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Structure and Physical Properties of Two Perchlorate Salts Derived from a Novel Twin Donor. Bis(4',5'-ethylenedithio-5-methylthiotetrathiafulvalenyl-4-thio)methane

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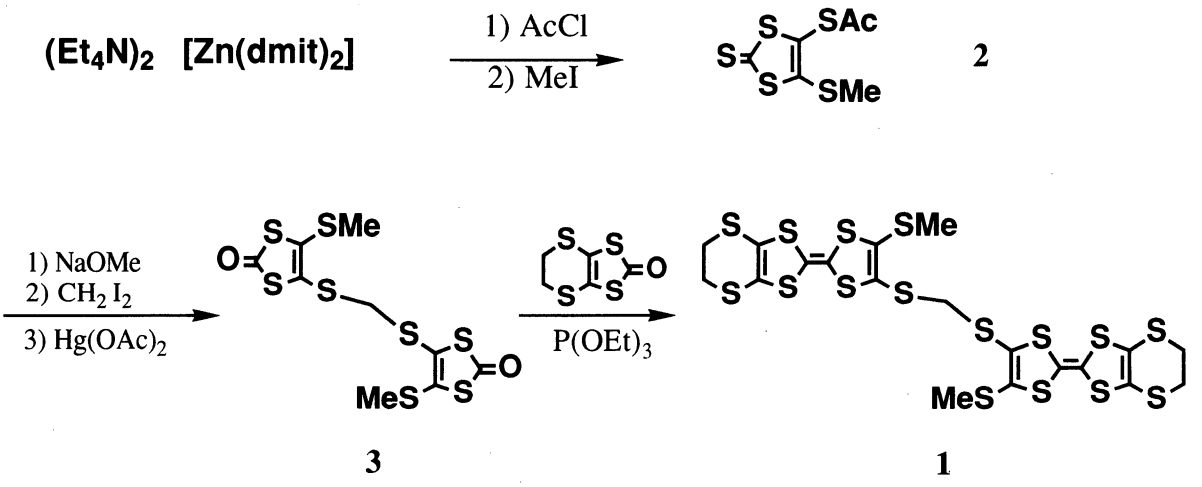
A twin donor (**1**) which consists of two BEDT-TTF moieties linked by a methylenedithio bridge was prepared. Two radical salts of ClO_4^- with the stoichiometry of 1:1 and 2:1 were obtained through electrochemical crystallization. In the salt of **1**$\bullet ClO_4$, the donor has a phane-like conformation. A magnetic behavior of the salt was interpreted by the one-dimensional antiferromagnetic Heisenberg model. On the other hand, the donor exist as a twist phane like conformation in the salt of **1**$\bullet(ClO_4)_{0.5}$ and the salt is a semiconductor ($\sigma_{rt} = 0.1$ S cm^{-1}) with an activation energy of 5×10^{-2} eV.

Most of conventional donors are flat in shape. If two donor units are jointed by an alkyl chain(s), a resulted twin donor ought to have conformational flexibility. Since intramolecular electronic interaction of two donor units depends on their relative orientation, physical properties of its radical cation salts are considered to show conformational dependence.$^{1)}$ Besides, stoichiometry between donor units and counter ions in their salts may have a wider variety due to the presence of two donor units within the molecule. Not only to elucidate these two factors but also to realize unconventional crystal packings we have designed a twin donor (**1**) where two BEDT-TTF moieties are linked by a methylenedithio bridge.$^{2)}$ We report preparation of the twin donor **1** and characterization of two radical salts, **1**$\bullet ClO_4$ and **1**$\bullet(ClO_4)_{0.5}$, obtained through electrocrystallization.

The twin donor **1** was prepared as shown in Scheme 1. A hybrid sulfide (**2**) is the key compound to prepare unsymmetrically substituted TTF derivatives. The twin donor **1** was obtained by a usual cross-coupling method$^{3)}$ from diketone **3**. Separation of **1** was performed by gel-permeation chromatography and the isolated product was recrystallized from benzene:methanol (3:1 v/v).$^{4)}$ A cyclic voltammogram of **1** showed reversible potential waves of the first and second redox processes; $E^1_{1/2} = 0.47$ V, $E^2_{1/2} = 0.55$ V vs. Ag/AgCl.$^{5)}$ The splitting of the waves indicates that the two TTF moieties interact through bond and/or through space interaction.



Scheme 1.

Galvanostatic electrocrystallization of **1** was performed in CH_2Cl_2:THF (3:1) using Pt electrodes in the presence of n-Bu_4NClO_4 as a supporting electrolyte. Two radical salts, **1**•ClO_4 and **1**•$(ClO_4)_{0.5}$ were obtained in a same batch; black blocks (crystal *A*) and dark green needles (crystal *B*). The electrical transport property of crystal *A* was nearly insulating; $\sigma_{rt} = 1 \times 10^{-8}$ S cm^{-1}. An X-ray analysis of crystal *A*⁽⁶⁾ reveals that the cation radical of **1** (**1**$^{+\bullet}$) takes a phane-like conformation. The phanes form a dimeric pair, and they stack in a column along the a axis (Fig. 1). The shortest S•••S distance between donor units in the phane is only 3.09 Å. While the shortest interstack S•••S distance is 3.67 Å. Therefore the radical ion is considered to be stabilized largely within the phane. Temperature dependence of ESR signal intensities (g=2.0062) of the salt shows a thermal activation pattern, with a transition⁽⁷⁾ at 150 K. Temperature dependence of the susceptibility above 150 K was analyzed by a S-T model. An energy gap between the singlet and the triplet caused by the antiferromagnetic interaction among the unpaired electrons of the phane conformer was determined to be 0.05 eV.⁽⁸⁾

On the other hand, the crystal *B* is a semiconductor (σ_{rt} = 0.15 S cm^{-1}) down to 100 K with an activation energy of 5×10^{-2} eV. The donor takes a twist phane-like conformation in the crystal (Fig. 2).⁽⁹⁾ Namely one of the donor units of the phane-like conformer turns over and is twisted around C-S bond of the methylenedithio bridge. The donor arranges side-by-side to form a uniform column along the c axis. The shortest S•••S contacts of 3.4 Å are recognized in upper and lower edges of each donor units, which constitutes two parallel zig-zag conduction paths in the same direction.

We have obtained two kinds of twin donor salts which have magnetic and electric property depending on the crystal packing and the conformation of donor molecules. Since

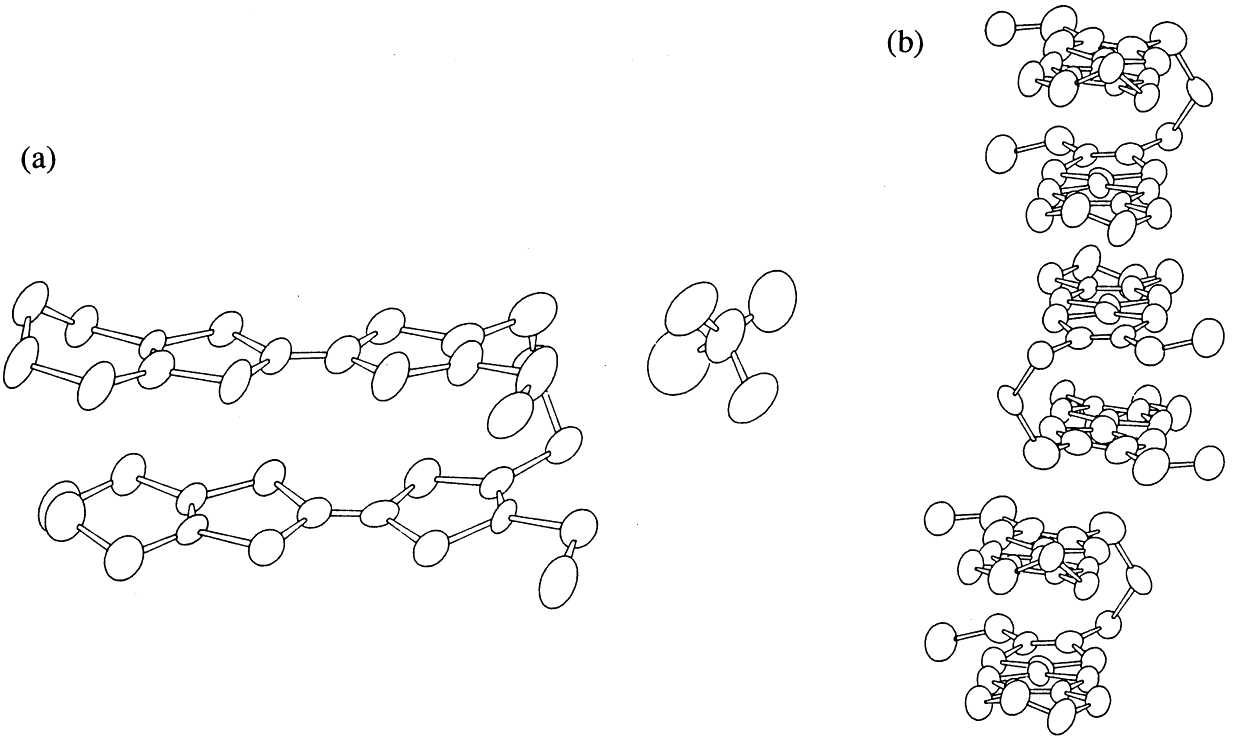


Fig. 1. (a) Molecular structure of cation radical of **1** and the position of ClO_4 anion in the crystal *A* (**1**•ClO_4). (b) Crystal packing of cation radical of **1** in the crystal *A* (**1**•ClO_4).

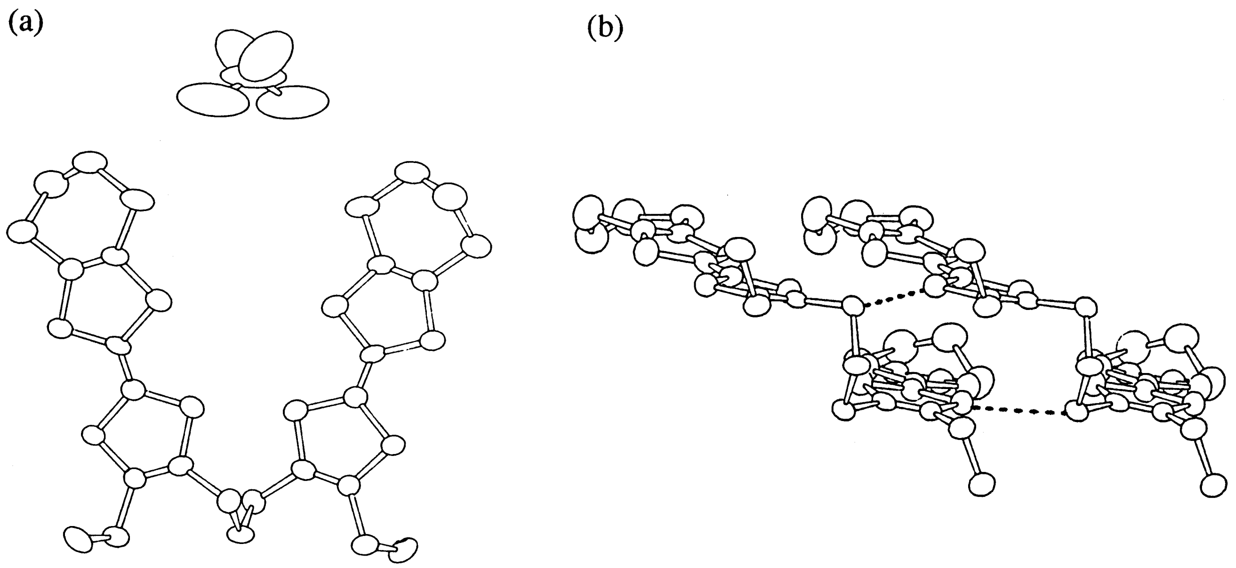


Fig. 2. (a) Molecular structure of cation radical of **1** and the position of ClO_4 anion in the crystal *B* (**1**•$(ClO_4)_{0.5}$). The counter ion is shared by two donors. (b) Crystal packing of cation radical of **1** in the crystal *B* (**1**•$(ClO_4)_{0.5}$). The shortest S•••S contacts are shown by doted lines.

twin donors can be considered as an elementary unit of the mixed valency of conductive salts, modification of the number and the length of the linking chain(s) of twin donors may afford some insights into the mixed valency at the molecular level.

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4) **1**: Mp 170 - 173 ℃(dec.). Anal. Found: C 30.42; H 2.18; S 67.46%. Calcd for $C_{19}S_{16}H_{16}$: C 30.14; H 2.13; S 67.74%. ^{1}H NMR (δ in $CDCl_3$) 2.45 (s, 6H, $-SCH_3$), 3.30 (s, 8H, $-SCH_2CH_2S-$), 4.15 (s, 2H, $-SCH_2S-$).

5) The averaged redox potentials of these waves are closed to the first one of BEDT-TTF ($E^1_{1/2}$ = 0.51 V). The third redox wave of **1** is irreversible and corresponds to a two-electron oxidation process; $E^3_{1/2}$ = 0.81 V.

6) Crystal data of **1**•ClO_4: $C_{19}S_{16}H_{16}ClO_4$ = 856.75, $P\bar{1}$, *triclinic*, a = 13.143(2), b = 14.554(1), c = 9.798(1)Å, α = 91.07(1), β = 102.86(1), γ = 119.812(7)°, V = 1566.7(3)Å^3, Z = 2, R = 0.082 for 2896 independent reflections.

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9) Crystal data of **1**•$(ClO_4)_{0.5}$: $C_{19}S_{16}H_{16}Cl_{0.5}O_2$ = 807.02, *C2/c*, *monoclinic*, a = 14.915(6), b = 30.47(1), c = 6.867(3)Å, β = 70.08(4)°, V = 3054(2)Å^3, Z = 4, R = 0.083 for 1958 independent reflections.

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