

Dication Salt of Bis(ethylenedithio)tetrathiafulvalene: Preparation and Crystal Structure of BEDT-TTF(ClO₄)₂

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Electrocrystallization of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) in an oxidizing solvent medium yields BEDT-TTF(ClO₄)₂, which is the first example of a salt in which BEDT-TTF is present only as the dication; bond length data from an X-ray structure determination of BEDT-TTF(ClO₄)₂ are used as a standard for assigning the +2 oxidation state to BEDT-TTF molecules in mixed-valent cation-radical salts.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is the basis of an important family of conducting and superconducting molecular solids.¹⁻⁴ Several BEDT-TTF-based superconductors are now known,¹⁻¹⁷ and a superconducting transition temperature, T_c , as high as 12.8 K (0.3 kbar) has recently been observed in the cation-radical salt (BEDT-TTF)₂Cu[N(CN)₂]Cl.⁶ Interest in the BEDT-TTF family of materials remains high because of the promise of investigating the structure-property relationships of superconducting solids by controlling molecular structure and intermolecular interactions. During the search for new molecular conductors and

superconductors, cation-radical salts of BEDT-TTF in several oxidation states from 0 to +1 have been isolated.¹⁻⁴ BEDT-TTF salts with oxidation states greater than +1, however, have scarcely been explored.^{18,19} We describe a new method for preparing high-oxidation-state salts of the BEDT-TTF family of donors. The procedure involves chemical oxidation of the donor and dissolution of the cation radical, followed by electrochemical oxidation to form the high-oxidation-state salt. Using this method, we have prepared BEDT-TTF(ClO₄)₂, the first example of a salt in which BEDT-TTF exists only as the dication. Characterization of a salt contain-

Table 1 Bond lengths^a of the TTF core in BEDT-TTF^{x+} cation-radical salts

Compound	<i>x</i>	Bond length/Å			
		A ^b	B	C	D
BEDT-TTF ^c	0	1.312(12)	1.757(7)	1.754(8)	1.332(7)
α-(BEDT-TTF) ₂ PF ₆ ^d	1/2	1.365(4)	1.740(2)	1.750(2)	1.345(3)
(BEDT-TTF) ₃ (ClO ₄) ₂ ^e	2/3	1.366(7)	1.731(7)	1.743(5)	1.345(9)
BEDT-TTF PF ₆ ^f	1	1.394(5)	1.722(4)	1.734(4)	1.362(5)
(BEDT-TTF) ₃ (ZnCl ₄) ₂ ^g		1.378(7)	1.721(6)	1.738(6)	1.360(6)
BEDT-TTF(ClO ₄) ₂	2	1.439(4)	1.683(3)	1.716(3)	1.379(5)
(BEDT-TTF) ₃ (ZnCl ₄) ₂ ^g		1.438(7)	1.680(6)	1.710(6)	1.369(7)
(BEDT-TTF) ₃ (MnCl ₄) ₂ ^h		1.431	1.685	1.715	1.361
(BEDT-TTF) ₅ Hg ₅ Br ₁₁ ^h		1.43	1.68	1.71	1.34
(BEDT-TTF) ₅ Hg ₅ Br ₁₁ ^h		1.41	1.69	1.72	1.37

^a Bond lengths are averaged assuming D_{2h} symmetry for the TTF core. ^b Bonds refer to the labels in Fig. 2. ^c Ref. 24. ^d Ref. 25. ^e Ref. 26. ^f Ref. 27. ^g Ref. 18. ^h ref. 19.

ing only the BEDT-TTF dication will now allow greater certainty in using structural data to assess the degree of oxidation in cation-radical salts of the BEDT-TTF donor.^{18–22}

BEDT-TTF(ClO₄)₂ was isolated at the working electrode of a standard constant-current electrocrystallization cell. The crystals used for the data reported here were obtained using a solvent mixture of 10% CS₂ in ClCH₂COCl,[†] and we have also isolated the dication salt from a 10% ClCH₂COCl in benzonitrile mixture. Optical spectroscopy shows that BEDT-TTF is slowly oxidized by ClCH₂COCl,²³ indicating that BEDT-TTF⁺ is first formed in the electrolytic medium before electrochemical oxidation to the dication and precipitation with the electrolyte anion. BEDT-TTF(ClO₄)₂ forms as either very thin hexagonal plates or thin needles, and the crystals exhibit a blue tint if thin enough to be translucent.[‡] A view of the crystal structure in Fig. 1 shows the packing of the cations

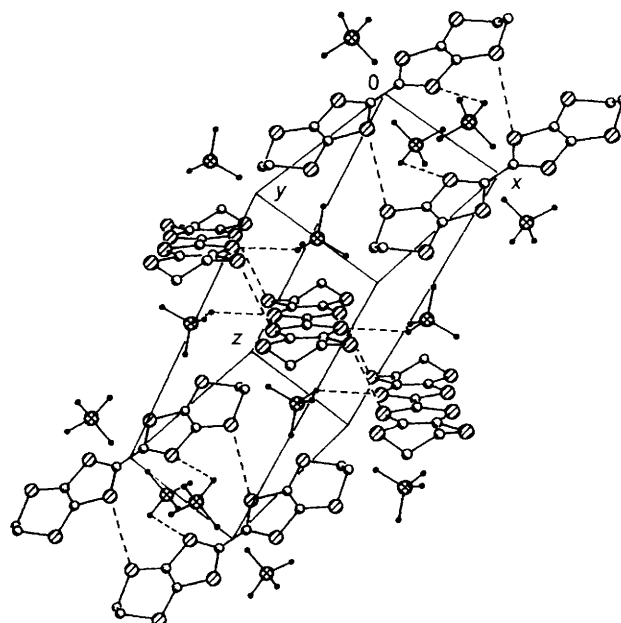


Fig. 1 Crystal structure of BEDT-TTF(ClO₄)₂ showing the packing of the donor and counterion

[†] BEDT-TTF(ClO₄)₂ BEDT-TTF (10 mg) was placed in the working electrode arm of a two-electrode H-cell containing a total of 25 ml of 6×10^{-2} mol dm⁻³ tetraethylammonium perchlorate in 10% CS₂ in ClCH₂COCl. A current density of $1 \mu\text{A cm}^{-2}$ was maintained between the working and counter electrodes that were separated by two glass frits. Crystals were harvested after 28 days.

[‡] Crystal data for C₁₀H₈S₈²⁺ (ClO₄⁻)₂ monoclinic, space group $P2_1/n$, $a = 5.867(1)$, $b = 9.579(2)$, $c = 17.669(3)$ Å, $\beta = 92.06(2)^\circ$, $V = 992.4(3)$ Å³, $Z = 2$, $D_c = 1.953$ g cm⁻³, $T = 298$ K, Mo-K α radiation, $\lambda = 0.71073$ Å. 2053 reflections were collected using the ω -scan method (1.2° scan range and 2–4° min⁻¹ scan speed depending on intensity). Data were collected out to $2\theta = 50^\circ$. The structure was solved by direct methods in SHELXTL plus (Sheldrick, 1990) from which the locations of the non-H atoms were obtained. The structure was refined in SHELXTL plus using full-matrix least squares. The non-H atoms were treated anisotropically. The CH₂CH₂ units of the cation are disordered [site occupation factors were refined to 0.65 for the C(4)–C(5) unit and 0.35 for the C(4')–C(5') unit with an e.s.d. of 0.03]. Each of the disordered CH₂ units has a H-atom of full occupancy ([H(4) or H(5) common to both disordered units] and a disordered H-atom [H(4a) and H(4a') on C(4) and C(4'), respectively; H(5a) and H(5a') on C(5) and C(5'), respectively]. H(4a') and H(5a') were calculated in idealized positions and their isotropic thermal parameters fixed at 0.08. H(4), H(5), H(4a) and H(5a) were refined freely without any constraints. The refinement converged to $R = 0.0331$ and $R_w = 0.0407$ in the last cycle of refinement in which 1385 observed reflections [$F > 4\sigma(F)$] were used of 1742 unique reflections. (Sheldrick, SHELXTL plus; Siemens XRD Corp., Madison, WI 1990). 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.

and anions. All BEDT-TTF dications are equivalent, and are surrounded by six counterions in a distorted octahedron. The nearest intermolecular S–S contact is 3.621 Å from an inner ring sulfur [S(1)] to an outer ring sulfur [S(4)] on adjacent molecules.

The BEDT-TTF²⁺ ion is characterized by a long central C–C double bond, 1.439(4) Å, and short C–S bonds in the fulvalene rings (Table 1). These trends are similar to structural changes observed upon oxidation of the fulvalene donor, tetramethyltetrathiafulvalene.²⁸ Table 1 compares bond lengths of the tetrathiafulvalene (TTF) core of BEDT-TTF in BEDT-TTF(ClO₄)₂ with bond lengths observed in a series of salts with differing BEDT-TTF formal oxidation states. Molecular orbital calculations^{29,30} on neutral BEDT-TTF show that the highest electron density is on the TTF core and that the HOMO has nodes on the C–S bonds. Upon oxidation, the C–C double bonds of BEDT-TTF become longer, and the C–S bonds become shorter.

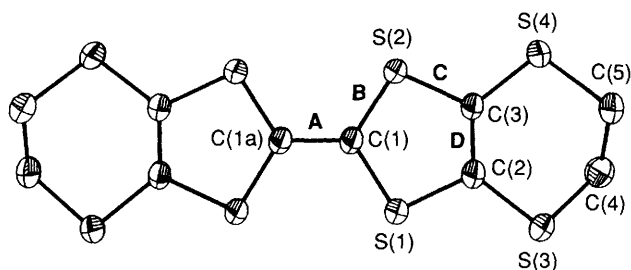


Fig. 2 Molecular structure of BEDT-TTF²⁺ in the salt BEDT-TTF(ClO₄)₂, with 50% probability ellipsoids, showing the atom numbering scheme. The bond lengths for the bonds labelled A–D are listed in Table 1.

Bond lengths are frequently used to estimate the degree of oxidation of donor molecules in charge-transfer complexes and cation-radical salts.^{18–22,31} The length of the central C–C double bond is most often used in these correlations, as it is the bond most sensitive to changes in oxidation state.^{18–22,31} However, until now there has not been a standard for the BEDT-TTF dication, although a charge of +2 has been proposed for BEDT-TTF molecules in mixed-valent salts.^{18,19,22} Table 1 also lists bond-length data for several mixed-valent salts thought to contain the BEDT-TTF dication for comparison with BEDT-TTF(ClO₄)₂. For example, comparing bond lengths for the salt (BEDT-TTF)₃(ZnCl₄)₂¹⁸ with the data reported here confirms the assignment¹⁸ that both localized mono- and di-cations coexist in a mixed-valent salt.

Room temperature EPR studies on both single crystals and powders of BEDT-TTF(ClO₄)₂ show the dication to be diamagnetic in agreement with removing two electrons from the singly degenerate HOMO.^{29,30} The dication salt has no partially filled electronic levels, and is not expected to be the basis of a conductor. Optical spectroscopy confirms that BEDT-TTF(ClO₄)₂ is insulating as no plasma edge is observed down to the far-IR. It would be of great interest to prepare salts with non-integral oxidation state above +1, and we are currently investigating the methods described here as a possible route for preparing examples of these materials. We have also recently isolated dication salts with BF₄[–] and PF₆[–] counterions, so the method described here for preparing high-oxidation-state salts appears to be general.

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