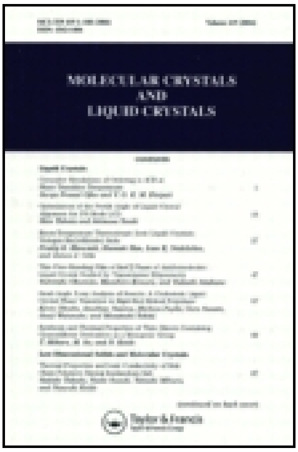

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The Crystal and Molecular Structure of (BEDT-TTF)Ag_xBr_3 ($x \approx 2.4$)

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THE CRYSTAL AND MOLECULAR STRUCTURE OF (BEDT-TTF)-Ag_xBr_3 ($x \approx 2.4$)

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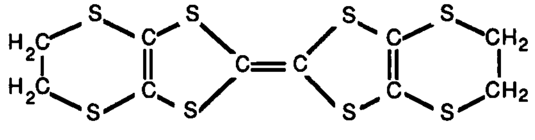
Abstract The synthesis, electrocrystallization, and crystal structure of the organic conductor (BEDT-TTF)Ag_xBr_3 ($x \approx 2.4$; BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) are reported. The crystal structure contains layers of donor cations (charge per molecule: +0.6) interspersed with layers of silver bromide complex anions. The latter are polymeric and consist of a double layer of bromine atoms, with Ag^+ cations distributed over at least five interstitial sites of variable occupancy. Crystal data: orthorhombic, space group $P2_12_12_1$, $a = 4.2316(14)$ Å, $b = 11.699(5)$ Å, $c = 40.287(17)$ Å, $V_c = 1994(1)$ Å^3, $Z = 4$.

INTRODUCTION

The organic donor molecule bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF or ET (1), has proven extremely useful in the synthesis of organic conducting and



(1)

superconducting materials.[1] Charge transfer salts of BEDT-TTF have yielded insulators, semiconductors, metals, and superconductors,[1] among them the organic superconductor with the highest transition temperature, T_c, i. e., κ-$(ET)_2Cu(NCS)_2$, with $T_c \approx 10$–11 K.[2] The copper thiocyanate salt is just one example of a series of BEDT-TTF salts with polymeric anions, the latter formed by a (d^{10}) or ($d^{10}s^2$) metal cation and bridging halide or pseudo-halide anions. We have reported elsewhere on $(ET)Ag_4(CN)_5$,[3] $(ET)_3Ag_{6.4}I_8$,[4] $(ET)Ag_{1.6}(SCN)_2$,[5] $(ET)Cu_2(NCS)_3$,[5] $(ET)_2HgBr_3(TCE)$,[6] and $(ET)BiI_4$.[7] Other examples include κ-$(ET)_2Ag(CN)_2(H_2O)$,[8] $(ET)_2Cu_5I_6$,[9] $(ET)_4Hg_{3-x}Br_8$,[10] and $(ET)_4Hg_{3-x}Cl_8$.[11]

In some of the silver-containing salts, i. e., $(ET)_3Ag_{6.4}I_8$[4] and $(ET)Ag_{1.6}(SCN)_2$,[5] we have found that the silver+1 cations partially occupy many interstitial sites between closely packed I^- or SCN^- anions, leading to non-stoichiometric compounds. Such a finding is characteristic of a class of ionic conductors (for a review, see ref. 12). We have examined the role of ionic conduction in $(ET)_3Ag_{6.4}I_8$, and concluded that the higher electronic conduction in the BEDT-TTF donor layers effectively shorts out any ionic conduction *via* the anion layer.[4] In this article we present a new charge transfer salt of BEDT-TTF with a polymeric silver bromide anion, which also shares the characteristic structural features of an ionic conductor, as described above.

EXPERIMENTAL

Crystals of $(BEDT\text{-}TTF)Ag_xBr_3$ were grown by electrocrystallization of 1.2 mM BEDT-TTF (Strem Chemical Co.) and 55 mM $[(n\text{-}C_4H_9)_4N]AgBr_2$ (prepared under reflux conditions from tetrabutylammonium bromide and AgBr in acetonitrile and recrystallized in 3:1 ether/acetonitrile) in dry tetrahydrofuran. Small, black elongated plate-like crystals grew after 4 days under a current density of 1.25 $\mu A/cm^{-2}$. ESR measurements at room temperature gave a single signal with a peak-to-peak line width of 48–64 G.

One such plate ($0.3 \times 0.2 \times 0.05$ mm^3) was mounted first on a Weissenberg film camera, and then on a Nicolet P3 four-circle diffractometer. The orthorhombic unit cell, a = 4.2316(14) Å, b = 11.699(5) Å, c = 40.287(17) Å, V_c = 1994(1) $Å^3$, was obtained from a least-squares analysis of the setting angles of 25 carefully centered reflections. 3423 intensity data were collected in two octants ($0 \leq h \leq 4$, $0 \leq k \leq 13$, $-44 \leq l \leq 46$, $4° \leq 2\theta \leq 48°$), using ω-scans of 1.1° width at variable speeds of 1.5–12°min^{-1}. 3 standards were measured every 192 reflections with no indication of crystal decay. The non-centrosymmetric space group $P2_12_12_1$ was uniquely determined by the systematic absences. The data were corrected for Lorentz, polarization, and absorption effects (Gaussian integration, μ = 90.8 cm^{-1}, T_{min} = 0.150, T_{max} = 0.635). For the structure solution, the equivalent data were averaged according to the point group *mmm* (R_{ave} = 0.063, wR_{ave} = 0.030, 1932 unique and allowed reflections), whereas for the refinement (in order to take advantage of anomalous dispersion effects) the data were averaged according to the non-centrosymmetric point group 222 (R_{ave} = 0.032, wR_{ave} = 0.018, 3130 unique and allowed reflections, 2443 with $F_o > 3\sigma(F_o)$ used in the refinement).

The structure was solved by direct methods, yielding the positions of the bromine atoms and of Ag1, and completed over several cycles of alternating refinement and difference Fourier maps. The diffuse electron density between the bromine atoms was modeled by four disordered silver atomic positions (refined occupancy factors: 0.534(10), 0.414(7), 0.271(11), and 0.169(8), for Ag2–5, respectively). All bromine and sulfur atoms, as well as Ag1–3, were refined with anisotropic thermal parameters, whereas Ag4, Ag5 and the carbon atoms were refined isotropically (Ag4 and Ag5 were constrained to have the same thermal parameter, in order to reduce correlation effects), for a total of 178 variables. Hydrogen atoms were observed on a difference map and subsequently fixed at their calculated positions (d_{C-H} = 1.0 Å, B_{iso}(H) = 5). No extinction effects were evident from a comparison of calculated and observed structure amplitudes. Convergence was obtained with agreement factors: $R(F_o)$ = 0.076, $wR(F_o)$ = 0.064, "goodness of fit" = 2.32. Final atomic coordinates are given in Table I. Anisotropic thermal parameters and structure factor tables are available from the authors upon request.

TABLE I Positional and isotropic (or equivalent isotropic) thermal parameters for (BEDT-TTF)Ag$_x$Br$_3$. $U_{eq} = 1/3\Sigma_{ij} U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Atom	x	y	z	$U_{eq} \times 10^4$
Br1	0.4990(5)	0.8738(2)	0.28283(5)	587(8)
Br2	0.8928(6)	0.1904(2)	0.29787(5)	537(8)
Br3	0.8950(6)	0.5647(2)	0.29471(5)	556(8)
Ag1	0.9660(5)	0.8732(2)	0.23980(5)	918(9)
Ag2	0.628(2)	0.5834(5)	0.2272(2)	1303(37)
Ag3	0.347(2)	0.6773(5)	0.2765(2)	1060(31)
Ag4	0.523(3)	0.6414(8)	0.2480(3)	476(26)*
Ag5	0.418(4)	0.6123(13)	0.2559(4)	476**
S1	0.5651(14)	0.6572(3)	0.52961(11)	439(18)
S2	0.2839(13)	0.4367(4)	0.54737(11)	408(18)
S3	0.5779(13)	0.5735(4)	0.45191(11)	412(18)
S4	0.2959(13)	0.3574(4)	0.47248(11)	452(18)
S5	0.6145(13)	0.7444(4)	0.59753(12)	425(18)
S6	0.3038(13)	0.4743(4)	0.61959(11)	371(18)
S7	0.5845(13)	0.5191(3)	0.38019(11)	369(17)
S8	0.2573(13)	0.2565(4)	0.40616(11)	374(17)
C1	0.435(5)	0.5229(13)	0.5169(4)	355(46)*
C2	0.434(4)	0.4888(13)	0.4838(4)	315(43)*
C3	0.507(3)	0.6319(13)	0.5727(3)	240(36)*
C4	0.391(4)	0.5309(13)	0.5798(4)	332(45)*
C5	0.483(4)	0.4747(12)	0.4200(4)	291(42)*
C6	0.370(4)	0.3765(13)	0.4299(4)	260(36)*
C7	0.438(4)	0.7001(12)	0.6361(4)	327(43)*
C8	0.509(5)	0.5766(13)	0.6449(4)	402(49)*
C9	0.395(5)	0.4115(13)	0.3556(4)	439(51)*
C10	0.446(4)	0.2882(11)	0.3671(4)	254(40)*

* U_{iso}

** Constrained to be equal to U(Ag4)

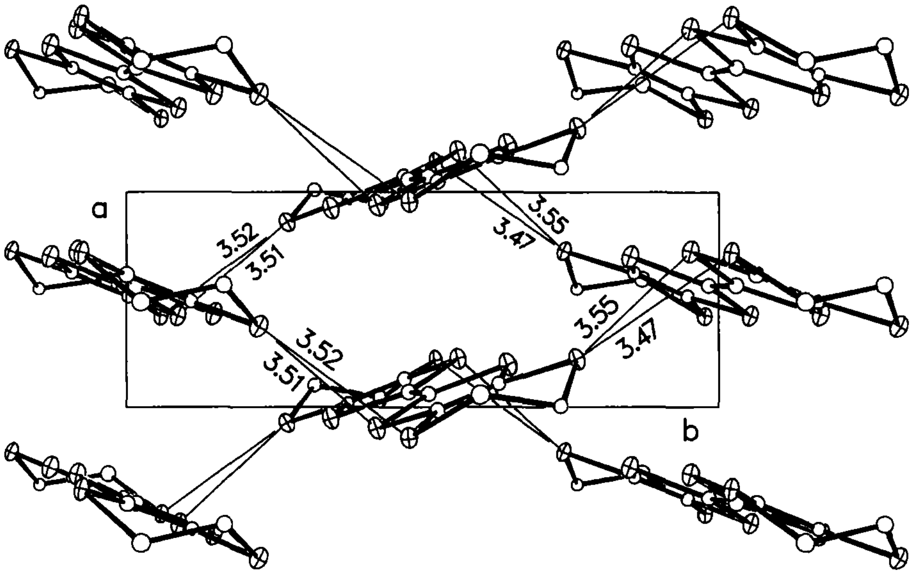


FIGURE 1 BEDT-TTF donor molecular layer in (BEDT-TTF)Ag_x Br_3. Intermolecular S···S contacts shorter than 3.6 Å are indicated with thin lines, and hydrogen atoms are omitted for clarity.

CRYSTAL STRUCTURE DESCRIPTION

The crystal structure of (BEDT-TTF)Ag_xBr_3 contains alternating layers of donor-cation molecules and polymeric silver bromide anions (two each per unit cell) parallel to the *ab*-plane. Within a given donor layer, two loosely bound BEDT-TTF molecular stacks, with a repeat unit of one donor molecule along the *a*-axis, are discernible. No short intermolecular contacts are found along the stacking direction, *a*, but several S···S contacts shorter than the sum of the van der Waals radii (r_{vdW} = 1.8 Å for sulphur) connect molecules located on adjacent stacks. These contacts, which are indicated in Figure 1, all involve at least one "outer" sulphur atom of the BEDT-TTF molecule (i. e., S5–8). The arrangement of the donor radical cations within the sheet is of the θ-type, such as in θ-$(ET)_2I_3$,[13] i. e., the stacking is uniform, and the angle of the normal to the molecular plane on adjacent stacks with respect to the stacking axis alternates (between +23.7° and –23.7°).

TABLE II Bond distances and angles in (ET)Ag$_x$Br$_3$.

Bond Distances (Å)

Ag1–Br1	2.629(3)	Ag5–Br3	2.614(11)	C6–S4	1.76(2)
Ag1–Br2	2.690(3)	Ag5–Br2	2.694(11)	C6–S8	1.76(2)
Ag1–Br3	2.701(3)	Ag5–Br3	2.77(2)	C7–S5	1.80(2)
Ag1–Br1	2.845(3)	C1–S1	1.74(2)	C8–S6	1.80(2)
Ag2–Br1	2.543(7)	C1–S2	1.71(2)	C9–S7	1.79(2)
Ag2–Br2	2.588(7)	C2–S3	1.73(2)	C10–S8	1.80(2)
Ag2–Br2	2.729(6)	C2–S4	1.71(2)	C1–C2	1.39(2)
Ag2–Br3	2.953(7)	C3–S1	1.779(14)	C3–C4	1.31(2)
Ag3–Br1	2.401(6)	C3–S5	1.714(15)	C5–C6	1.31(2)
Ag3–Br3	2.436(6)	C4–S2	1.77(2)	C7–C8	1.52(2)
Ag3–Br3	2.767(8)	C4–S6	1.77(2)	C9–C10	1.53(2)
Ag4–Br3	2.612(7)	C5–S3	1.77(2)		
Ag4–Br2	2.616(7)	C5–S7	1.74(2)		

Bond Angles (°)

Br1–Ag1–Br2	122.77(11)	C5–S7–C9	100.9(8)
Br1–Ag1–Br3	120.05(11)	C6–S8–C10	100.9(7)
Br1–Ag1–Br1	101.19(9)	C2–C1–S2	121.2(12)
Br2–Ag1–Br3	108.70(9)	C2–C1–S1	122.7(12)
Br2–Ag1–Br1	99.77(10)	S2–C1–S1	116.0(10)
Br3–Ag1–Br1	97.98(10)	C1–C2–S4	120.9(12)
Br1–Ag2–Br2	124.7(4)	C1–C2–S3	123.0(12)
Br1–Ag2–Br2	102.3(2)	S4–C2–S3	116.0(9)
Br1–Ag2–Br3	98.97(14)	C4–C3–S5	131.6(12)
Br2–Ag2–Br2	105.4(2)	C4–C3–S1	114.5(12)
Br2–Ag2–Br3	95.5(2)	S5–C3–S1	113.9(8)
Br2–Ag2–Br3	133.2(4)	C3–C4–S2	119.7(13)
Br1–Ag3–Br3	134.2(4)	C3–C4–S6	127.7(13)
Br1–Ag3–Br3	101.7(2)	S2–C4–S6	112.5(9)
Br3–Ag3–Br3	108.7(2)	C6–C5–S7	129.3(12)
Br3–Ag4–Br2	171.7(5)	C6–C5–S3	115.8(12)
Br3–Ag5–Br2	158.5(10)	S7–C5–S3	114.7(9)
Br3–Ag5–Br3	103.7(6)	C5–C6–S4	118.3(12)
Br2–Ag5–Br3	97.6(5)	C5–C6–S8	129.4(12)
C1–S1–C3	95.3(7)	S4–C6–S8	112.3(9)
C1–S2–C4	93.9(8)	C8–C7–S5	113.3(12)
C2–S3–C5	94.9(7)	C7–C8–S6	114.0(13)
C2–S4–C6	94.8(8)	C10–C9–S7	115.7(12)
C3–S5–C7	99.9(7)	C9–C10–S8	113.3(11)
C4–S6–C8	99.4(8)		

The internal geometry (see Table II) of the BEDT-TTF donor molecule is in agreement with that found in most ET salts. From the composition, the average charge state of the ET molecule is calculated to be approximately +0.6. Correlations have been found between bond lengths and charge of the donor molecule, i. e., C–C bond lengths increase, but C–S distances decrease upon increasing the charge.[1] In addition, the conjugated portion of the molecule tends to be more planar in the charged species. In the present crystal structure, the standard deviations of the bond lengths are large enough to preclude an unambiguous assignment of the charge from the geometrical parameters. However, the central C–C bond is among the longest, and the innermost C–S bond lengths among the shortest observed, indicating ET^{+1}, rather than a partially charged cation. The discrepancy may be due to an overestimation of the silver population parameters, as discussed below.

The polymeric anion (shown in Figure 2) consists of a double layer of almost close packed bromide ions, with most silver+1 ions occupying tetrahedral interstitial sites. Of the latter, only Ag1 is fully occupied, whereas the other positions are only partially occupied. From the distances between these sites, it is impossible for Ag2–4 to be occupied in a particular unit cell where silver atom Ag5 is present, and

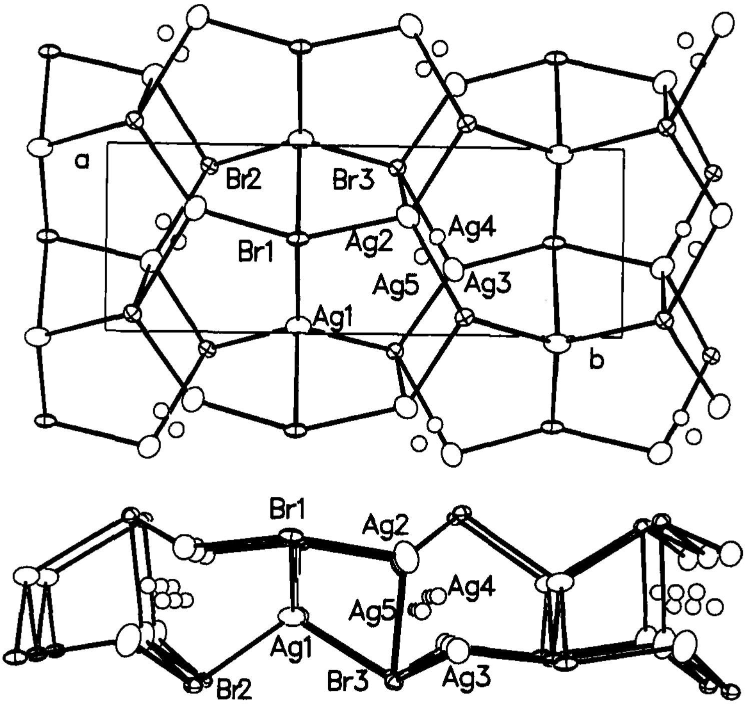


FIGURE 2 Two perpendicular views of the polymeric silver bromide anion layer in (BEDT-TTF)Ag_xBr_3.

correspondingly for Ag4. However, the major positions are Ag2 and Ag3, with refined populations of 0.5 and 0.4 each. Their separation (2.6 Å) is still slightly shorter than the Ag–Ag distance in silver metal (2.9 Å), but occasional simultaneous occupation of both sites, as required by the model, seems possible. However, the possibility that correlation and Fourier series truncation effects lead to an overestimation of the silver atomic population factors cannot be excluded.

A curious observation in the crystal structure of (BEDT-TTF)Ag_xBr_3 is the presence of two different kinds of pseudo-symmetry. The donor layer (Fig. 1) exhibits non-crystallographic inversion symmetry, with pseudo-centers of inversion at the center of the donor molecules, and half-way in between molecules. On the other hand, the anion layer (Fig. 2) appears mirror-symmetric, with a pseudo-reflection plane perpendicular to the *b*-axis and passing through atoms Ag1 and Br1. However, it must be noted that neither pseudo-symmetry carries over into the other parts of the structure. Furthermore, if these symmetries were exact, the combination of screw axes and inversion centers would generate glide planes, leading to systematic absences for reflections which are clearly observed. Therefore, we are confident that we have not overlooked any missing symmetry elements, and the structure is truly non-centrosymmetric.

CONCLUSIONS

Polymeric anions are frequently found in salts of BEDT-TTF with complex anions composed of metal cations with full *d*-shell (Ag^+, Au^+, Cu^+, Hg^{2+}, Bi^{3+} etc.) and halide or pseudo-halide anions. Silver complexes often exhibit the further complication that the Ag^+ ions randomly occupy a number of crystallographic interstitial sites. The title compound encompasses both of these characteristics. The non-centrosymmetric space group is another unusual, but not unprecedented feature of the present crystal structure. Additional physical measurements will be carried out as more and larger crystals will become available.

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