

Fig. 2. Stereoscopic representation of the unit cell viewed slightly oblique to the a axis, with b horizontal, illustrating hydrogen bonds.

guaianolides of the ambrosanolide class, having five-membered rings *trans*-fused at C(1)–C(5). The r.m.s. difference between the seven endocyclic torsion angles found here (Table 2) and those of hysterin (Declercq, Germain, Van Meerssche, Demuynck, Declercq & Vandewalle, 1980) is 1.7° , with the largest individual difference $3.1 (5)^\circ$. Similar conformations are also found in bippinatin: r.m.s. deviation 7.2° and parthenin: r.m.s. deviation 9.3° (Fronczek, Vargas, Fischer, Chiari, Balza & Towers, 1988).

C–H distances range $0.89 (2)$ – $1.03 (2)$ Å and average $0.96 (4)$ Å, while the O–H distance is $0.83 (2)$ Å. Molecules interact in the crystal through a hydrogen bond, with hydroxyl group O(5) as donor and spiro-lactone carbonyl O(4) of a molecule related by the 2_1 axis at $1, y, \frac{3}{4}$ as acceptor. Geometrical parameters of this hydrogen bond are O...O $2.883 (2)$, H...O $2.09 (2)$ Å and O–H...O angle $161 (2)^\circ$. The spiral chains formed by this interaction are depicted in Fig. 2. No other intermolecular interactions shorter than 3.35 Å between heavy atoms exist.

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Structures of Two Semiconducting Charge-Salts Based on 4,5-Methylenedithio-4',5'-propylenedithiotetrathiafulvalene (MPT): (MPT)₂ClO₄(THF) and (MPT)₂PF₆(THF)

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Abstract. $2C_{10}H_8S_8^{1/2+}.ClO_4^-(C_4H_8O)$, $M_r = 940.933$, triclinic, $P\bar{1}$, $a = 9.110 (2)$, $b = 12.501 (4)$, $c = 16.611 (6)$ Å, $\alpha = 104.46 (2)$, $\beta = 88.47 (2)$, $\gamma =$

$102.42 (2)^\circ$, $V = 1788 (1)$ Å³, $Z = 2$, $D_x = 1.747$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.04$ mm⁻¹, $F(000) = 962$, $T = 298$ K, $R(F) = 0.088$ for 8261 observed reflections. $2C_{10}H_8S_8^{1/2+}.PF_6^-(C_4H_8O)$, $M_r = 986.446$, triclinic, $P\bar{1}$, $a = 9.215 (3)$, $b = 12.528 (4)$, $c = 17.110 (7)$ Å, $\alpha = 105.03 (3)$, $\beta = 91.14 (3)$, $\gamma = 103.56 (2)^\circ$, $V = 1848 (1)$ Å³, $Z = 2$, $D_x = 1.773$ Mg m⁻³, $\lambda(\text{Mo } K\alpha)$

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$= 0.71073 \text{ \AA}$, $\mu = 0.99 \text{ mm}^{-1}$, $F(000) = 1002$, $T = 298 \text{ K}$, $R(F) = 0.073$ for 5739 observed reflections. In these isostructural salts the partially oxidized MPT donor molecules occur in stacks along the a axis and are linked by weak interstack intermolecular $S \cdots S$ contacts along the b direction to form layers in the ab plane. These two-dimensional donor sheets are separated by alternating stacks made up of ClO_4^- or PF_6^- anions and THF molecules. The ClO_4^- salt is semiconducting, with $E_a = 170 \text{ meV}$ and $\sigma_{300} = 1 \times 10^{-3} (\Omega \text{ cm})^{-1}$.

Introduction. The charge-transfer salts based on bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) include metals, semiconductors and superconductors (Williams, Beno, Wang, Leung, Emge, Geiser & Carlson, 1985; Williams *et al.*, 1987). These salts consist of stacks of relatively planar donor molecules which are linked by short [compared with the van der Waals radii sum, 3.6 \AA (Bondi, 1964)] inter- and intrastack $S \cdots S$ interactions. The size and symmetry of the counteranions (Emge *et al.*, 1986; Wang *et al.*, 1987) as well as the donor- $CH_2 \cdots$ anion hydrogen-bonding interactions (Leung, Emge, Beno, Wang, Williams, Petřiček & Coppens, 1985; Whangbo, Williams, Schultz, Emge & Beno, 1987) have been elucidated as some of the factors that determine the transport properties of these salts. An alternative method of tuning the intermolecular $S \cdots S$ contact distances, and hence the electrical properties of a charge-transfer salt, is by modification of the donor molecules. One approach by which this may be accomplished is the substitution of the terminal ethylene groups by other alkylene groups containing a different number of $-CH_2-$ units (Kini, Beno & Williams, 1987; Kini, Tytko, Hunt & Williams, 1987). We report here the structures of the first charge-transfer salts derived from the unsymmetrical donor MPT (see Fig. 1).

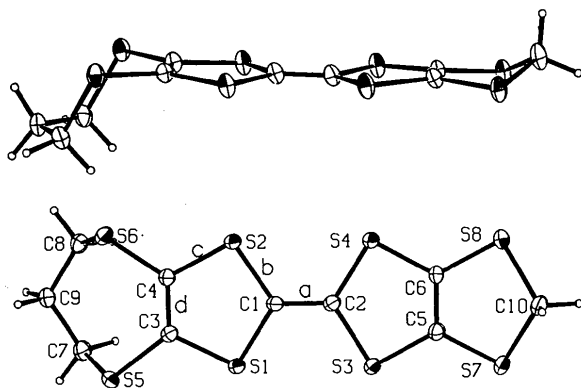


Fig. 1. Configuration of the MPT molecule and atomic numbering scheme for molecule *A*. The atom numbering used for molecule *B* is similar with 10 added to each atom number. The thermal ellipsoids are drawn at the 25% probability level with H atoms reduced to $B_{iso} = 1.0 \text{ \AA}^2$ for clarity.

Experimental. The neutral donor, 4,5-methylenedithio-4',5'-propylenedithiotetrathiafulvalene (MPT), was synthesized as reported by Kini, Tytko, Hunt & Williams (1987) and purified by flash chromatographic separation (silica, CS_2). Crystals of $(MPT)_2ClO_4(THF)$ were grown by electrocrystallization on a Pt electrode, $1.0 \mu\text{A cm}^{-2}$, 294 K , with 0.9 mM MPT and 0.06 M $[N(n-C_4H_9)_4]ClO_4$ in THF. Small black plates, $0.50 \times 0.41 \times 0.03 \text{ mm}$, were produced. For $(MPT)_2PF_6(THF)$, $0.27 \times 0.12 \times 0.05 \text{ mm}$ black plates were produced by electrocrystallization ($1.0 \mu\text{A cm}^{-2}$, 296 K) of 0.8 mM MPT and 0.05 M $[N(n-C_4H_9)_4]PF_6$ in THF. Nicolet *P2*, automated diffractometer. Unit-cell dimensions from least squares based on the setting angles of 25 reflections ($10 < 2\theta < 20^\circ$). Intensity data were collected using the θ - 2θ scan technique with monochromatized Mo $K\alpha$ radiation and variable scan speeds of 2 to $12^\circ \text{ min}^{-1}$ to $(\sin\theta)/\lambda = 0.59 \text{ \AA}^{-1}$, $0 \leq h \leq 10$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$ for the PF_6^- salt and to $(\sin\theta)/\lambda = 0.65 \text{ \AA}^{-1}$, $0 \leq h \leq 11$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$ for the ClO_4^- salt. Three standard reflections measured every 100 reflections showed $< 4\%$ intensity variation. Data were corrected for Lorentz and polarization effects, a Gaussian absorption correction ($8 \times 8 \times 8$) procedure was used and multiply measured reflections (standards and $0kl$ zone) were averaged. For $(MPT)_2PF_6(THF)$, $T_{min} = 0.88$, $T_{max} = 0.95$ with $R_{int}(F_o) = 0.024$ for 1018 reflections. In the case of $(MPT)_2ClO_4(THF)$, $T_{min} = 0.68$, $T_{max} = 0.97$ with $R_{int}(F_o) = 0.029$ for 1325 reflections. The centrosymmetric space group was indicated by intensity statistics and confirmed by the successful structure solution. The structure of $(MPT)_2PF_6(THF)$ was solved using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier methods; that of the ClO_4^- salt by analogy. H atoms, which could be observed in Fourier maps, were included at calculated positions with $B_{iso} = 5.0 \text{ \AA}^2$ for the two independent MPT molecules in the asymmetric unit and 7.0 \AA^2 for the THF solvent molecule. The calculated electron density around the Cl atom in $(MPT)_2ClO_4(THF)$ showed a double maximum near one O atom so the O atoms were modeled by three fully occupied and two partially occupied oxygen positions [O(4) and O(5) populations are 0.5]. All non-hydrogen atoms were refined with anisotropic temperature factors. The function minimized was $\sum w(1F_o - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$ and $\sigma(F_o) = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{1/2}/2F_o$, with the value of $\sigma(F_o^2)$ based on counting statistics. $\Delta/\sigma \leq 0.05$ in the final least-squares cycle resulted in $R(F_o) = 0.088$, $wR(F_o) = 0.066$ and $S = 2.07$ for 425 variable parameters and 8261 data with $F_o \geq 0.0$ in the case of $(MPT)_2ClO_4(THF)$ and $R(F_o) = 0.073$, $wR(F_o) = 0.050$ and $S = 1.67$ for 433 refined parameters and 5739 observed data in the case of $(MPT)_2PF_6(THF)$. Electrical conductivity measurements on $(MPT)_2ClO_4(THF)$ in an arbitrary direction in the ab plane using a

two-probe technique gave thermally activated conductivity with $\sigma_{300} = 0.001 (\Omega \text{ cm})^{-1}$ and $E_a = 170 \text{ meV}$. Atomic scattering factors including anomalous contributions were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed using a local modification of the *UCLA Crystallographic Package* (Strouse, 1978).

Discussion. The final positional and equivalent isotropic thermal parameters are given in Table 1.* Bond distances and angles along with intermolecular S...S contact distances are given in Table 2. The atomic numbering scheme used for MPT molecule *A* and the conformation of the molecule are shown in Fig. 1. Bond lengths for the anions and THF molecules are in the expected range (*Molecular Structures and Dimensions*, 1972).

The MPT molecules stack face-to-face in an $\cdots A \cdots B \cdots A \cdots B \cdots$ arrangement along the *a* axis with methylene groups stacked over methylene groups and propylene groups over propylene groups as shown in Fig. 2. Stacks containing alternatively THF molecules and $\text{PF}_6^-(\text{ClO}_4^-)$ anions separate the donor molecules along the *c* direction. Short interstack S...S contacts (see Table 2) less than the van der Waals radii sum of 3.6 Å (Bondi, 1964) link the donor stacks along the *b* direction. However, no short contacts occur along the stacking axis. As is shown in Fig. 3, the resulting two-dimensional donor sheet with two MPT molecules stacked along the *a* axis, two stacks/unit cell along the *b* direction and one donor sheet/unit cell along the *c* direction is similar to that found in $(\text{BEDT-TTF})_2\text{ClO}_4$ (TCE) $_{0.5}$ (Kobayashi, Kobayashi, Sasaki, Saito, Enoki & Inokuchi, 1983) and $(\text{BEDT-TTF})_2\text{BrO}_4$ (TCE) $_{0.5}$ (Beno, Blackman, Leung, Carlson, Copps & Williams, 1985). While also lacking short intrastack S...S contacts, the structure observed for $(\text{BEDT-TTF})_2\text{ClO}_4$ (TCE) $_{0.5}$ results in a two-dimensional metal (Mori, Kobayashi, Sasaki, Kobayashi, Saito & Inokuchi, 1982). Electrical conductivity measurements indicate that $(\text{MPT})_2\text{ClO}_4$ (THF) is a semiconductor. Similar electrical properties are expected for $(\text{MPT})_2\text{PF}_6$ (THF) because of the nearly identical structural parameters which are observed for this salt.

While independent of the counter-anion, the two independent MPT molecules in both the ClO_4^- and PF_6^- salts possess slightly different conformations. Molecule *A* is in a chair conformation (as shown in Fig. 1) while in molecule *B* the methylene group is found in the molecular plane (see Fig. 2). The central portions of the molecules (S1–S8 and C1–C6) are quite planar with the

* Lists of structure factors, anisotropic thermal parameters, and calculated H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44814 (46 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters*

The complete temperature factor is $\exp[-8\pi^2 U_{\text{eq}}(\sin^2\theta)/\lambda^2]$, where $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ in units of Å².

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ² × 10 ⁴)
(MPT)₂ClO₄(THF)				
MPT molecule A				
S(1)	0.2725 (2)	0.18728 (10)	-0.45595 (8)	397 (5)
S(2)	0.2849 (2)	0.42342 (10)	-0.46108 (8)	419 (5)
S(3)	0.0539 (2)	0.09711 (10)	-0.62016 (8)	433 (5)
S(4)	0.0587 (2)	0.33576 (10)	-0.62199 (8)	431 (5)
S(5)	0.50024 (15)	0.25073 (11)	-0.31649 (8)	404 (5)
S(6)	0.5135 (2)	0.52228 (10)	-0.32126 (8)	417 (5)
S(7)	-0.1593 (2)	0.01307 (11)	-0.77380 (9)	471 (5)
S(8)	-0.1630 (2)	0.25116 (11)	-0.77196 (8)	444 (5)
C(1)	0.2153 (5)	0.2793 (4)	-0.5069 (3)	344 (17)
C(2)	0.1199 (5)	0.2425 (4)	-0.5735 (3)	346 (17)
C(3)	0.3946 (5)	0.2938 (4)	-0.3843 (3)	351 (17)
C(4)	0.4011 (5)	0.4022 (4)	-0.3864 (3)	366 (18)
C(5)	-0.0465 (5)	0.1199 (4)	-0.6996 (3)	342 (17)
C(6)	-0.0458 (5)	0.2281 (4)	-0.6994 (3)	364 (18)
C(7)	0.4320 (6)	0.3097 (4)	-0.2145 (3)	433 (19)
C(8)	0.4353 (6)	0.5149 (4)	-0.2200 (3)	427 (19)
C(9)	0.4917 (6)	0.4364 (4)	-0.1770 (3)	437 (19)
C(10)	-0.1802 (7)	0.1085 (4)	-0.8371 (3)	510 (21)
MPT molecule B				
S(11)	-0.1818 (2)	0.36449 (10)	-0.43285 (8)	387 (5)
S(12)	-0.19087 (15)	0.13095 (10)	-0.42910 (8)	380 (4)
S(13)	-0.4094 (2)	0.27471 (10)	-0.59388 (8)	401 (5)
S(14)	-0.4009 (2)	0.04021 (10)	-0.59488 (8)	400 (5)
S(15)	0.0317 (2)	0.46637 (10)	-0.28788 (8)	428 (5)
S(16)	0.0189 (2)	0.19264 (11)	-0.28265 (8)	428 (5)
S(17)	-0.6066 (2)	0.18987 (11)	-0.75319 (9)	511 (5)
S(18)	-0.5861 (2)	-0.04690 (11)	-0.75778 (9)	540 (6)
C(11)	-0.2457 (5)	0.2219 (4)	-0.4791 (3)	331 (17)
C(12)	-0.3398 (5)	0.1831 (4)	-0.5491 (3)	342 (17)
C(13)	-0.0760 (5)	0.3450 (4)	-0.3537 (3)	341 (17)
C(14)	-0.0796 (5)	0.2369 (4)	-0.3524 (3)	333 (17)
C(15)	-0.5102 (5)	0.1681 (4)	-0.6724 (3)	330 (17)
C(16)	-0.5052 (5)	0.0599 (4)	-0.6734 (3)	346 (17)
C(17)	-0.0392 (6)	0.4601 (4)	-0.1857 (3)	494 (21)
C(18)	-0.0560 (6)	0.2545 (5)	-0.1834 (3)	481 (21)
C(19)	0.0127 (7)	0.3772 (5)	-0.1446 (3)	518 (22)
C(20)	-0.6739 (7)	0.0415 (4)	-0.8005 (4)	685 (26)
THF molecule				
C(21)	0.2130 (11)	0.1184 (6)	0.0196 (5)	1082 (42)
C(22)	0.2364 (9)	0.2023 (8)	-0.0305 (4)	1031 (41)
C(23)	0.2574 (10)	0.3123 (7)	0.0325 (5)	1083 (43)
C(24)	0.1969 (8)	0.2882 (5)	0.1082 (4)	744 (29)
O(6)	0.1866 (5)	0.1714 (3)	0.1030 (3)	723 (19)
ClO₄⁻ anion				
Cl	0.7037 (2)	0.2582 (2)	1.00612 (10)	767 (8)
O(1)	0.6333 (8)	0.2351 (10)	0.9333 (4)	2097 (58)
O(2)	0.8230 (11)	0.2083 (11)	0.9932 (5)	2860 (74)
O(3)	0.6148 (6)	0.2346 (6)	1.0707 (4)	1459 (35)
O(4)	0.707 (5)	0.374 (3)	1.007 (3)	2836 (227)
O(5)	0.806 (3)	0.353 (3)	1.0402 (9)	1509 (125)
(MPT)₂PF₆(THF)				
MPT molecule A				
S(1)	0.27131 (15)	0.18572 (9)	-0.45789 (7)	420 (5)
S(2)	0.28570 (15)	0.42204 (9)	-0.46336 (7)	432 (5)
S(3)	0.0347 (2)	0.08711 (10)	-0.61686 (7)	454 (5)
S(4)	0.04257 (15)	0.32535 (9)	-0.62138 (7)	443 (5)
S(5)	0.51174 (14)	0.25566 (10)	-0.32115 (7)	443 (5)
S(6)	0.52874 (14)	0.52733 (10)	-0.32678 (7)	433 (5)
S(7)	-0.1973 (2)	-0.00589 (10)	-0.76585 (8)	483 (5)
S(8)	-0.19499 (15)	0.23112 (10)	-0.76800 (7)	472 (5)
C(1)	0.2091 (5)	0.2752 (3)	-0.5085 (3)	379 (17)
C(2)	0.1071 (5)	0.2352 (4)	-0.5726 (3)	387 (17)
C(3)	0.4017 (5)	0.2961 (4)	-0.3878 (3)	367 (17)
C(4)	0.4087 (5)	0.4037 (4)	-0.3906 (3)	388 (17)
C(5)	-0.0718 (5)	0.1060 (4)	-0.6951 (3)	383 (17)
C(6)	-0.0703 (5)	0.2135 (4)	-0.6960 (2)	364 (17)
C(7)	0.4557 (5)	0.3186 (4)	-0.2212 (3)	467 (19)
C(8)	0.4642 (5)	0.5247 (4)	-0.2269 (3)	441 (18)
C(9)	0.5236 (5)	0.4460 (4)	-0.1863 (3)	450 (18)
C(10)	-0.2156 (6)	0.0855 (4)	-0.8308 (3)	523 (20)

Table 1 (cont.)

	x	y	z	U _{eq} (Å ² × 10 ⁴)
MPT molecule B				
S(11)	-0.17418 (14)	0.37128 (9)	-0.43257 (7)	406 (4)
S(12)	-0.18454 (14)	0.13759 (9)	-0.42930 (7)	378 (4)
S(13)	-0.41807 (15)	0.27410 (9)	-0.59017 (7)	410 (5)
S(14)	-0.41357 (14)	0.03984 (9)	-0.58984 (7)	393 (4)
S(15)	0.05276 (15)	0.47876 (10)	-0.29030 (8)	445 (5)
S(16)	0.04177 (14)	0.20513 (10)	-0.28773 (7)	435 (5)
S(17)	-0.6344 (2)	0.18169 (10)	-0.74474 (8)	510 (5)
S(18)	-0.6192 (2)	-0.05535 (10)	-0.74689 (8)	533 (5)
C(11)	-0.2447 (5)	0.2272 (3)	-0.4777 (2)	333 (16)
C(12)	-0.3468 (5)	0.1849 (3)	-0.5451 (3)	343 (16)
C(13)	-0.0612 (5)	0.3545 (4)	-0.3561 (3)	365 (17)
C(14)	-0.0658 (5)	0.2463 (4)	-0.3549 (2)	339 (16)
C(15)	-0.5289 (5)	0.1637 (4)	-0.6656 (2)	358 (17)
C(16)	-0.5259 (5)	0.0564 (4)	-0.6658 (2)	353 (17)
C(17)	-0.0115 (6)	0.4714 (4)	-0.1909 (3)	516 (20)
C(18)	-0.0200 (6)	0.2656 (4)	-0.1896 (3)	515 (20)
C(19)	0.0471 (6)	0.3922 (4)	-0.1514 (3)	488 (20)
C(20)	-0.7079 (7)	0.0308 (4)	-0.7902 (3)	667 (24)
THF molecule				
C(21)	0.1485 (8)	0.2682 (5)	0.1176 (4)	872 (30)
C(22)	0.1803 (8)	0.2930 (6)	0.0389 (4)	1014 (35)
C(23)	0.1672 (8)	0.1781 (6)	-0.0203 (4)	877 (30)
C(24)	0.2001 (8)	0.1067 (5)	0.0338 (4)	819 (28)
O(6)	0.1516 (5)	0.1530 (3)	0.1110 (2)	742 (17)
PF₆⁻ anion				
P(1)	-0.3330 (2)	0.2609 (2)	-0.00712 (9)	734 (7)
F(1)	-0.3824 (8)	0.2144 (6)	0.0643 (3)	2336 (44)
F(2)	-0.4355 (8)	0.3398 (6)	0.0122 (5)	2454 (46)
F(3)	-0.1993 (7)	0.3477 (5)	0.0411 (4)	1993 (35)
F(4)	-0.2907 (6)	0.3050 (6)	-0.0828 (3)	1966 (37)
F(5)	-0.2330 (7)	0.1802 (5)	-0.0349 (5)	2378 (47)
F(6)	-0.4681 (6)	0.1703 (6)	-0.0592 (3)	1767 (32)

Table 2 (cont.)

Intermolecular S...S distances (Å)	ClO ₄ ⁻ salt		PF ₆ ⁻ salt	
	ClO ₄ ⁻ salt	PF ₆ ⁻ salt	ClO ₄ ⁻ salt	PF ₆ ⁻ salt
S(1)-S(14)	3.585 (2)	3.642 (2)	S(2)-S(13 ⁱⁱ)	3.585 (2)
S(3)-S(16)	3.503 (2)	3.494 (2)	S(4)-S(11 ⁱⁱ)	3.570 (2)
S(4)-S(15 ⁱⁱ)	3.439 (2)	3.458 (2)	S(5)-S(14)	3.492 (2)
S(5)-S(18)	3.332 (2)	3.357 (2)	S(6)-S(13 ⁱⁱ)	3.496 (2)
S(6)-S(17 ⁱⁱ)	3.423 (2)	3.422 (2)	S(7)-S(16)	3.437 (2)
S(6)-S(17 ⁱⁱ)	3.374 (2)	3.429 (2)		3.455 (2)

Symmetry code: (i) -x, -y, -1-z; (ii) -x, 1-y, -1-z.

MPT molecule A	ClO ₄ ⁻ salt		PF ₆ ⁻ salt		MPT molecule B	ClO ₄ ⁻ salt		PF ₆ ⁻ salt	
	ClO ₄ ⁻ salt	PF ₆ ⁻ salt	ClO ₄ ⁻ salt	PF ₆ ⁻ salt		ClO ₄ ⁻ salt	PF ₆ ⁻ salt	ClO ₄ ⁻ salt	PF ₆ ⁻ salt
C(3)-S(1)-C(1)	95.3 (2)	95.7 (2)	C(11)-S(11)-C(13)	95.7 (2)	95.6 (2)	C(11)-S(12)-C(14)	95.2 (2)	95.2 (2)	
C(4)-S(2)-C(2)	95.5 (2)	95.6 (2)	C(15)-S(13)-C(12)	94.5 (2)	94.6 (2)	C(16)-S(14)-C(12)	94.8 (2)	94.6 (2)	
C(5)-S(3)-C(2)	94.3 (2)	93.9 (2)	C(13)-S(15)-C(17)	103.4 (2)	102.8 (2)	C(14)-S(16)-C(18)	102.0 (2)	102.8 (2)	
C(6)-S(4)-C(2)	94.1 (2)	94.1 (2)	C(15)-S(17)-C(20)	94.5 (2)	94.3 (2)	C(16)-S(18)-C(20)	94.6 (2)	94.7 (2)	
C(3)-S(5)-C(7)	103.3 (2)	103.5 (2)	C(12)-C(11)-S(11)	122.6 (3)	123.2 (3)	C(12)-C(11)-S(12)	122.1 (3)	121.6 (3)	
C(4)-S(6)-C(8)	101.2 (2)	102.2 (2)	S(11)-C(11)-S(12)	115.3 (2)	115.1 (2)	C(11)-C(12)-S(14)	121.8 (3)	122.1 (3)	
C(5)-S(7)-C(10)	92.9 (2)	92.1 (2)	C(11)-C(12)-S(14)	121.8 (3)	122.1 (3)	C(11)-C(12)-S(13)	116.1 (3)	115.8 (2)	
C(6)-S(8)-C(10)	92.4 (2)	91.9 (2)	C(14)-C(13)-S(11)	116.4 (3)	116.7 (3)	C(14)-C(13)-S(15)	126.5 (3)	126.0 (3)	
C(2)-C(1)-S(2)	122.6 (3)	123.1 (3)	C(14)-C(13)-S(15)	117.5 (3)	117.1 (3)	S(11)-C(13)-S(15)	116.9 (3)	117.2 (2)	
C(2)-C(1)-S(1)	122.8 (3)	122.9 (3)	S(11)-C(13)-S(12)	117.0 (3)	116.9 (3)	C(13)-C(14)-S(12)	117.0 (3)	116.9 (3)	
S(2)-C(1)-S(1)	114.6 (3)	113.9 (2)	C(13)-C(14)-S(16)	126.3 (4)	126.2 (3)	S(12)-C(14)-S(16)	116.8 (3)	116.9 (2)	
C(1)-C(2)-S(4)	122.4 (3)	122.6 (3)	C(16)-C(15)-S(13)	117.4 (3)	117.3 (3)	C(16)-C(15)-S(17)	117.9 (3)	118.0 (3)	
C(1)-C(2)-S(3)	122.0 (3)	121.7 (3)	S(13)-C(15)-S(17)	124.6 (3)	124.5 (3)	C(15)-C(16)-S(14)	117.2 (3)	117.7 (3)	
S(4)-C(2)-S(3)	115.6 (2)	115.6 (2)	C(15)-C(16)-S(18)	118.3 (3)	118.5 (3)	C(15)-C(16)-S(18)	118.3 (3)	118.5 (3)	
C(4)-C(3)-S(5)	125.4 (4)	126.0 (3)	S(14)-C(16)-S(18)	124.1 (3)	123.5 (3)	C(19)-C(17)-S(15)	117.0 (4)	116.4 (3)	
C(4)-C(3)-S(1)	117.5 (3)	117.1 (3)	C(19)-C(17)-S(15)	117.0 (4)	116.4 (3)	C(19)-C(18)-S(16)	116.0 (4)	116.2 (3)	
S(5)-C(3)-S(1)	117.1 (3)	116.9 (2)	C(7)-C(9)-C(8)	115.4 (4)	116.1 (4)	C(18)-C(19)-C(17)	114.1 (4)	115.0 (4)	
C(3)-C(4)-S(6)	125.9 (3)	125.4 (4)	S(7)-C(10)-S(8)	110.0 (3)	109.3 (2)	S(18)-C(20)-S(17)	113.1 (3)	113.2 (3)	
C(3)-C(4)-S(2)	116.7 (3)	117.4 (3)							
S(6)-C(4)-S(2)	117.4 (3)	117.3 (2)							
C(6)-C(5)-S(3)	117.6 (4)	118.1 (3)							
C(6)-C(5)-S(7)	117.9 (4)	117.7 (3)							
S(3)-C(5)-S(7)	124.3 (3)	123.8 (3)							
C(5)-C(6)-S(4)	118.4 (3)	118.3 (3)							
C(5)-C(6)-S(8)	117.7 (4)	117.5 (3)							
S(4)-C(6)-S(8)	123.6 (3)	124.0 (3)							
C(9)-C(7)-S(5)	116.4 (4)	115.3 (3)							
C(9)-C(8)-S(6)	116.1 (3)	115.3 (3)							
C(7)-C(9)-C(8)	115.4 (4)	116.1 (4)							
S(7)-C(10)-S(8)	110.0 (3)	109.3 (2)							

Table 2. Interatomic distances (Å) and angles (°)

MPT molecule A	ClO ₄ ⁻ salt		PF ₆ ⁻ salt		MPT molecule B	ClO ₄ ⁻ salt		PF ₆ ⁻ salt	
	ClO ₄ ⁻ salt	PF ₆ ⁻ salt	ClO ₄ ⁻ salt	PF ₆ ⁻ salt		ClO ₄ ⁻ salt	PF ₆ ⁻ salt	ClO ₄ ⁻ salt	PF ₆ ⁻ salt
S(1)-C(3)	1.752 (5)	1.760 (4)	S(11)-C(13)	1.746 (4)	1.741 (4)				
S(1)-C(11)	1.754 (4)	1.766 (4)	S(11)-C(11)	1.733 (5)	1.727 (4)				
S(2)-C(1)	1.754 (5)	1.764 (4)	S(12)-C(11)	1.723 (4)	1.734 (4)				
S(2)-C(4)	1.756 (4)	1.761 (5)	S(12)-C(14)	1.748 (5)	1.738 (4)				
S(3)-C(5)	1.738 (5)	1.741 (5)	S(13)-C(15)	1.730 (5)	1.727 (4)				
S(3)-C(2)	1.766 (5)	1.770 (4)	S(13)-C(12)	1.740 (4)	1.745 (4)				
S(4)-C(6)	1.738 (5)	1.735 (4)	S(14)-C(16)	1.730 (4)	1.729 (4)				
S(4)-C(2)	1.759 (4)	1.763 (4)	S(14)-C(12)	1.731 (5)	1.733 (4)				
S(5)-C(3)	1.751 (4)	1.755 (5)	S(15)-C(13)	1.746 (5)	1.753 (4)				
S(5)-C(7)	1.822 (5)	1.827 (5)	S(15)-C(17)	1.814 (6)	1.829 (5)				
S(6)-C(4)	1.750 (5)	1.757 (5)	S(16)-C(14)	1.744 (4)	1.752 (4)				
S(6)-C(8)	1.825 (5)	1.826 (5)	S(16)-C(18)	1.820 (6)	1.816 (5)				
S(7)-C(5)	1.736 (5)	1.753 (5)	S(17)-C(15)	1.730 (4)	1.743 (4)				
S(7)-C(10)	1.817 (5)	1.822 (5)	S(17)-C(20)	1.801 (5)	1.803 (5)				
S(8)-C(6)	1.747 (4)	1.758 (4)	S(18)-C(16)	1.729 (5)	1.734 (4)				
S(8)-C(10)	1.817 (5)	1.825 (5)	S(18)-C(20)	1.780 (5)	1.785 (5)				
C(1)-C(2)	1.347 (6)	1.339 (6)	C(11)-C(12)	1.384 (6)	1.379 (6)				
C(3)-C(4)	1.353 (6)	1.347 (6)	C(13)-C(14)	1.350 (6)	1.352 (5)				
C(5)-C(6)	1.350 (6)	1.348 (6)	C(15)-C(16)	1.358 (6)	1.349 (6)				
C(7)-C(9)	1.532 (7)	1.522 (6)	C(17)-C(19)	1.531 (7)	1.523 (7)				
C(8)-C(9)	1.524 (7)	1.533 (6)	C(18)-C(19)	1.508 (7)	1.521 (6)				
THF molecule									
C(21)-O(6)	1.417 (8)	1.426 (6)	C(21)-C(22)	1.474 (10)	1.478 (8)				
C(22)-C(23)	1.484 (10)	1.506 (9)	C(23)-C(24)	1.434 (9)	1.516 (8)				
C(24)-O(6)	1.423 (7)	1.423 (6)							
ClO₄⁻ anion									
Cl-O(1)	1.322 (6)		Cl-O(2)	1.353 (7)					
Cl-O(3)	1.380 (5)		Cl-O(4)	1.44 (2)					
Cl-O(5)	1.348 (14)								
PF₆⁻ anion									
P(1)-F(1)	1.519 (5)	P(1)-F(2)	1.501 (5)						
P(1)-F(3)	1.499 (5)	P(1)-F(4)	1.557 (5)						
P(1)-F(5)	1.517 (5)	P(1)-F(6)	1.550 (5)						

largest deviations from the molecular plane, 0.11 and 0.15 Å, observed in molecules A and B, respectively, for (MPT)₂ClO₄(THF) and 0.10 and 0.17 Å observed for (MPT)₂PF₆(THF). The intramolecular distances in the MPT molecules are also independent of the counteranion but show considerable differences between the two independent MPT molecules. In BEDT-TTF salts systematic variations in bond lengths are observed for

different oxidation states of the donor molecule (Beno *et al.*, 1987). The central TTF portion of the MPT molecule is expected to be electronically very similar to that in the BEDT-TTF molecule so that the C—C double bonds and the central C—S distance [e.g. C(1)—S(1)], which were found to depend most sensitively on the oxidation state of the BEDT-TTF donor, are expected to possess similar lengths for the MPT donor and to vary systematically in the same manner. The average intramolecular bond lengths for the central TTF portion of the MPT molecule as given in Table 3 are consistent with molecule *A* having charge MPT^0 while MPT molecule *B* has an oxidation state of $1+$. This charge localization, which does not occur in the metallic $(BEDT-TTF)_2ClO_4(TCE)_{0.5}$ salt, results in the opening of a gap and is the apparent cause for the semiconducting properties of these MPT salts.

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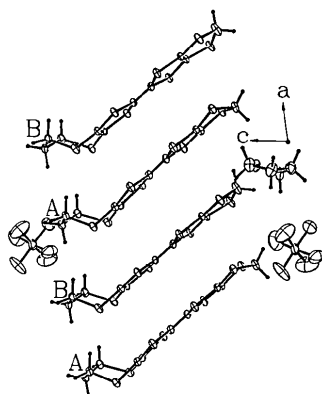


Fig. 2. Molecular stacking in $(MPT)_2PF_6(THF)$ shows the $\dots A \dots B \dots A \dots B \dots$ repeat of the MPT molecules along the axis with anions and THF solvent molecules separating the stacks along *c*. In the PF_6^- salt the anions are ordered but the ClO_4^- anion disorders in the cell.

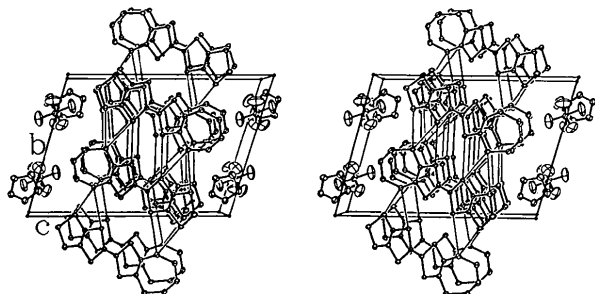


Fig. 3. Packing diagram for $(MPT)_2PF_6(THF)$. Intermolecular S...S contacts less than 3.6 Å indicated by the thin lines occur only between the stacks; no short intrastack contacts are observed.

Table 3. Average intramolecular distances (Å)

	<i>a</i> *	<i>b</i>	<i>c</i>	<i>d</i>
BEDT-TTF ⁰⁺	1.32	1.76	1.75	1.33
BEDT-TTF ^{1/2+}	1.366	1.742	1.756	1.356
BEDT-TTF ^{2/3+}	1.373	1.730	1.747	1.353
BEDT-TTF ¹⁺	1.38	1.72	1.73	1.37
(MPT) ₂ ClO ₄ (THF)				
Molecule <i>A</i>	1.347 (6)‡	1.758 (6)§	1.746 (9)§	1.352 (6)‡
Molecule <i>B</i>	1.384 (6)	1.732 (7)	1.739 (10)	1.354 (6)
(MPT) ₂ PF ₆ (THF)				
Molecule <i>A</i>	1.339 (6)	1.766 (3)	1.749 (13)	1.348 (6)
Molecule <i>B</i>	1.379 (6)	1.735 (8)	1.734 (7)	1.350 (6)

* Labels *a*...*d* refer to Fig. 1.

† Data for BEDT-TTF taken from Beno *et al.* (1987). Standard deviations are approximately 0.01 Å for 0 and 1+ charge states and 0.005 Å for others.

‡ Standard deviations from Table 2.

§ Standard deviations from averaging.

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