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Structure and Conductivity of Di[3,4;3'4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium] Tetrabromomercurate(II)-1,1,2-Trichloroethane, (BEDT-TTF)₂HgBr₄.TCE

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Abstract. [C₁₀H₈S₈]₂[HgBr₄].C₂H₃Cl₃, $M_r = 1423.01$, monoclinic, $C2/c$, $a_A = 56.13$ (1), $b_A = 4.202$ (1), $c_A = 22.306$ (4) Å, $\beta = 100.88$ (2)°, $b_B = 2b_A$, where the A lattice represents C₁₀H₈S₈, the B lattice the remainder of the atoms, $V_A = 5166$ (3) Å³, $Z_A = 4$, $D_x = 1.83$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 68.4$ cm⁻¹, $F(000) = 2712$, as summed over the volume of the A cell and including the B atoms of the B lattice, room temperature, $R(F) = 0.076$, $wR(F) = 0.091$ for 1430 unique reflections. The superlattice layers corresponding to $b_B = 8.404$ Å are diffuse indicating short-range ordering of the HgBr₄ structure. The structure consists of sheets of BEDT-TTF cations [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]

parallel to the bc plane, separated along the a direction by columns of anions and solvent molecules. Short S—S contacts are found within the cation layers. Tetrahedral HgBr₄ anions form discrete columns with twice the repeat period along the b direction. Four-probe conductivity measurements indicate the solid to be a narrow-band-gap semiconductor.

Introduction. Because of their unusual transport properties salts of BEDT-TTF have attracted considerable attention (Williams *et al.*, 1987). Of particular interest are the organomineral salts, which show the highest superconducting transition temperatures in the BEDT-TTF family or in other organic salts. We report here on the crystal structure

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and properties of a newly synthesized bromo-mercurate salt (BEDT-TTF)₂HgBr₄.TCE (TCE = 1,1,2-trichloroethane).

Experimental. Crystal structure analysis. Crystals of (BEDT-TTF)₂HgBr₄.TCE were grown by electro-crystallization (Pt electrodes) in a 1,1,2-trichloroethane solution of 0.4 mM BEDT-TTF, 4 mM (Et₄N)₂HgBr₄ and 0.1 M [CH₃(CH₂)₃]₄NPF₆ with a current of 0.8 μA. All single crystals were black shiny thin plates. (Et₄N)₂HgBr₄ was prepared by mixing excess Et₄NBr with HgBr₂ in ethanol, and subsequently purified by recrystallization in CH₃CN. Commercial BEDT-TTF and [CH₃(CH₂)₃]₄NPF₆ were directly used without further purification. The presence of solvent molecules was indicated by electron fluorescence microprobe analysis (EDX), which unequivocally showed the presence of Cl atoms, with an S:Cl ratio of about 16:3, *i.e.* one solvent molecule per two BEDT-TTF molecules. The incorporation of solvent molecules explains the failure to produce the same crystals from THF solutions.

An elongated plate, 0.24 × 0.13 × 0.038 mm, was mounted on top of a glass fiber. Oscillation photographs around the *b* axis show diffuse layers intermediate between the sharp layers of the 4.202 Å repeat period. In the subsequent analysis the layers were identified as originating from the bromo-mercurate ions. A Weissenberg photograph of the first diffuse layer shows not quite continuous diffuse streaks along the *a** direction, indicating only short-range correlation of the Hg *y* parameters between columns separated in the *a* direction.

Room-temperature intensity data were collected on a CAD-4 diffractometer with the $\theta/2\theta$ scan technique and graphite-monochromatized Mo *K* α radiation. From Weissenberg photographs, the space group was determined to be either *C2/c* or *Cc*. 3377 symmetry-allowed reflections with $2 < \theta < 22^\circ$ were measured ($h = -58, 58; k = 0, 4; l = 0, 20$), and averaged to give 2690 unique reflections; the internal agreement factor $R(F) = 0.035$. Three standard reflections monitored throughout the data collection showed very small changes in intensity (less than 3%). Despite the long *a* axis, the resolution of Mo *K* α radiation is adequate because the reflections are separated by systematic absences. Analysis of peak profiles showed no overlap among reflection peaks. Numerical absorption corrections were applied. Programs of the Enraf-Nonius (1985) *VAX-SDP* 3.0 package were used. The structure was solved by the Patterson method, additional atoms were located in difference Fourier maps. Scattering factors (including anomalous contributions) were taken from *International Tables for X-ray Crystallography* (1974). The program *LINEX84* (1984) was used for the final full-matrix refinement. 1430 unique

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} / <i>U</i> _{iso} (Å ²)
Hg	-0.08677 (4)	0.1692 (7)	0.1836 (1)	0.052 (2)
Br1	-0.0395 (1)	0.205 (2)	0.1900 (3)	0.074 (6)
Br2	-0.0960 (1)	0.152 (2)	0.2935 (3)	0.071 (5)
Br3	-0.10407 (7)	0.664 (1)	0.1257 (2)	0.080 (3)
S1	0.7055 (1)	0.310 (2)	0.1629 (3)	0.045 (5)
S2	0.7060 (1)	0.012 (2)	0.0448 (3)	0.048 (5)
S3	0.7642 (1)	0.306 (2)	0.1916 (3)	0.048 (5)
S4	0.7640 (1)	0.017 (2)	0.0725 (3)	0.048 (5)
S5	0.6523 (1)	0.302 (2)	0.1508 (3)	0.049 (5)
S6	0.6532 (1)	-0.029 (2)	0.0064 (3)	0.048 (5)
S7	0.8171 (1)	0.305 (2)	0.2298 (3)	0.046 (5)
S8	0.8162 (1)	-0.033 (2)	0.0861 (3)	0.050 (6)
C1	0.7225 (4)	0.150 (7)	0.112 (1)	0.038 (7)
C2	0.7471 (4)	0.168 (7)	0.125 (1)	0.039 (7)
C3	0.6771 (5)	0.214 (7)	0.119 (1)	0.045 (8)
C4	0.6783 (5)	0.073 (7)	0.063 (1)	0.042 (8)
C5	0.7917 (4)	0.210 (7)	0.172 (1)	0.038 (7)
C6	0.7915 (5)	0.075 (6)	0.118 (1)	0.037 (7)
C7	0.6272 (5)	0.121 (7)	0.097 (1)	0.051 (8)
C8	0.6291 (5)	0.172 (7)	0.033 (1)	0.043 (7)
C9	0.8410 (5)	0.114 (7)	0.201 (1)	0.046 (8)
C10	0.8403 (5)	0.165 (8)	0.134 (1)	0.053 (8)

Hg, Br and S atoms were refined anisotropically.

Table 2. Bond lengths (Å) and bond angles (°)

Hg—Br1	2.636 (7)	Hg—Br2	2.603 (7)
Hg—Br3'	2.576 (5)	Hg—Br3	2.542 (5)
S1—C1	1.75 (3)	S1—C3	1.76 (3)
S2—C1	1.71 (2)	S2—C4	1.70 (3)
S3—C2	1.71 (2)	S3—C5	1.73 (3)
S4—C2	1.76 (3)	S4—C6	1.70 (2)
S5—C3	1.72 (3)	S5—C7	1.83 (3)
S6—C4	1.76 (2)	S6—C8	1.78 (3)
S7—C5	1.78 (2)	S7—C9	1.78 (3)
S8—C6	1.74 (3)	S8—C10	1.76 (3)
C1—C2	1.36 (4)	C3—C4	1.39 (4)
C5—C6	1.32 (4)	C7—C8	1.49 (4)
C9—C10	1.51 (4)		
Br1—Hg—Br2	109.1 (2)	S3—C2—C1	126 (2)
Br1—Hg—Br3	105.4 (2)	S4—C2—C1	120 (2)
Br2—Hg—Br3	112.1 (2)	S1—C3—S5	116 (2)
Br1—Hg—Br3'	110.8 (2)	S1—C3—C4	114 (2)
Br2—Hg—Br3'	109.0 (2)	S5—C3—C4	130 (2)
Br3—Hg—Br3'	110.4 (2)	S2—C4—S6	116 (2)
C1—S1—C3	95 (1)	S2—C4—C3	118 (2)
C1—S2—C4	96 (1)	S6—C4—C3	125 (2)
C2—S3—C5	95 (1)	S3—C5—S7	113 (1)
C2—S4—C6	95 (1)	S3—C5—C6	118 (2)
C3—S5—C7	103 (1)	S7—C5—C6	129 (2)
C4—S6—C8	102 (1)	S4—C6—S8	115 (1)
C5—S7—C9	101 (1)	S4—C6—C5	117 (2)
C6—S8—C10	102 (1)	S8—C6—C5	128 (2)
S1—C1—S2	116 (1)	S5—C7—C8	113 (2)
S1—C1—C2	120 (2)	S6—C8—C7	117 (2)
S2—C1—C2	124 (2)	S7—C9—C10	114 (2)
S3—C2—S4	115 (1)	S8—C10—C9	114 (2)

reflections with $I > 3\sigma(I)$ were used. The refinement was based on centrosymmetric space group *C2/c* with anisotropic thermal parameters for Hg, Br, S. Cl atoms could be located in the *h0l* projection, but are extended over the whole repeat period in the *b*

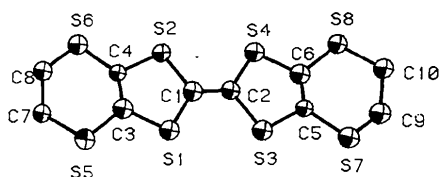


Fig. 1. Molecular diagram of the BEDT-TTF molecule showing the labelling of the atoms.

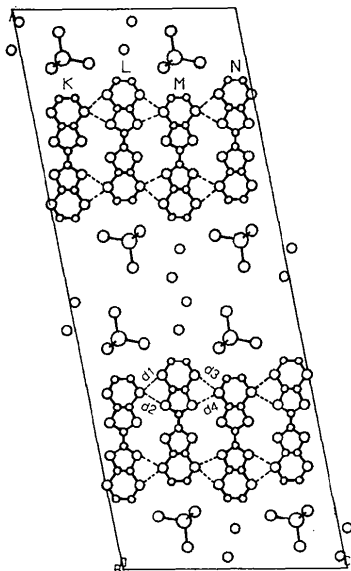


Fig. 2. Crystal structure projected onto the ac plane. Two Br atoms of the tetrahedral HgBr_4^{2-} are superimposed in projection. The unconnected circles represent the position of Cl atoms in the solvent molecules. Four BEDT-TTF molecules are labelled K, L, M, N . Symmetry operations in BEDT-TTF sublattice are $K: x, y, z$; $L: \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $M: x, 1 - y, \frac{1}{2} + z$; $N: \frac{1}{2} - x, \frac{1}{2} - y, 1 - z$. The intermolecular $\text{S}\cdots\text{S}$ contact distances are: $d_1 = 3.56$, $d_2 = 3.68$, $d_3 = 3.45$, $d_4 = 3.57$ Å.

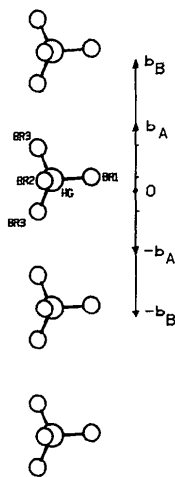


Fig. 3. The molecular arrangement within a column of HgBr_4^{2-} anions.

direction. As a result there is poor agreement between F_{obs} and F_{cal} for the $h0l$ reflections when Cl atoms are not included in the refinement. 149 variables were refined, minimizing the function $\sum[w(|F_{\text{obs}}| - k|F_{\text{cal}}|)]$, where $w = 1/\sigma^2(F)$; $\sigma(F) = \sigma(F^2)/2F$; $\sigma(F^2) = [\sigma_{\text{counting}}^2 + (0.02|F|^2)^2]^{1/2}$. Parameter shifts in the final least-squares cycles were smaller than 0.02σ . The positions of H atoms were calculated and included in the structure-factor calculation. For all 1430 unique reflections, $R(F) = 0.076$, $wR(F) = 0.091$, $\text{GOF} = 2.80$; for 303 $h0l$ reflections, $R(F) = 0.092$, $wR(F) = 0.117$. The Cl atoms in the TCE molecule can be located in the $h0l$ projection. In the refinement of the Cl-atom positions with the $h0l$ data, $R(F)$, $wR(F)$ values of 0.067 and 0.075 respectively were obtained.

Final atomic coordinates and thermal parameters are listed in Table 1,* while bond lengths and angles are given in Table 2. Fig. 1 shows a molecular diagram indicating the atomic labelling scheme. The projection of the unit cell onto the ac plane is illustrated in Fig. 2. Fig. 3 shows a column of HgBr_4^{2-} anions along the b axis.

Conductivity measurements. Four-probe measurements of the conductivity along the needle (b) axis were performed on a single crystal in the 160–300 K temperature range. The results are shown in Fig. 4. A plot of $\ln R$ ($R = \text{resistance}$) versus $1/T$ (Fig. 4, insert) gives a straight line with a slope of 1050 K, and an intercept (equal to R at $T = \infty$) of 288 Ω. The temperature dependence indicates that the solid is a semiconductor with a narrow band gap of 89.9 meV.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52839 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

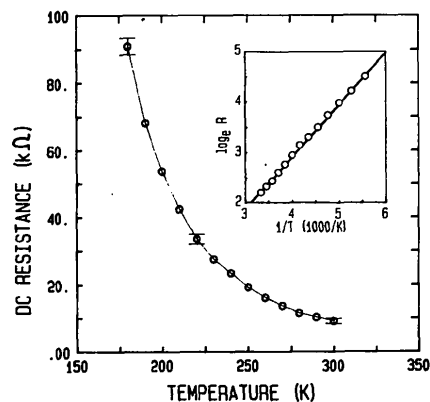


Fig. 4. DC resistance (R) of a single crystal as a function of temperature. The horizontal lines on three of the points are error bars. The insert shows the $\ln R$ vs $1/T$ dependence, the straight line is a least-squares fit to the experimental points.

Discussion. The unit cell of the *A* lattice contains eight crystallographically equivalent BEDT-TTF cations, four HgBr₄ anions, and four disordered TCE molecules. The BEDT-TTF long molecular axis is parallel to the *ac* plane, while the molecular plane is tilted out of the *ac* plane by about 25°. The molecules are stacked along the short 4.202 Å axis. The stacks are interlinked by short S...S interactions to form sheets parallel to the *bc* plane (Fig. 2). The shortness of the *b* axis repeat [shorter than any repeat listed by Williams *et al.* (1987)] limits the tilting of the molecules, and thereby the occurrence of S...S distances much shorter than the translation period. In terms of the classification of Williams *et al.* (1987) the stacking is type *a* with a negligible offset, while the interstack arrangement is described by *L* and *W* for center of symmetry and screw-axis related molecules respectively. In terms of the same classification the unit cell can be described as (1,4,2).

HgBr₄ anions form ordered columns along the *b* axis, with a repeat period twice that of the BEDT-TTF lattice. This leads to half occupancy for Hg, Br1 and Br2. The separation of the two Br3 atoms of the HgBr₄ anion is almost exactly equal to *y*_A, giving full occupancy for this atom (Fig. 3).

The occurrence of diffuse reciprocal-lattice lines at $b_B^* = 0.5b_A^*$ indicates the existence of ordered domains of limited size. From the length of the segments along *a*^{*}, the correlation length is estimated to be about two unit cells, *i.e.* approximately eight HgBr₄ columns. The solvent molecules are interspersed between the anions in a highly disordered arrangement. The inclusion of disordered TCE solvent molecules has also been reported for (BEDT-TTF)₂-ClO₄.0.5TCE (Kobayashi, Kobayashi, Sasaki, Saito, Enoki & Inokuchi, 1983).

A number of other bromomercurate salts of BEDT-TTF have been described in the literature. Lyubovskaya *et al.* (1987) describe the low-

temperature superconductor (BEDT-TTF)₄Hg_{2.89}Br₈ with an apparently composite structure, while Mori, Wang, Imaeda, Enoki & Inokuchi (1987) report a semiconductor and a conductor, (BEDT-TTF)HgBr₃ and (BEDT-TTF)₅Hg₃Br₁₁. In the latter compound, BEDT-TTF ions with several different charges coexist, as shown by the analyses of the bond lengths (Mori *et al.*, 1987; Umland, Allie, Kuhlmann & Coppens, 1988). The bond lengths in the present structure are not sufficiently accurate for a reliable prediction, but we note that the BEDT-TTF molecules carry a formal charge of +1.

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Structure and Molecular Mechanics of Ferrirhodin

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Abstract. C₄₁H₆₄FeN₉O_{17.7}·7½H₂O, *M*_r = 1146.0, orthorhombic, *P*2₁2₁2₁, *a* = 9.740 (7), *b* = 16.764 (10), *c* = 32.632 (17) Å, *V* = 5328 (6) Å³, *Z* = 4, *D*_x = 1.43 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ =

3.26 cm⁻¹, *F*(000) = 2428, *T* = 138 (2) K, *R* = 0.0986 for 3543 observed reflections. Ferrirhodin, a ferrichrome siderophore (iron transport agent) was isolated from low-iron cultures of *Aspergillus*

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