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Urs Geiser [a] , Hau H. Wang [a] , Stephanie Kleinjan [a] & Jack M. Williams [a]

[a] Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, IL, 60439, USA

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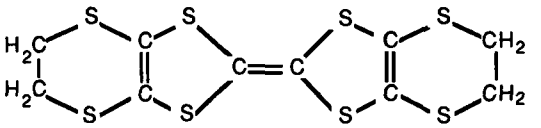
THE CRYSTAL AND MOLECULAR STRUCTURE OF (BEDT-TTF)$_4$(Hg_2Br_6)(1,1,2-TRICHLOROETHANE)

URS GEISER, HAU H. WANG, STEPHANIE KLEINJAN, AND JACK M. WILLIAMS
Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, IL 60439 (USA)

Abstract The synthesis, electrocrystallization, and crystal structure of the organic conductor (BEDT-TTF)$_4$(Hg_2Br_6)(TCE) (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene; TCE = 1,1,2-trichloroethane) are reported. The crystal structure contains layers of two stacks per unit cell of BEDT-TTF donor molecules. Within the stacks, eight donor units are found per unit cell. The anion consists of a dimeric species formed by two edge-sharing distorted [$HgBr_4$] tetrahedra. Crystal data: monoclinic, space group $P2_1/n$, a = 19.344(5) Å, b = 13.401(3) Å, c = 29.418(10) Å, β = 103.87(2)°, V_c = 7403(3) Å^3, Z = 4.

INTRODUCTION

Numerous charge transfer salts based on the organic donor molecule bis(ethylenedithio)tetrathiafulvalene (short, BEDT-TTF or ET; **1**) have been synthesized. Many



BEDT-TTF, or ET **(1)**

of them are metallic conductors, and about a dozen are superconductors.[1] One of these superconductors is (ET)$_4$$Hg_{3-x}Br_8$ with a transition temperature, T_c, of 4.3 K at ambient pressure.[2]

In our efforts to synthesize crystals of (ET)$_4$$Hg_{3-x}Br_8$, we discovered several other phases in the ET-Hg-Br system, in addition to the compounds (ET)$HgBr_3$,[3] ζ-(ET)$_3$($HgBr_3$)$_2$,[4] (ET)$_5$$Hg_3Br_{11}$ ≡ (ET)$_5$($HgBr_4$)$_2$($HgBr_3$),[3] and (ET)$_2$$HgBr_4$(TCE).[5] Among them is the title compound, (ET)$_4$(Hg_2Br_6)(TCE) whose crystal structure is described here. Another one, (ET)$_2$$HgBr_3$(TCE), will be reported elsewhere.[6]

EXPERIMENTAL

Black, shiny crystals of $(ET)_4(Hg_2Br_6)(TCE)$ were grown by electrocrystallization of a solution of 1.39 mM ET, 20.8 mM $[(n\text{-}C_4H_9)_4N]Br$, and 20.8 mM $HgBr_2$ in TCE (1,1,2-trichloroethane) at a current density of 0.5 μAcm^{-2}. The batch yielded other modifications as well, but the title compound is the predominant phase under these growth conditions. It has a characteristic ESR peak-to-peak line width of ~5 G at room temperature, and the crystals typically exhibit growth steps parallel to the direction of fastest crystal growth (b-axis) on the prominent $\bar{1}01$-faces.

The crystal selected for the crystal structure determination ($0.53\times0.27\times0.045$ mm^3) was cut from a larger, rectangular plate and mounted on a Nicolet P3/F automated four-circle diffractometer. Lattice parameters at room temperature were determined from the setting angles of 25 well-centered reflections with $18° < 2\theta < 23°$: monoclinic, a = 19.344(5) Å, b = 13.401(3) Å, c = 29.418(10) Å, β = 103.87(2)°, V_c = 7403(3) $Å^3$. The space group, $P2_1/n$, was determined uniquely by the systematic absences. Intensity data were collected using ω-scans of 1° width at 1–8°min^{-1} in the angle range $4° < 2\theta < 50°$ for reflections with $-23 \le h \le 22$, $-1 \le k \le 15$, $0 \le l \le 34$. Three standard reflections (406, 144, $\bar{4}25$), monitored every 100 reflections, showed no significant decay. 15,608 reflections were measured, corrected for Lorentz, polarization, and absorption (Gaussian integration based on crystal shape, $Z = 4$, $\mu = 83.6$ cm^{-1}, $T_{min} = 0.124$, $T_{max} = 0.698$) effects, and averaged (R_{ave} = 0.054, $wR_{ave} = 0.025$) to yield 13,003 unique reflections after removing systematic absences. The structure was solved by use of direct methods, resulting in positional parameters for the Hg and Br atoms, and completed by subsequent cycles of least-squares refinement and difference Fourier maps. Residual density near (0.6, 0.0, 0.1) was identified as a disordered trichloroethane molecule. No hydrogen atoms were included in the calculations. The final full-matrix least-squares structure refinement of 760 variable parameters (all atoms except C28 and C41 with anisotropic thermal parameters, one scale factor, no secondary extinction) using the 7035 reflections with $F_o > 4\sigma(F_o)$ gave agreement factors, $R(F_o) = 0.077$, $wR(F_o) = 0.059$, and "goodness of fit" = 2.00. Two positions with approximately equal probability were found for atom C28, reflecting the disordered nature of some of the ethylene end groups of the ET molecule. Two sites, C28A and C28B, were refined with a common isotropic thermal parameters. Atomic positions are given in Table I. Thermal parameters and structure factors are available from the authors upon request.

TABLE I Atomic positions in $(ET)_4(Hg_2Br_6)(TCE)$.

Atom	x	y	z	Atom	x	y	z
		Anion		C20	0.6787(9)	0.3915(14)	0.3957(6)
Hg1	0.10189(5)	0.05417(6)	0.62394(3)			Molecule 3	
Hg2	0.09604(5)	–0.23639(6)	0.61327(3)	S21	0.2278(3)	0.1539(4)	0.1836(2)
Br1	0.16241(12)	–0.0937(2)	0.57509(8)	S22	0.1846(3)	0.3615(4)	0.1829(2)
Br2	0.02199(10)	–0.0995(2)	0.65076(7)	S23	0.0694(3)	0.0856(4)	0.1906(2)
Br3	0.01353(12)	0.1371(2)	0.56034(8)	S24	0.0300(3)	0.2937(4)	0.1934(2)
Br4	0.19707(11)	0.0910(2)	0.69498(8)	S25	0.3794(3)	0.1956(4)	0.1881(2)
Br5	0.00754(12)	–0.3403(2)	0.55419(8)	S26	0.3258(3)	0.4434(5)	0.1842(3)
Br6	0.18542(11)	–0.3303(2)	0.67703(7)	S27	–0.0582(3)	0.0081(4)	0.2172(2)
		Molecule 1		S28	–0.1009(3)	0.2583(4)	0.2256(2)
S1	0.4352(3)	0.0841(4)	0.3178(2)	C21	0.1614(10)	0.2360(14)	0.1848(6)
S2	0.4788(3)	0.2929(4)	0.3169(2)	C22	0.0947(10)	0.2083(15)	0.1884(6)
S3	0.2795(3)	0.1561(4)	0.3300(2)	C23	0.2948(9)	0.2443(15)	0.1863(6)
S4	0.3210(3)	0.3651(4)	0.3235(2)	C24	0.2738(10)	0.3387(13)	0.1849(7)
S5	0.5463(3)	0.0071(4)	0.2736(2)	C25	–0.0099(10)	0.1105(13)	0.2061(6)
S6	0.6019(3)	0.2500(4)	0.2751(2)	C26	–0.0276(9)	0.2044(14)	0.2092(6)
S7	0.1253(3)	0.1988(4)	0.3146(2)	C27	0.4277(11)	0.306(2)	0.1741(8)
S8	0.1712(3)	0.4391(4)	0.3036(2)	C28A*	0.412(2)	0.400(2)	0.1995(12)
C1	0.4106(9)	0.2090(14)	0.3200(6)	C28B†	0.397(2)	0.392(3)	0.161(2)
C2	0.3456(9)	0.2392(12)	0.3222(6)	C29	–0.1471(9)	0.0634(13)	0.2041(7)
C3	0.5076(9)	0.1099(13)	0.2935(6)	C30	–0.1513(10)	0.1499(14)	0.2357(7)
C4	0.5286(9)	0.2019(14)	0.2940(6)			Molecule 4	
C5	0.2099(10)	0.2439(13)	0.3171(6)	S31	0.6748(3)	0.1986(4)	0.5609(2)
C6	0.2296(9)	0.339(2)	0.3133(6)	S32	0.6323(2)	0.4088(4)	0.5591(2)
C7	0.6336(12)	0.046(2)	0.2678(10)	S33	0.5205(3)	0.1312(4)	0.5723(2)
C8	0.6580(11)	0.137(2)	0.2893(9)	S34	0.4763(3)	0.3413(4)	0.5695(2)
C9	0.0779(10)	0.3054(14)	0.3300(7)	S35	0.8155(2)	0.2360(4)	0.5422(2)
C10	0.1125(13)	0.401(2)	0.3380(9)	S36	0.7648(3)	0.4855(4)	0.5386(2)
		Molecule 2		S37	0.3849(3)	0.0503(4)	0.5836(2)
S11	0.3715(2)	0.0856(4)	0.4542(2)	S38	0.3309(3)	0.3000(4)	0.5796(2)
S12	0.3254(3)	0.2921(4)	0.4487(2)	C31	0.6086(9)	0.2852(12)	0.5616(5)
S13	0.5262(3)	0.1548(4)	0.4433(2)	C32	0.5425(9)	0.2563(13)	0.5658(6)
S14	0.4814(3)	0.3633(4)	0.4398(2)	C33	0.7349(9)	0.2883(13)	0.5494(6)
S15	0.2373(3)	0.0046(4)	0.4695(2)	C34	0.7154(8)	0.3821(13)	0.5484(6)
S16	0.1808(3)	0.2520(4)	0.4599(2)	C35	0.4342(10)	0.1562(14)	0.5764(6)
S17	0.6684(3)	0.1946(4)	0.4282(2)	C36	0.4134(8)	0.2508(14)	0.5746(6)
S18	0.6150(3)	0.4450(4)	0.4250(2)	C37	0.8681(10)	0.3458(14)	0.5362(7)
C11	0.3927(10)	0.2069(14)	0.4498(6)	C38	0.8551(9)	0.4367(14)	0.5623(7)
C12	0.4599(9)	0.2391(14)	0.4455(6)	C39	0.3172(10)	0.104(2)	0.6096(7)
C13	0.2854(9)	0.1096(13)	0.4596(6)	C40	0.2803(10)	0.188(2)	0.5843(8)
C14	0.2634(9)	0.2023(15)	0.4575(6)			Solvent	
C15	0.5890(8)	0.2437(14)	0.4360(6)	C11	0.5210(3)	0.0897(5)	0.1413(2)
C16	0.5679(9)	0.3393(14)	0.4337(6)	C12	0.6716(4)	0.1490(6)	0.1512(2)
C17	0.1473(10)	0.050(2)	0.4462(9)	C13	0.6636(3)	0.0631(5)	0.0529(2)
C18	0.1276(11)	0.138(2)	0.4639(9)	C41	0.608(2)	0.058(2)	0.1178(10)
C19	0.7167(10)	0.3070(15)	0.4218(7)	C42	0.578(2)	0.097(2)	0.0798(11)

* Occupation factor: 0.58(3).

† Occupation factor: 0.42 = 1.00 – 0.58.

STRUCTURE DESCRIPTION

The crystal structure of $(ET)_4(Hg_2Br_6)(TCE)$ contains layers (parallel to a plane formed by the *b*-axis and the (*a*+*c*)-diagonal, i. e., the crystallographic $10\bar{1}$ direction) of ET donor molecules separated by layers of dimeric $Hg_2Br_6^{2-}$ anions and TCE solvent molecules, see Fig. 1. The donor-molecule layers are formed of two

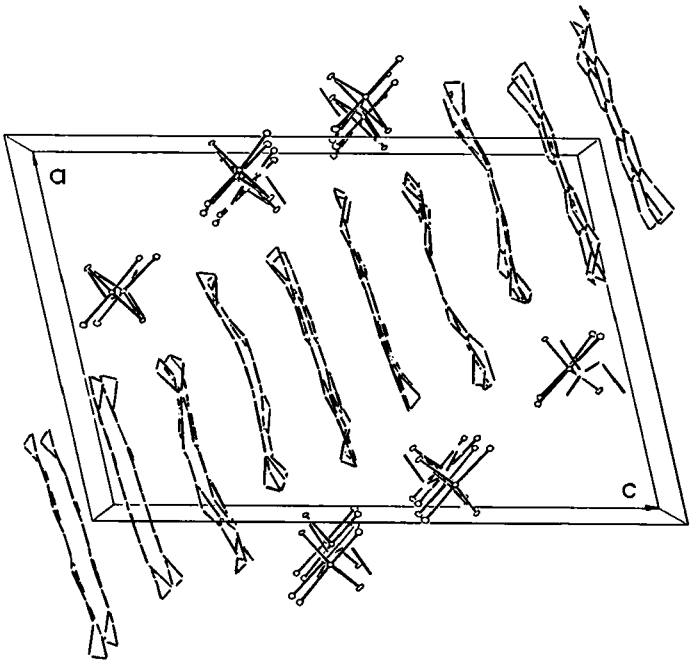


FIGURE 1 Perspective view of the structure of $(ET)_4(Hg_2Br_6)(TCE)$ along the *b*-axis showing the segregated donor and anion/solvent layers.

symmetry-related stacks of ET entities, consisting of eight molecules along the repeat stacking axis (*a*+*b*). Within these stacks, the molecules form a unique packing pattern: pairs of molecules located near the edge of the unit cell (molecules i and viii, in a numbering scheme starting at x=0, z=0 and ending at x=1, z=1; in terms of the numbering scheme of Table I, molecules i–viii correspond to 4', 3, 1, 2, 4, 3', 1', 2', respectively, where the prime indicates a glide-reflection operation) and near the center of the cell (molecules iv and v) are parallel to each other forming face-to-face

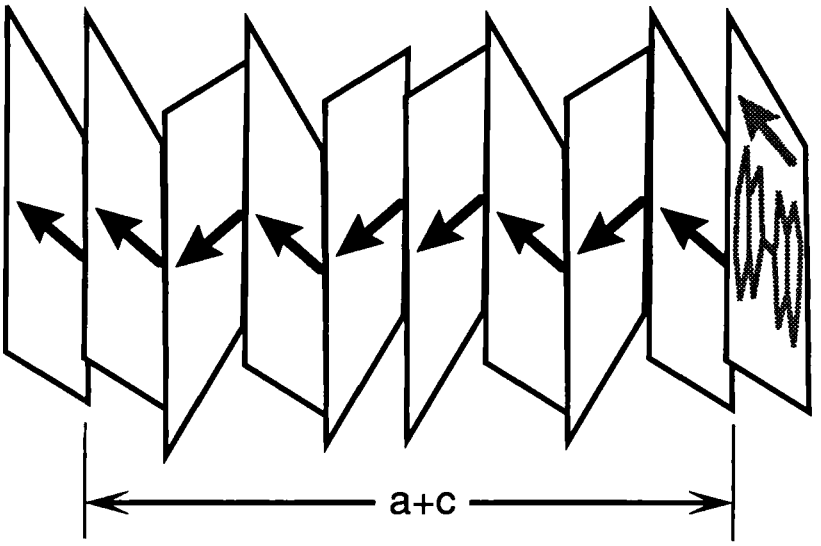


FIGURE 2 Schematic illustration of the molecular stacking pattern in $(ET)_4(Hg_2Br_6)(TCE)$. The perspective rectangles represent the ET molecules, and the direction of the principal molecular axis is indicated by the arrows.

dimers (*A*-type overlap in the nomenclature of ref. 1), whereas in all other adjacent pairs (i and ii, ii and iii, iii and iv, v and vi, vi and vii, vii and viii) the long molecular axes or the central C=C bonds are twisted with respect to each other (*C*-type overlap according to ref. 1). This situation is shown schematically in Fig. 2, where each perspective rectangle represents an ET molecule, and the arrows denote the direction of the central C=C bonds.

All inter-donor S···S contacts shorter than the sum of the van der Waals radii (r_{vdw} = 1.8 Å for sulfur[7]) are found between molecules on adjacent stacks. Some are as short as 3.38 Å (S15···S37), and every pair of neighbors has 4 contacts shorter than 3.67 Å (in fact, all but S16···S36 are shorter than 3.60 Å), i. e., two "inner"–"outer" and two "outer"–"outer" S···S contacts. Furthermore, these interstack interactions all take place approximately in the plane of the donor molecules involved ("side-by-side" contacts). The *intra*stack interactions are considerably longer, on the order 3.7–3.8 Å. Nevertheless, the intrastack contacts may be as important to the electronic overlap integrals as the *inter*stack contacts, because π-type molecular orbitals elongated along the stacking direction are involved. Due to the large size of the unit cell, no band electronic structure calculation has been carried out yet, in order

to determine if the electronic properties are expected to be one- or two-dimensional. In the title compound the interstack packing and the twisting of ET molecules with respect to each other are very similar to the α'-$(ET)_2X$ family of salts (X^- = $AuBr_2^-$, $Au(CN)_2^-$, and $Ag(CN)_2^-$; also $CuCl_2^-$),[8,9] except for the occurence of parallel paired ET molecules after every four donor molecules.

The internal geometry of the ET molecules is summarized in Table II. On the average, all donors carry a charge of +1/2 per molecule. In very accurate crystal

TABLE II Bond lengths averaged over chemically equivalent bonds in the four ET molecules in $(ET)_4(Hg_2Br_6)(TCE)$. For individual interatomic distances, the *esd*'s are on the approximately 0.02 Å. The *esd*'s indicated are *rmsd*'s from averaging. Typical values for $ET^{+1/2}$ are also given (from ref. 1).

Molecule	Central C=C	Central C–S	Inner S–Outer C	Outer C=C	Outer C–S
1	1.37	1.75(1)	1.76(2)	1.32(4)	1.74(2)
2	1.41	1.72(2)	1.75(1)	1.32(2)	1.74(1)
3	1.37	1.72(2)	1.75(2)	1.32(1)	1.74(1)
4	1.37	1.74(1)	1.75(1)	1.32(1)	1.76(1)
All	1.38(2)	1.73(2)	1.75(1)	1.32(2)	1.75(1)
$ET^{+1/2}$	1.35–1.38	1.74–1.76	1.75–1.76	1.34–1.36	—

structure determinations, often at low temperature, it is sometimes possible to deduce the charge state of an ET or related molecule from the bond lengths. In general, C=C distances increase and C–S distances decrease with increasing charge, with bonds near the center of the molecule being more affected than those near the ends. In the title compound, however, the statistical uncertainties are too large to discern unequal charge states between the four molecules. In particular, the slightly longer central C=C length in molecule 2 is not statistically significant. The consistently short outer C=C distances may be due to a vibrational effect which tends to lead to short bond lengths if the thermal motion of the atoms involved is correlated. In most ET salts, the ethylene end groups are the main points of interaction between the donor molecules and the anions, often determining the packing arrangement of the donors. The conformation of the ethylene groups with respect to the planar portion of the 6-membered outer rings of the ET molecule is one of the variables used to describe these interactions. Comparing both sides of the molecule, the end groups

are usually parallel to each other if viewed along the long ET molecular axis (eclipsed conformation), if they are at all ordered, but occasionally the staggered arrangement (end groups are twisted with opposing sense with respect to the molecular plane) is observed. In $(ET)_4(Hg_2Br_6)(TCE)$, the ethylene groups of molecule 1 are disordered (indicated by large thermal parameters and apparent C–C distances around 1.4 Å) but tending towards an eclipsed conformation; in molecule 2 they are somewhat disordered but rather staggered than eclipsed; in molecule 3 one end is completely disordered whereas the other is not, allowing for both conformations; and in molecule 4 they are almost completely ordered with a staggered arrangement. It appears, therefore, that the eclipsed vs. staggered conformations are not intrinsic properties of the ET molecule but result from the packing arrangement, rather than determining it.

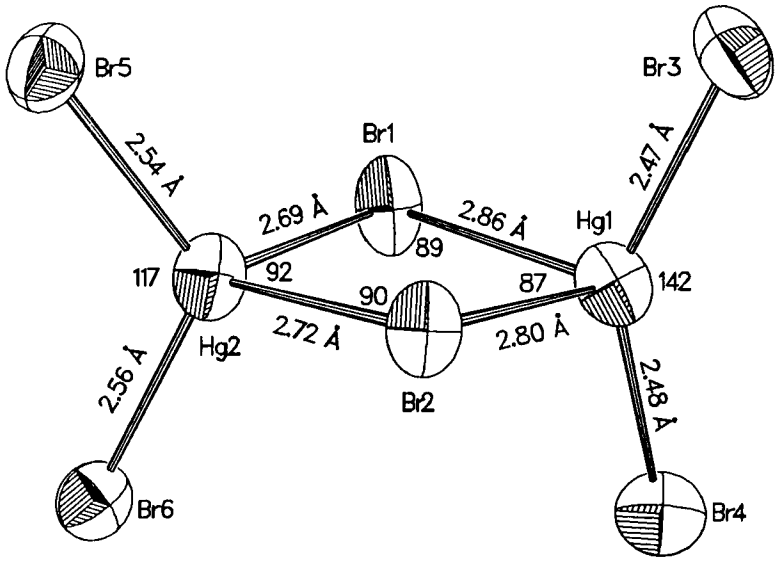


FIGURE 3 The dimeric $Hg_2Br_6^{2-}$ anion in $(ET)_4(Hg_2Br_6)(TCE)$. Bond lengths and angles are indicated, and ellipsoids are drawn at the 50% probability level.

The geometry of the dimeric $Hg_2Br_6^{2-}$ anion is shown in Fig. 3. The anion is formed by edge-sharing tetrahedra analogous to that found in a number of other salts[10–12] and similar to the chloromercurate anion found in $(ET)_3(Hg_2Cl_6)$.[13] The same ion has also been postulated in $[(n\text{-}C_4H_9)_4N]HgBr_3$,[14] based on spectroscopic evidence. The anion bond lengths and the bridging geometry are comparable to the

published structures,[10–12] but, unlike those salts, in the title compound the anion is not located on a symmetry element, and considerable unsymmetry is noticeable in the Br–Hg–Br bond angles. In particular, the coordination around atom Hg1 is quite distorted from tetrahedral geometry with an exceptionally large Br3–Hg1–Br4 angle of 142°, almost as if to make room for a fifth, weakly bound ligand. However, no non-hydrogen atom outside the complex anion is found within a distance of 4 Å, and, as there is no electronic reason for the large distortion, we assume that packing forces acting on the terminal bromide ligands (Br3 and Br4) cause the unusual bond angle.

CONCLUSIONS

The ET-Hg-Br system contains a wide variety of modifications, depending on the crystal growth conditions. TCE as a solvent, equimolar mixtures of $HgBr_2$ and Br^-, with a large excess of ET present, leads primarily to the title compound, $(ET)_4(Hg_2Br_6)(TCE)$. Its structure contains the anion in a dimeric form, and the ET donor molecule packing is surprisingly complex. However, much of the packing is related to that found in the α'-$(ET)_2X$ salts (X^- = $AuBr_2^-$, $Au(CN)_2^-$, $Ag(CN)_2^-$, and $CuCl_2^-$).[8,9] The structure is among the largest ever reported for any ET salt, with four donor molecules in each asymmetric unit. Measurements of the physical properties of this compound are currently in progress and will be reported at a later date.

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