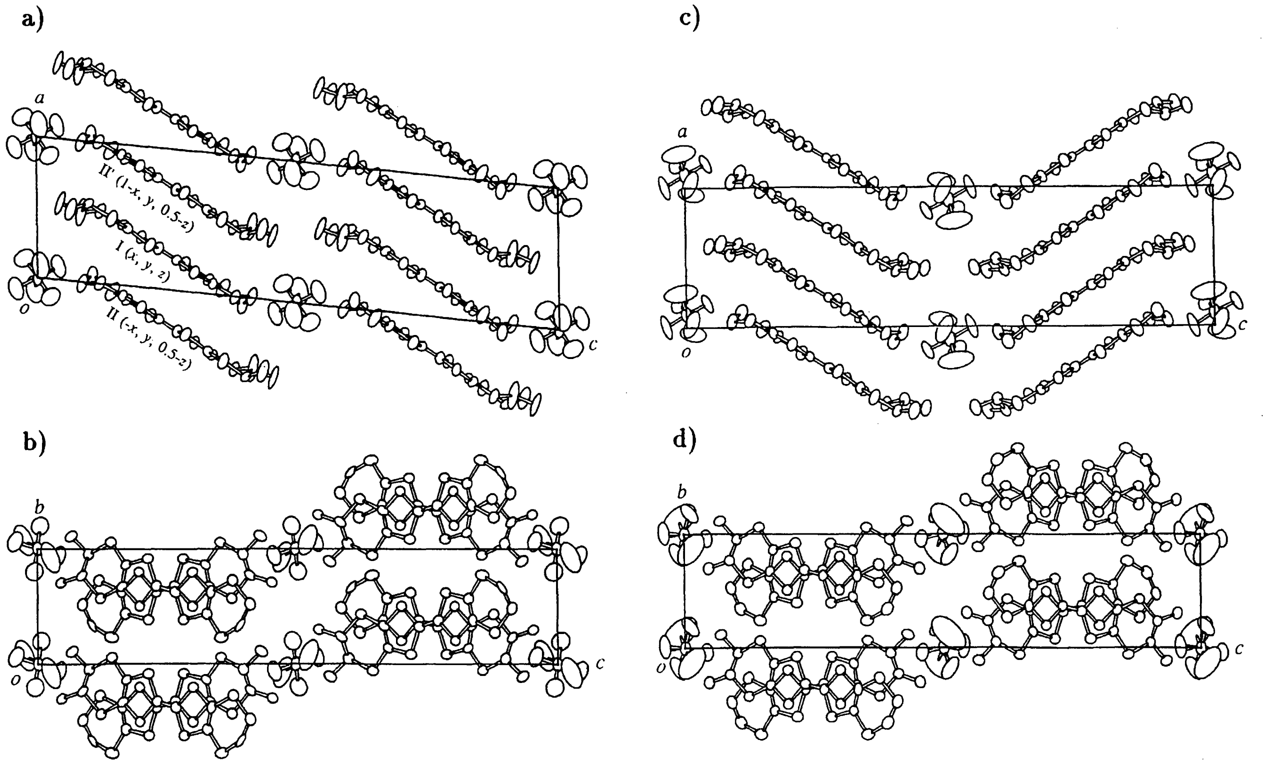

Fig. 1. (a) Crystal structure of $(\mathbf{1}_R)(\mathbf{1}_S)\mathrm{PF}_6$ viewed along the *b* axis. (b) Crystal structure of $(\mathbf{1}_R)(\mathbf{1}_S)\mathrm{PF}_6$ viewed along the *a* axis. (c) Crystal structure of $(\mathbf{1}_R)_2\mathrm{PF}_6$ viewed along the *b* axis. (d). Crystal structure of $(\mathbf{1}_R)_2\mathrm{PF}_6$ viewed along the *a* axis.

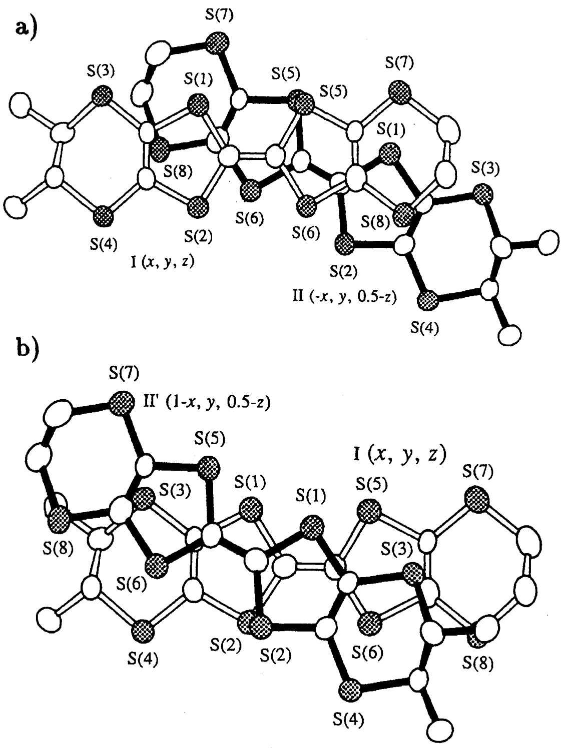

Fig. 2. The two types of molecular stacking in the donor column. (a) pair 1; I(*x*, *y*, *z*) – II(−*x*, *y*, 0.5−*z*). (b) pair 2; I(*x*, *y*, *z*) – II′(1−*x*, *y*, 0.5−*z*).

The chiral donor $\mathbf{1}_R$ also forms the hexafluorophosphates of 2:1 stoichiometry. The donor molecules of the chiral salt $(\mathbf{1}_R)_2\mathrm{PF}_6$ are stacked to form the twist column as in the case of racemic salt $(\mathbf{1}_R)$ $(\mathbf{1}_S)\mathrm{PF}_6$ (Fig. 1c). The side-by-side arrangement of the donor columns along the *b* axis is similar to that of the racemic salt (Fig. 1d). The most prominent difference between the crystal structures of the chiral and the racemic salts is the arrangement of the donor columns along the *c* axis. While the enantiomeric columns are related by inversion symmetry in the racemic salt, the facing donor columns of the chiral salt are related by a twofold rotational symmetry, therefore the direction of inclination of the facing donors is reversed. The donor arrangement form a corrugated sheet along the *bc* plane (Fig. 1c).

The anion is surrounded by methylated and unsubsituted dihydrodithiin rings, as in the racemic salt (Fig. 4b). Because the crystal is made of the donors of single chirality, the cavity thus formed becomes chiral. There is no disorder of methyl groups in the chiral salt, the conformation of the methylated dihydrodithiin ring being a sofa form (similar to the ring A of the chiral salt). The phosphorus atom of the anion is placed on the twofold axis of the crystal. The fluorine atoms of the anion are fixed to the two disordered orientations by the occupation ratio of 1:1 (related by twofold symmetry: the disordered atoms are shown in open and filled circles in Fig. 4b).

The C–H···anion contact[12] is observed in these

Table 7. Short Intermolecular C–H···X (X=F or O) Contacts

Compound	Shortest C···X length/Å	Shortest H···X length/Å[a)]	Number of short H···X contacts per anion[b)]
$(\mathbf{1}_R)(\mathbf{1}_S)PF_6$	3.40(3)	2.30	8
$(\mathbf{1}_R)_2PF_6$	3.30(3)	2.33	6
$(\mathbf{1}_R)_2ClO_4$	3.45(2)	2.46	6
$(\mathbf{1}_R)_2ReO_4$	3.30(2)	2.35	10

a) Interatomic distances are estimated by using the calculated positions for hydrogen atoms. b) The lengths shorter than 2.8 Å are listed.

Me_2ET salts between the methylene or methine hydrogens and the fluorine atoms of the counter anion (the number of short contacts and the shortest distances are listed in Table 7).[13)] This interaction may explain the fixed orientation of the PF_6 anion and the difference in anion ordering between the chiral and racemic salts. Because the donor columns around the anion are related by the inversion symmetry in the racemic salt, the inversion-related fluorines of the PF_6 anion can equally interact with the donor on each side. On the other hand, the fluorines of the anion in the chiral salt can not equally interact with the donors on both sides, because the donor columns are related by a C_2 symmetry. This may be the reason for the disordered orientaion of the anion in the chiral salt.

The crystal structures of $(\mathbf{1}_R)_2ClO_4$ and $(\mathbf{1}_R)_2ReO_4$ are very similar to that of $(\mathbf{1}_R)_2PF_6$ (Tables 4 and 5). The XO_4 anion (X=Cl or Re) is placed directing its twofold axis along the *a* axis (the twofold axis of the crystal), therefore the oxygen atoms of the anion are orientationally ordered. The C–H···O short contacts are also observed in the crystals of $(\mathbf{1}_R)_2ClO_4$ and $(\mathbf{1}_R)_2ReO_4$, the shortest contact being 2.35 Å (Table 7).

The similarity in the crystal structure of $(Me_2ET)_2X$ ($X=PF_6$, ClO_4, and ReO_4) shows a sharp contrast with the polymorphism of the ion radical salts of ET, which is commonly observed regardless of the shape of anions.[1,2)] This structural singularity suggests that the packing style of Me_2ET is largely determined by the steric factor of the donor itself.

The electrical conductivity of these four salts is very

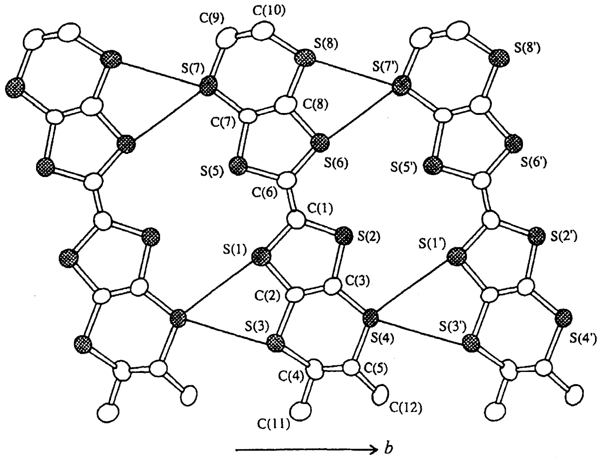

Fig. 3. Short intermolecular S–S contacts of Me_2ET along the *b* axis. For each S–S distance, see Table 6.

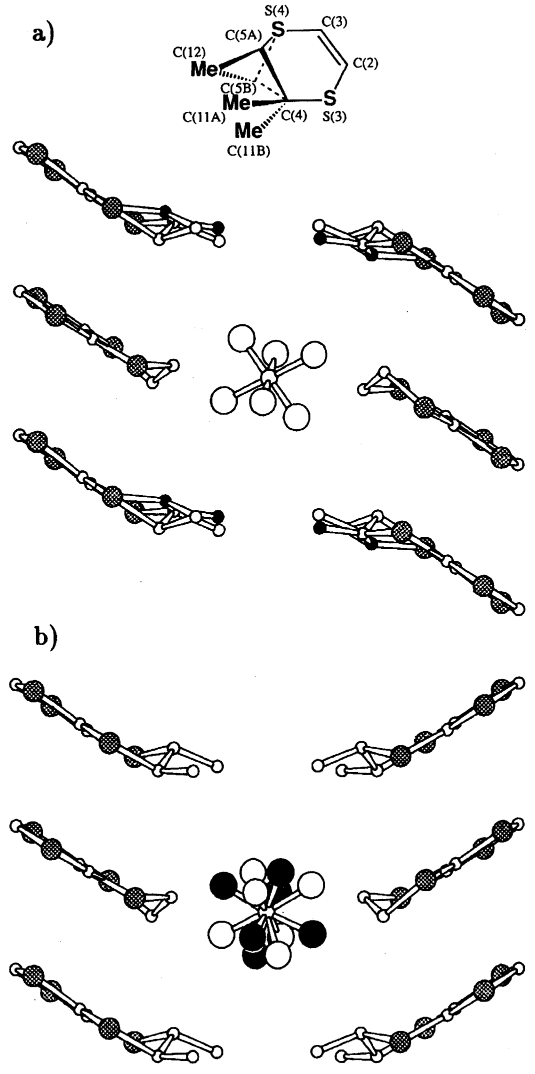

Fig. 4. The arrangement of donor columns around the anion. Only a half of the donor molecules surrounding the anion are depicted. (a) $(\mathbf{1}_R)(\mathbf{1}_S)PF_6$. The carbon atoms constituting ring B (C(5B) and C(11B)) are shown as filled circles. In Figs. 1a and 1b, the methylated dihydrodithiin rings are drawn as ring A for clarity. (b) $(\mathbf{1}_R)_2PF_6$. The two orientation of the fluorines are shown with open and filled circles.

similar (semiconductor, $\sigma_{\rm RT}\approx 0.2$ S cm^{-1} and $E_{\rm a}\approx 0.2$ eV for the temperature range of 77—300 K), reflecting the similarity of the packing of donors in these crystals.

In the crystal of neutral Me$_2$ET, the donor molecules form a head-to-tail dimer with their long axes parallel.[3)] The steric repulsion of the methyl groups can also be avoided by constituting this dimeric structure. In fact, similar dimerization is discovered in the salt of $(\mathbf{1}_S)_2$ClO$_4$, reported recently. The salt has the κ-type structure and exhibits superconducting behavior under pressure.[14)]

In summary, Me$_2$ET forms radical salts of both one dimensional and two dimensional conductors. The arrangement of donors in the former salt is characterized by the twist-type columnar structure, while in the latter salt the κ-type structure is recognized. The methyl groups in both cases play an important role of controlling the crystal structure and of providing a cavity for the anion.

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