

## Structure of Bis(ethylenedithio)tetrathiafulvalenium Tribromodicuprate(I), (BEDT-TTF<sup>+</sup>)Cu<sub>2</sub>Br<sub>3</sub>: Coordination of the Organic Radical Cation to the Metal Ions

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X-Ray crystal analysis has revealed that two sulfur atoms of a bis(ethylenedithio)tetrathiafulvalene radical cation, BEDT-TTF<sup>+</sup>, are coordinated to copper(I) atoms in a –Cu–Br–Cu–(μ-Br)<sub>2</sub>–Cu– chain, in which each copper atom has a distorted tetrahedral coordination with a sulfur atom and three bromine atoms.

A series of bis(ethylenedithio)tetrathiafulvalene (abbreviated as BEDT-TTF) complexes formed with anionic copper compounds exhibit interesting physical properties including metallic charge transport and superconductivity.<sup>1–12</sup> Copper(II) halides readily oxidize tetrathiafulvalene and its analogues, and provide a variety of complexes that have quite different structural and electrical properties.<sup>5–15</sup> The compositions of products in this type of reaction depend on the relative concentrations of the donor and the anionic copper compound that are employed. In the present study, a redox reaction between BEDT-TTF and [CuBr<sub>4</sub>]<sup>2–</sup> was carried out under such conditions that the copper complex was always in excess throughout the course of reaction,<sup>†</sup> and a new compound (BEDT-TTF)Cu<sub>2</sub>Br<sub>3</sub> was obtained. An X-ray crystal analysis<sup>‡</sup> of this compound showed that two sulfur atoms of a BEDT-TTF<sup>+</sup> cation were coordinated to different copper(I)

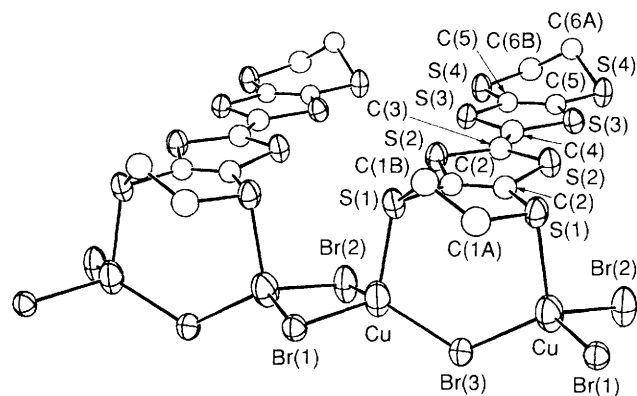
ions. This is the first example of coordination-bond formation between a radical cation and a metal ion.

As shown in Fig. 1, each copper atom is coordinated to three bromine atoms and a sulfur atom of the ethylenedithio group of BEDT-TTF. The resulting tetrahedrons share the sides and the apexes alternately, constructing a –Cu–Br(1)–Br(2)–Cu–Br(3)–Cu– chain along the crystal *c* axis: the Cu–Br distances are 2.419–2.478 Å, and the Cu–S distances are 2.931 Å. All BEDT-TTF molecules are crystallographically equivalent. Two sulfur atoms that belong to the same ethylenedithio group in each BEDT-TTF molecule are coordinated to two copper atoms [Cu–S(1) = 2.439 Å] that are linked with each other by a Br(3) atom; the sulfur atoms, S(4)s, of the other ethylenedithio group are not bonded to copper. The shortest intermolecular S–S distances are practically identical with the value 3.70 Å of the van der Waals S–S contact: S(1)–S(1) and S(4)–S(4) contacts parallel to the molecular plane are 3.714 and 3.696 Å, respectively; S(2)–S(4) and S(3)–S(3) contacts perpendicular to the molecular plane are 3.709 and 3.710 Å, respectively. The electrical resistivity determined by a two-probe method was of the order of 10 kΩ cm. This low conductivity is due to the absence of a close S–S contact between BEDT-TTF cations.

All the copper atoms are crystallographically equivalent, and have the tetrahedral coordination geometry that is characteristic of the Cu<sup>I</sup> species. The copper atoms are, therefore, in the Cu<sup>I</sup> state, and the compound is formulated as (BEDT-TTF)<sup>+</sup>Cu<sub>2</sub>Br<sub>3</sub>. The interatomic distance between the central carbon atoms, C(3)–C(4), of BEDT-TTF can be used as a diagnostic test for the determination of charge occupation of the donor; 1.32 Å in BEDT-TTF<sup>0</sup> and 1.38 Å in BEDT-TTF<sup>+</sup>.<sup>16</sup> The distance in the present compound is 1.40 Å, which shows the presence of BEDT-TTF<sup>+</sup>, consistent with the proposed compound formula. The Cu–S distance, 2.439 Å, is close to the typical Cu<sup>I</sup>–S coordination bond distances,

<sup>†</sup> Single crystals were grown by diffusing [Me<sub>4</sub>N<sup>+</sup>]<sub>2</sub>[CuBr<sub>4</sub>]<sup>2–</sup> and BEDT-TTF in 1,2-dichloroethane in an H-shaped cell, in which the compartments of the starting materials were connected with a capillary. All crystals grown in the compartment of the copper compound had an identical crystal shape, which was apparently different from that of crystals formed in the other compartment.

<sup>‡</sup> A dark crystal of C<sub>10</sub>H<sub>8</sub>Br<sub>3</sub>Cu<sub>2</sub>S<sub>8</sub> (*M* = 751.49) with approximate dimensions of 0.25 × 0.23 × 0.17 mm was used for the data collection, which was performed at 23°C with monochromated Mo-Kα (*λ* = 0.71073 Å) on a Syntex P2<sub>1</sub> diffractometer with Crystal Logic automatic system. Data processing was carried out using UCLA Crystallographic Computing Package (C. Strouse). The orthorhombic cell parameters and calculated volume were: *a* = 13.997(2), *b* = 19.370(2), *c* = 7.178(1) Å and *V* = 1946.1 Å<sup>3</sup>. For *Z* = 4, *D*<sub>c</sub> = 2.56 g cm<sup>–3</sup>, which agreed with the density 2.53 g cm<sup>–3</sup> determined by flotation in a bromoform–carbon tetrachloride mixture. The systematic absences (*h*0*l*, *h* + *l* = 2*n* + 1; 0*kl*, *k* + *l* = 2*n* + 1) showed that the space group was either the *Pnmm* (No. 58) or *Pmm2* (No. 34). Inspection of the correlation coefficients from the least-squares refinements (W. H. Baur and E. Tillmanns, *Acta Crystallogr., Sect. B*, 1986, 42, 95) led to the conclusion that the space group was *Pnmm* in which half the molecule was unique. The 0–20 scan method was used in the range, 0 < 2θ ≤ 50°. A total of 2013 reflections were collected, 1871 of which were unique and not systematically absent. *μ* = 91.2 cm<sup>–1</sup>. An empirical absorption correction based on a series of *ψ*-scans was applied to the data. The copper and bromine atoms were located by direct methods. The remaining atoms were located in succeeding difference Fourier syntheses. A mirror plane that existed perpendicular to the molecular plane of a BEDT-TTF molecule along its long axis resulted in the disorder of the ethylene carbon atoms within the rings. This was modelled assuming that each of the ethylene carbon atoms occupied two positions with 0.5 multiplicity. The non-hydrogen atoms except carbon were anisotropically refined. The refinement was performed by a full-matrix least-squares analysis using 1077 reflections with *I* > 3σ(*I*) for 94 variables. After this refinement, the hydrogen atoms were visible in the difference map. The hydrogens were placed in idealized positions and were included in the refinements with fixed thermal parameters and their coordinates 'riding' on the carbon to which they are bonded. The final cycle of refinement converged with *R* = 0.031 and *R*<sub>w</sub> = 0.041. All calculations were performed on a VAX computer with an SPD/VAX program. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 1** Chain structure and (BEDT-TTF)–Cu coordination bonds in (BEDT-TTF<sup>+</sup>)Cu<sub>2</sub>Br<sub>3</sub>. A distorted coordination geometry is formed around each copper atom with bond lengths (Å) and angles (°): Cu–S(1) 2.439(2), Cu–Br(1) 2.455(1), Cu–Br(2) 2.478(1), Cu–Br(3) 2.419(1); S(1)–Cu–Br(1) 104.36(6), S(1)–Cu–Br(2) 99.73(6), S(1)–Cu–Br(3) 109.40(6), Br(1)–Cu–Br(2) 105.51(4), Br(1)–Cu–Br(3) 117.09(5), Br(2)–Cu–Br(3) 118.53(5). The C(1) and C(6) atoms are disordered between two positions; one of the possible conformations of the ethylene groups is shown.

2.31–2.42 Å, reported for copper(I) complexes with thiourea and thioacetamide.<sup>17,18</sup> The bond length suggests that Cu–S coordination bonds are formed, despite the positive charge on the BEDT-TTF molecules which should result in an electrostatic repulsion between the metal and the ligand ions. The formation of a  $\sigma$ -type dative bond is conceivable between a sulfur p orbital and a copper  $sp^3$  orbital, on the basis of the following facts: (i) the Cu–S coordination bond is approximately perpendicular to the averaged molecular plane of BEDT-TTF, and (ii) the highest occupied molecular orbital of BEDT-TTF has a large electron population in the p orbitals of the sulfur atoms.<sup>19</sup> This dative bond, however, is expected to be weak, because the molecular orbital that may form the dative bonds is not completely filled in BEDT-TTF<sup>+</sup>. This new type of coordination should be stabilized by the back donation of Cu d electrons to BEDT-TTF molecular orbitals.

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