Structure of 3,4;3′,4′-Bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalenium–Hydrogensulfate (3/2). A (BEDT-TTF) Charge-Transfer Salt Containing a Tetrahedral Anion

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Abstract. $3C_{10}H_8S_8 \cdot 2HSO_4$, $M_r = 1348 \cdot 1$, triclinic, $P\bar{1}$, $a = 7 \cdot 633$ (1), $b = 9 \cdot 440$ (1), $c = 16 \cdot 607$ (1) Å, $\alpha = 92 \cdot 28$ (1), $\beta = 94 \cdot 97$ (1), $\gamma = 83 \cdot 13$ (1)°, $V = 1181 \cdot 8$ (3) Å^3, $Z = 1$, $D_x = 1 \cdot 89$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0 \cdot 71073$ Å, $\mu = 1 \cdot 175$ mm^{-1}, $F(000) = 686$, $T = 298$ K. Electrocrystallization of BEDT-TTF with $[N(C_4H_9)_4][HSO_4]$ in 1,1,2-trichloroethane yields a charge-transfer salt containing BEDT-TTF cations and $(HSO_4)^-$ anions in a 3:2 ratio. This product consists of segregated stacks of BEDT-TTF cations with $(HSO_4)^-$ anions located in the cavities formed by the H atoms associated with the ethylenedithiol groups of the BEDT-TTF donors. The asymmetric unit contains two crystallographically independent BEDT-TTF molecules in a lattice which is highly cross linked with multiple intermolecular S–S contacts $\le 3 \cdot 5$ Å. Convergence to conventional R values of $R = 0 \cdot 043$ and $wR = 0 \cdot 049$ was obtained using 3114 averaged reflections ($R_{int} = 0 \cdot 021$) with $F_o^2 > 0 \cdot 0\sigma(F_o^2)$ and 289 variable parameters.

Introduction. The use of X-ray and neutron diffraction data, in conjunction with tight-binding band calculations, has provided considerable insight into some of the factors governing the conductivity behavior of several organic charge-transfer compounds with metal-like magnetic and electrical properties. Among the most intensively studied systems are a large number containing tetrathiafulvalene or a derivative in which tetrathia- or tetraselenafulvalene forms part of the molecular framework (Williams, Wang, Emge, Geiser, Beno, Leung, Carlson, Thorn & Schultz, 1987). For one series of charge-transfer compounds containing bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) cations and linear centrosymmetric monovalent anions, a direct correlation between anion length and the onset temperature of superconductivity has been established (Emge, Leung, Beno, Wang, Firestone, Webb, Carlson, Williams, Venturini, Azevedo & Schirber, 1986). This type of correlation not only provides a means of fine-tuning the electrical properties of the system by the

judicious selection of anion, but also provides a pathway for the rational development of new materials with specific conductivity properties.

As part of an ongoing project aimed at exploring structure–conductivity relationships in BEDT-TTF salts, we recently prepared a new product containing the monovalent $(HSO_4)^-$ anion. In this paper we report the room-temperature crystal structure of the 3:2 charge-transfer salt $(BEDT\text{-}TTF)_3(HSO_4)_2$.

Experimental. Black multifaceted crystals of approximate dimensions $0 \cdot 20 \times 0 \cdot 24 \times 0 \cdot 13$ mm obtained by electrocrystallization of BEDT-TTF at a constant current of $0 \cdot 42$ µA in 1,1,2-trichloroethane using H-cells equipped with platinum electrodes and $[N(C_4H_9)_4][HSO_4]$ as the supporting electrolyte. Triclinic symmetry suggested on the basis of interaxial angles and confirmed by a Delaunay reduction. Refined cell parameters obtained from the setting angles of 25 reflections with $30 \le 2\theta \le 35°$. θ–2θ-scan data collection carried out at ambient temperature using a Nicolet *P*3*F* diffractometer and graphite-monochromated Mo $K\alpha$ radiation. Scan rate variable, 2–12° min^{-1}; scan range $-1 \cdot 2°$ in 2θ from $K\alpha_1$ to $+1 \cdot 1°$ from $K\alpha_2$. 6648 reflections (± 8, ± 10, ± 17) measured with $4 \le 2\theta \le 45°$ and averaged to give 3114 unique reflections with $wR_{int} = 0 \cdot 021$. Three standards ($1\bar{2}\bar{1}$, $1\bar{1}4$, $21\bar{2}$) measured every 47 data showed no significant variation over the period of data collection. The data were corrected for absorption, Lorentz and polarization effects. Absorption corrections applied using a Gaussian quadrature procedure following careful measurement of crystal dimensions and assignment of indices to the crystal faces. Minimum and maximum transmission $0 \cdot 770$ and $0 \cdot 861$, respectively. Structure solution and refinement carried out using a locally modified version of the UCLA collection of crystallographic software (Strouse, 1986). S-atom positions from *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); remaining non-H-atom positions from difference-Fourier maps. H atoms associated with the BEDT-TTF donors were placed in idealized positions with fixed isotropic thermal

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for* $(BEDT\text{-}TTF)_3(HSO_4)_2$

	x	y	z	U_{eq}*(Å² × 10⁴)
S1	0.55060 (14)	0.30153 (10)	0.46229 (6)	344 (3)
S2	0.74217 (13)	0.01360 (10)	0.47352 (6)	343 (3)
S3	0.67437 (14)	0.36554 (10)	0.65078 (6)	340 (3)
S4	0.88104 (13)	−0.08395 (10)	0.65764 (5)	308 (3)
S5	0.41051 (15)	0.26880 (11)	0.29390 (6)	389 (4)
S6	0.63221 (15)	−0.07915 (10)	0.30721 (6)	388 (4)
S7	0.75045 (13)	0.44539 (10)	0.82198 (6)	326 (3)
S8	0.99560 (14)	0.10863 (11)	0.83264 (6)	371 (4)
S9	−0.15158 (13)	0.61179 (10)	0.39938 (6)	332 (3)
S10	0.02707 (14)	0.32135 (10)	0.41327 (6)	346 (3)
S11	−0.26671 (14)	0.58504 (10)	0.22596 (6)	347 (3)
S12	−0.06140 (14)	0.23215 (10)	0.24529 (6)	382 (4)
S13	0.61432 (14)	0.78779 (10)	0.99850 (6)	358 (4)
O1	0.4420 (4)	0.8383 (3)	0.9532 (2)	460 (10)
O2	0.5873 (4)	0.7542 (3)	1.0795 (2)	569 (12)
O3	0.7218 (4)	0.9172 (3)	1.0017 (2)	540 (11)
O4	0.7122 (4)	0.6765 (3)	0.9542 (2)	697 (13)
C1	0.6845 (5)	0.1779 (4)	0.5210 (2)	271 (12)
C2	0.7418 (5)	0.2062 (4)	0.6006 (2)	264 (12)
C3	0.5363 (5)	0.1907 (4)	0.3756 (2)	267 (12)
C4	0.6242 (5)	0.0569 (4)	0.3814 (2)	274 (12)
C5	0.7833 (4)	0.3173 (4)	0.7447 (2)	251 (12)
C6	0.8773 (5)	0.1868 (4)	0.7482 (2)	271 (12)
C7	0.3921 (5)	0.1194 (4)	0.2237 (2)	366 (14)
C8	0.5603 (5)	0.0207 (4)	0.2171 (2)	368 (14)
C9	0.8633 (7)	0.3614 (5)	0.9092 (3)	671 (20)
C10	0.8711 (6)	0.1972 (5)	0.9114 (3)	534 (17)
C11	−0.1589 (5)	0.5029 (4)	0.3112 (2)	262 (12)
C12	−0.0765 (5)	0.3678 (4)	0.3191 (2)	269 (12)
C13	−0.2909 (5)	0.4329 (4)	0.1573 (2)	344 (13)
C14	−0.1234 (5)	0.3283 (4)	0.1530 (2)	355 (14)
C15	−0.0274 (5)	0.4857 (4)	0.4600 (2)	269 (12)

* The complete temperature factor is $\exp(-8\pi^2 U_{eq}\sin^2\theta/\lambda^2)$, where:
$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Bond lengths* (Å) *and angles* (°) *for* $(BEDT\text{-}TTF)_3(HSO_4)_2$

S1—C1	1.729 (4)	S10—C12	1.738 (4)
S2—C4	1.744 (3)	S12—C12	1.738 (3)
S4—C2	1.726 (4)	S13—O2	1.432 (3)
S5—C7	1.805 (4)	C1—C2	1.381 (5)
S7—C5	1.741 (3)	C7—C8	1.504 (5)
S8—C10	1.803 (4)	C13—C14	1.524 (5)
S10—C15	1.728 (3)	S2—C1	1.738 (3)
S11—C13	1.815 (4)	S3—C5	1.753 (3)
S13—O4	1.431 (3)	S5—C3	1.730 (4)
S13—O3	1.548 (3)	S6—C8	1.810 (4)
C5—C6	1.350 (5)	S8—C6	1.741 (3)
C11—C12	1.359 (5)	S9—C11	1.755 (3)
S1—C3	1.749 (3)	S11—C11	1.737 (3)
S3—C2	1.736 (3)	S12—C14	1.812 (4)
S4—C6	1.758 (3)	S13—O1	1.493 (3)
S6—C4	1.743 (3)	C3—C4	1.360 (5)
S7—C9	1.784 (4)	C9—C10	1.546 (6)
S9—C15	1.729 (3)	C15—C15	1.384 (7)
C1—S1—C3	95.6 (2)	C3—C4—S2	117.1 (3)
C2—S4—C6	95.6 (2)	C6—C5—S3	116.7 (3)
C5—S7—C9	103.8 (2)	C5—C6—S4	116.6 (3)
C15—S10—C12	95.6 (2)	C7—C8—S6	113.9 (3)
O4—S13—O2	115.0 (2)	C12—C11—S11	129.4 (3)
O2—S13—O1	110.5 (2)	C11—C12—S12	127.6 (3)
C2—C1—S1	122.8 (3)	C14—C13—S11	114.4 (3)
C1—C2—S4	122.4 (3)	C15—C15—S9	122.6 (4)
C4—C3—S5	129.2 (3)	C2—S3—C5	95.6 (2)
C3—C4—S6	127.6 (3)	C4—S6—C8	101.2 (2)
C6—C5—S7	128.8 (3)	C15—S9—C11	96.0 (2)
C5—C6—S8	127.2 (3)	C12—S12—C14	102.4 (2)
C8—C7—S5	114.8 (3)	O4—S13—O3	106.1 (2)
C9—C10—S8	112.1 (3)	O1—S13—O3	104.7 (2)
S11—C11—S9	115.1 (2)	S1—C1—S2	115.5 (2)
S12—C12—S10	114.7 (2)	S4—C2—S3	115.4 (2)
C15—C15—S10	122.1 (4)	S5—C3—S1	114.4 (2)
C1—S2—C4	95.3 (2)	S6—C4—S2	115.3 (2)
C3—S5—C7	102.4 (2)	S7—C5—S3	114.5 (2)
C6—S8—C10	99.9 (2)	S8—C6—S4	116.2 (2)
C11—S11—C13	101.5 (2)	C10—C9—S7	116.9 (3)
O4—S13—O1	111.3 (2)	C12—C11—S9	115.5 (3)
O2—S13—O3	108.6 (2)	C11—C12—S10	117.6 (3)
C2—C1—S2	121.7 (3)	C13—C14—S12	113.2 (3)
C1—C2—S3	122.2 (3)	S10—C15—S9	115.3 (2)
C4—C3—S1	116.4 (3)		

parameters. All non-H atoms refined anisotropically using full-matrix least-squares refinement. Refinement based on F with weights of the form $w^{-1} = \sigma(F_o)^2$, where $\sigma(F_o) = [\sigma(F_o^2)^2 + (0.02F_o^2)^2]^{1/2}/2F_o$. Neutral atomic scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974). Convergence to conventional R values of $R = 0.043$ and $wR = 0.049$ was obtained using 289 variable parameters and 3114 reflections with $F_o^2 \geq 0.0\sigma(F_o^2)$. For the final cycle, $\Delta/\sigma = 0.01$. Difference-Fourier map calculated after final refinement essentially featureless with maximum residual electron densities of ± 1.0 e Å⁻³.

Discussion. The product obtained from the electrocrystallization of BEDT-TTF in the presence of the tetra(n-butyl)ammonium salt of $(HSO_4)^-$ consists of discrete cations and anions with two crystallographically independent BEDT-TTF donors in the asymmetric unit. A view of the structure illustrating the atomic numbering scheme is shown in Fig. 1. Atomic positional and equivalent isotropic thermal parameters for all non-H atoms are presented in Table 1.* Selected

bond angles and distances are summarized in Table 2. In Fig. 2, a stereoview packing diagram projected down the crystallographic *b* axis is given.

The crystal structure of the product described here consists of segregated stacks of BEDT-TTF cations with $(HSO_4)^-$ anions located in cavities formed by the BEDT-TTF donors. The BEDT-TTF molecules form a highly cross-linked network of intermolecular S–S contacts ranging in length from 3.416 (1) to 3.752 (1) Å, the shortest of which involve contacts between the S atoms comprising the outer six-membered rings of the BEDT-TTF donors [S6···S11 = 3.423 (1), S8···S12 = 3.416 (1) Å]. One of the BEDT-TTF molecules resides on a special position and therefore possesses a crystallographically imposed center of symmetry. The TTF groups in both molecules are essentially planar, the C atoms comprising the outer six-membered rings of the BEDT-TTF donor being displaced slightly above and below the plane defined by the atoms of the central TTF fragment. The $(HSO_4)^-$ anions in this structure reside in cavities formed by the terminal ethylene H atoms of the BEDT-TTF donors and have S—O bond lengths ranging from 1.431 (2) to 1.548 (2) Å. It was not

possible to locate the anion H atom in this structure by means of conventional difference-Fourier techniques, and the calculated S—O bond lengths do not permit an unequivocal oxygen H-atom assignment to be made. The anions, however, do not appear to be subject to any significant degree of high amplitude thermal motion; therefore, the refined positions may reflect an average structure with the anions assuming two or more orientations.

As with tetrathiafulvalene and other tetrathiaful-valene-based organic donors, the intramolecular geometry of BEDT-TTF is correlated with its formal electronic charge. Molecular-orbital calculations have characterized the HOMO of BEDT-TTF as bonding with respect to the two C atoms in the center of the TTF fragment, the length of this bond increasing with increasing positive charge. Although crystallographically independent, the two BEDT-TTF molecules in this structure are essentially identical [C1—C2 = 1·381 (2), C15—C15′ = 1·384 (2) Å]. This system is, therefore, probably best described as being a charge-transfer salt where the positive charge is delocalized over all BEDT-TTF units, each possessing a formal charge of +2/3. Arguments for mixed-valence BEDT-TTF compounds have been made; however, reliable evidence has not yet been found (Mori, Kobayashi, Sasaki, Saito &

Inokuchi, 1984; Mori, Kobayashi, Sasaki, Kobayashi, Saito & Inokuchi, 1984).

The $(BEDT\text{-}TTF)_3(HSO_4)_2$ product described here is isostructural with several other 3:2 BEDT-TTF charge-transfer compounds containing tetrahedral anions. The tetra(n-butyl)ammonium salts of both $(ClO_4)^-$ and $(BrO_4)^-$ yield charge-transfer salts with BEDT-TTF that display metal-like room-temperature conductivities but are unstable with respect to a metal–insulator transition which occurs at 190 and 210 K, respectively (Kobayashi, Kato, Mori, Kobayashi, Sasaki, Saito, Enoki & Inokuchi, 1984; Beno, Blackman, Leung, Carlson, Copps & Williams, 1985). Electrocrystallization of BEDT-TTF in the presence of the monovalent perrhenate anion has yielded a multitude of phases, among which are included an isostructural 3:2 product and a 2:1 phase demonstrating pressure-induced superconductivity at 2 K (Parkin, Engler, Shumaker, Lagier, Lee, Scott & Greene, 1983). The conductivity behaviour of the $(HSO_4)^-$ product described here has not yet been examined; however, further investigations are in progress.
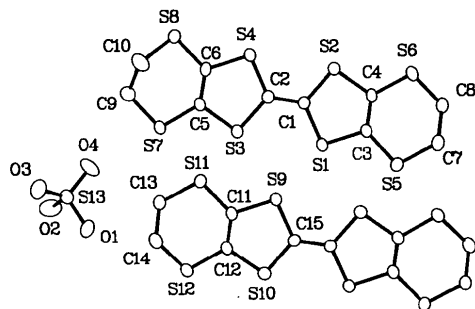
Fig. 1. A view of the $(BEDT\text{-}TTF)_3(HSO_4)_2$ structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. H atoms have been omitted for clarity.
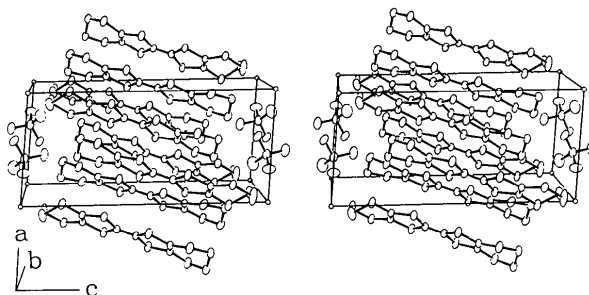

Fig. 2. A stereoview packing diagram projected down the crystallographic b axis.

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