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Structure of the Charge-Transfer Salt Bis(methylenedithio)tetrathiafulvalene Hexafluoroantimonate(V)

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Abstract. $C_8H_4S_8^+.AsF_6^-$, $M_r = 592{\cdot}38$, triclinic, $P\bar{1}$, $a = 5{\cdot}664\ (1)$, $b = 7{\cdot}488\ (1)$, $c = 9{\cdot}614\ (2)$ Å, $\alpha = 91{\cdot}24\ (2)$, $\beta = 91{\cdot}63\ (2)$, $\gamma = 100{\cdot}46\ (1)°$, $V = 400{\cdot}7\ (1)$ Å^3, $Z = 1$, $D_m = 2{\cdot}43$, $D_x = 2{\cdot}45$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 28{\cdot}0$ cm^{-1}, $F(000) = 285$, $T = 293$ K, $R = 0{\cdot}014$ for 1388 observed reflections. The cation radicals stack along **b** to form columns with intrastack separations of about 3·867 Å. Shortest interstack S···S separations range from 3·575 to 3·696 Å. The central C=C bond of the cation is 1·388 (4) Å.

Introduction. Charge-transfer salts derived from the π-electron donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and linear centrosymmetric charge-compensating anions exhibit superconductivity at atmospheric pressure and temperatures as high as 8 K [Schirber *et al.* (1986) and references cited therein]. The crystal structure of these organic superconductors consists of donor cation-radicals arranged in a 'corrugated sheet network" (Williams *et al.*, 1984) in which the short interstack S···S separations predominate and little or no columnar stacking occurs. These interstack interactions are thought to be responsible for the two-dimensional character exhibited by these materials. In view of the importance of these interstack interactions (Leung *et al.*, 1985) for stabilizing the tendency of these materials to undergo lattice distortions, we have concentrated on preparing charge-transfer salts based on the donor bis(methylenedithio)tetrathiafulvalene (BMDT-TTF). This choice was motivated by the belief that the highly symmetrical and planar structure of BMDT-TTF (Kato, Kobayashi, Kobayashi & Sasaki, 1985) is likely to lead to increased two-dimensional interactions. A similar approach has been reported for the preparation of two 3:1 complexes, $(\text{BMDT-TTF})_3\text{PF}_6(\text{DCE})$, DCE = dichloroethane (Kato, Kobayashi, Kobayashi & Sasaki, 1984), and $(\text{BMDT-TTF})_3\text{ClO}_4(\text{DCE})$ (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito & Inokuchi, 1985). We have previously reported preliminary structural data on a 2:1 complex, $(\text{BMDT-TTF})_2\text{Au(CN)}_2$ (Nigrey, Morosin, Kwak, Venturini & Baughman, 1986). In this paper, we report the crystal structure of the 1:1 complex, $(\text{BMDT-TTF})\text{SbF}_6$.

Experimental. The crystals were prepared by electrochemical oxidation of BMDT-TTF (1·4 mg) in 10 ml of

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^4$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij}.

	x	y	z	U_{eq}
Sb	0	0	0	237 (1)
F(1)	−732 (2)	2223 (2)	640 (1)	427 (4)
F(2)	3170 (2)	1166 (2)	−264 (2)	559 (5)
F(3)	825 (3)	−542 (2)	1833 (1)	470 (5)
C(1)	4793 (3)	744 (2)	4629 (2)	225 (5)
S(2)	2462 (1)	1869 (1)	5000 (1)	256 (1)
C(3)	3227 (3)	3497 (2)	3771 (2)	227 (5)
S(4)	1783 (1)	5338 (1)	3516 (1)	286 (2)
C(5)	3143 (4)	5827 (3)	1842 (2)	333 (7)
S(6)	6019 (1)	5088 (1)	1812 (1)	300 (2)
C(7)	5117 (3)	3369 (2)	2979 (2)	229 (6)
S(8)	6566 (1)	1569 (1)	3270 (1)	263 (1)
H(5*a*)	2147 (45)	5140 (32)	1102 (26)	54 (7)
H(5*b*)	3481 (49)	7063 (37)	1735 (28)	70 (9)

a 0·1 *M* ($(C_4H_9)_4NSbF_6$) solution of methylene chloride at a platinum electrode (0·127 cm diameter). A constant current density of 0·24 μA cm^{-2} was passed through a fine fritted-glass two-compartment electrochemical cell for 10 days yielding well-faceted black crystals. A selected black prismatic crystal of dimensions 0·069 × 0·092 × 0·207 mm was used for data collection. D_m was measured by flotation in a chloroform/bromoform mixture. A Syntex *P*3/*F* automated diffractometer equipped with a graphite monochromator was used. Lattice constants were obtained from a least-squares fit to the automatically centred settings for 25 reflections with $10{\cdot}67 < 2\theta < 37{\cdot}24°$. θ–2θ scan data were collected at room temperature [293 (2) K] for the entire sphere ($-6 \leq h \leq 6$, $-8 \leq k \leq 8$, $-11 \leq l \leq 11$) out to the 2θ limit of 50° [$(\sin\theta)/\lambda$ limit of 0·595 Å^{-1}]. The total background scan time to total scan time was set to 0·5. A variable scan speed of 4–30° min^{-1} was used. Three standard reflections (300, 060, 006) were monitored every 141 reflections and showed no signs of crystal deterioration. The data were corrected for Lorentz and polarization effects. The redundant data were averaged, with *R*(merge) = 1·15%. 2836 reflections were collected, 1418 unique, of which 1388 observed reflections with $F > 3\sigma(F)$ were used for refinement of the structure. A small empirical absorption correction based on 360 azimuthal (ψ) scans was applied to the data: *R*(before) = 1·37% and *R*(after) = 1·12% where *R*(before) and *R*(after) refer to the fit of the calculated intensities to the observed intensities of the azimuthal scans (*SHELXTL*; Sheldrick, 1983). The estimated maximum and minimum transmission factors are 0·454 and 0·423. The weights have the form $1/[\sigma(F_o)^2]$. Block-cascade least-squares refinement on *F* used anomalous-dispersion corrections for atoms with atomic numbers greater than 2. Neutral-atom scattering form factors from *International Tables for X-ray Crystallography* (1974) were used. The structure was solved by the heavy-atom method with Sb at (0,0,0) in the space group $P\bar{1}$. The Fourier map showed the positions of F atoms. Subsequent Fourier maps revealed positions for the S and C atoms. The BMDT-TTF ion was centered on ($\frac{1}{2}$,0,$\frac{1}{2}$). All H atoms were clearly seen after the non-hydrogen atoms were refined anisotropically. These H atoms were included in the refinements with positions variable and also isotropic *U* variable. For 144 variables and 1388 reflections the final agreement factors are: $R(F) = 0{\cdot}0136$, $wR(F) = 0{\cdot}0130$, $S = 1{\cdot}820$, $(\Delta/\sigma)_{\max} = 0{\cdot}012$ for C(3), $(\Delta\rho)_{\max} = 0{\cdot}314$, $(\Delta\rho)_{\min} = -0{\cdot}187$ e Å^{-3}. All computations and plotting were performed on a Data General computer using the *SHELXTL* crystallographic package (Sheldrick, 1983).

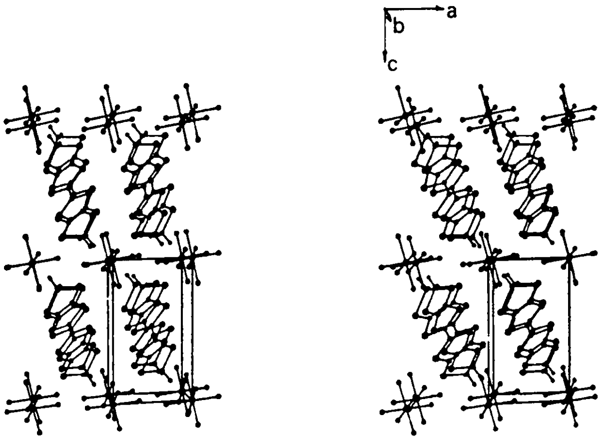

Fig. 1. Stereoview of the unit cell viewed down the *b* axis. The atoms are drawn at the 25% probability level.

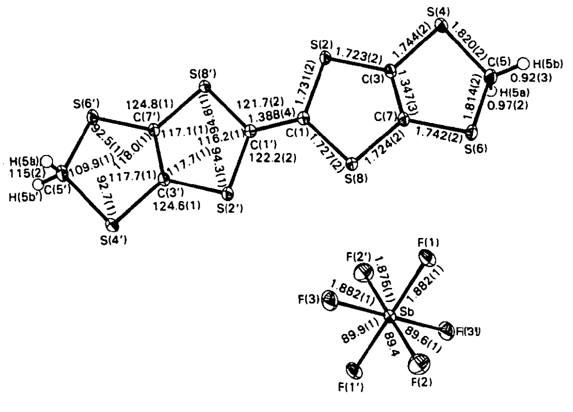

Fig. 2. Thermal-ellipsoid plot and numbering scheme for (BMDT-TTF)SbF_6 showing 25% probability ellipsoids for all atoms. The bond lengths (Å) and bond angles (°) for the BMDT-TTF cation and the SbF_6^- anion are indicated.

Discussion. The atomic coordinates are listed in Table 1.* A stereoview of the unit cell along the *b* axis is shown in Fig. 1. The cation radicals are stacked to form columns along the *b* axis in which the normals to the cation plane are essentially oriented along (111). The closest interplanar separation was 3·867 (3) Å which is only slightly longer than observed in neutral BMDT-TTF (3·80 Å) (Kato, Kobayashi, Kobayashi & Sasaki, 1985). The cations pack face-to-face. There are two S···S intermolecular distances (interstack separations) shorter than the 3·6 Å accepted van der Waals contact. In the notation of Fig. 2, the shortest two are 3·575 (1) [S(2)–S(2)] and 3·583 (1) Å [S(6)–S(4)]. Other close contacts between cations adjacent to one another along the *a* axis are given in Table 2. Similar short S···S contacts have been found in $(\text{BMDT-TTF})_2\text{Au(CN)}_2$ (Nigrey, Morosin, Kwak, Venturini & Baughman, 1986) where the cations each have a formal charge of $+\frac{1}{2}$ but have a different packing arrangement. Contacts between the cation layers are through the hexafluoroantimonate(V) anions located nearly in the *ab* plane. These involve two F–S contacts at 2·996 (1) [F(1)–S(8)] and 3·169 (2) Å [F(2)–S(6)]. Fig. 2 shows the bond lengths and bond angles of the BMDT-TTF cation and the SbF_6^- anion. The central C=C bond [C(1′)–C(1)] was found to be 1·388 (8) Å. This bond length was considerably longer than observed in either the $+\frac{1}{2}$ charged BMDT-TTF cation [1·353 (8) Å] or neutral BMDT-TTF (1·327 Å). In contrast, the two C–S bonds [C(1)–S(8) and C(7)–S(8)] with bond lengths of 1·727 (2) and 1·724 (2) Å, respectively, appear to become shorter with increasing formal charge. These results are consistent with extended molecular-orbital calculations (Kato, Kobayashi, Mori, Kobayashi & Sasaki, 1985) indicating that the central C=C bond lengths become longer and those of the C–S shorter with increasing formal charge on the molecule because the character of the highest occupied molecular orbital is bonding on the C=C bonds and antibonding on the C–S bonds. The outer C=C bond [C(3)–C(7)] length of 1·347 (3) Å appears to be relatively insensitive to formal charge since only slight changes in bond length were observed with increasing formal charge. This may indicate that most of the electronic charge density is located on the central tetrathioethylene moiety [S(2)–C(1)–S(8)–S(2′)–C(1′)–S(8′)]. The intramolecular S···S separation of the inner ring sulfur atoms [S(2)–S(8), S_i] was 2·935 Å with the outer ring sulfur atoms [S(4)–S(6), S_o] having a value of 2·975 Å. The ratio S_o/S_i gave a value of 1·014 for the +1 charged cation. This ratio was 1·007 for a $+\frac{1}{2}$ charged cation and 0·99 for the neutral BMDT-TTF molecule. A decreasing ratio with decreasing formal charge may be related, in part, to the deviation from planarity of the BMDT-TTF molecule upon being oxidized. The BMDT-TTF cation deviates from a planar configuration with the methylene groups [C(5′) and C(5)] lying above and below in a *trans*-like configuration. These configurational deviations may best be visualized by considering the planar deviations of the three parts of the cation: (1) the central tetrathioethylene moiety [S(2)–C(1)–S(8)–S(2′)–C(1′)–S(8′)]; (2) the outer tetrathioethylene moiety [S(2)–C(3)–S(4)–S(6)–C(7)–S(8)]; and (3) the dithiomethylene moiety [S(4)–C(5)–S(6)]. The angle formed by the normals to planes (1) and (2) was 5·1° while the angle formed by the normals to planes (3) and (2) was 31·3°. All angles are in a *trans*-like or accordion-like configuration.

Table 2. *Selected intermolecular separations* (Å)

$S(6^{i})$–$S(4^{ii})$	3·583 (1)	$S(2^{i})$–$S(2^{iii})$	3·575 (1)
$S(8^{i})$–$S(2^{ii})$	3·656 (1)	$F(2^{i})$–$S(6^{iv})$	3·169 (2)
$S(8^{i})$–$S(4^{ii})$	3·696 (1)	$F(1^{i})$–$S(8^{v})$	2·996 (1)

Symmetry code: (i) x, y, z; (ii) $1+x, y, z$; (iii) $-x, -y, 1-z$; (iv) $1-x, 1-y, -z$; (v) $x-1, y, z$.

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* Lists of structure factors, anisotropic thermal parameters and a complete list of atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43729 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.