

Synthesis, Structure and Conductivity of the New Charge-transfer Salt $(\text{ET})_2(\text{CH}_2=\text{CH}-\text{CH}_2-\text{SO}_3)\cdot\text{H}_2\text{O}$

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Abstract: Electro-oxidation of 3,4,3', 4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalen (abbr. ET) in the presence of allylsulfonate affords a new charge-transfer salt $(\text{ET})_2(\text{CH}_2=\text{CH}-\text{CH}_2-\text{SO}_3)\cdot\text{H}_2\text{O}$. The single crystal structure of the title compound is determined to be in orthorhombic crystal system, *Pma2* space group. This salt is a semiconductor and its room-temperature conductivity is $0.0489 \Omega^{-1}\cdot\text{m}^{-1}$.

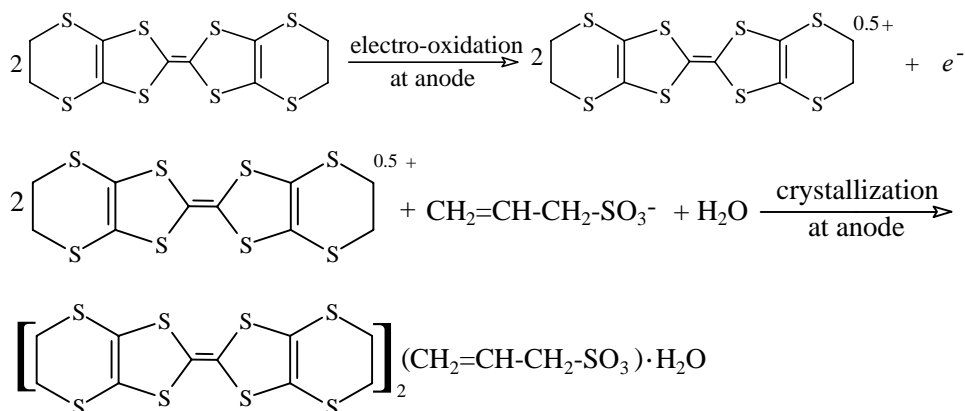
Keywords: ET, electro-oxidation, crystal structure, conductivity.

ET is one of the most famous electron-donor molecules, which forms charge-transfer complexes (abbr. CT-complexes) with various types of counterions. These complexes have received intense attention because a wide range of physical properties such as conductivity and superconductivity¹, ferromagnetism²⁻⁴ and nonlinear optical properties⁵ was found in these materials. Although the majority of the ET-based CT-complexes were prepared by combining with inorganic counterions, CT-complexes with organic counterions form a remarkable minority. To the best of our knowledge, the highest superconducting temperature of purely organic CT-complexes to date is obtained in $\beta''\text{-(ET)}_2\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3$ ($T_c = 5.2\text{K}$)⁶, which has given us inspiration to exploring new CT-salts containing sulfonate, and consequently the title organic conductor has been synthesized in our laboratory.

Synthesis and Structure

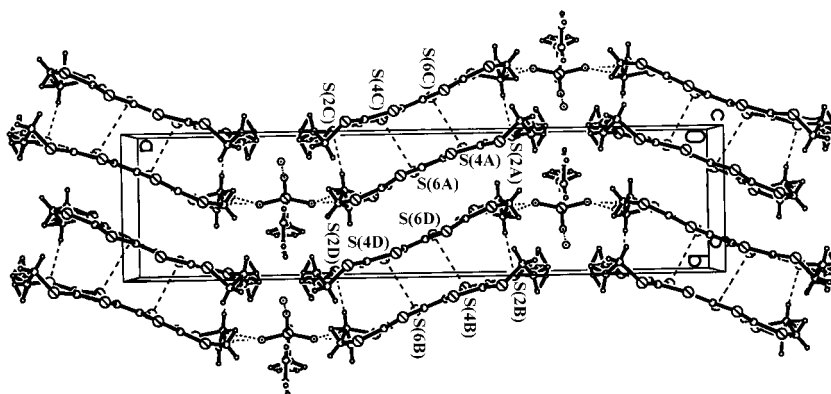
At a constant current of 1.5 μA , black rectangular plates were obtained by electro-chemical oxidation of a solution containing 7.3×10^{-4} mol/L of ET, 1.44×10^{-3} mol/L of allylsulfonic acid sodium salt (Tokyo Kasei Kogyo CO., LTD.) and 4.0×10^{-3} mol/L of 18-crown-6 ether in 1, 2-dichloroethane after 26 days. The oxidation process can be shown as follows:

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The X-ray diffraction data of the single crystal were collected on a Bruker P4 four-circle diffractometer and the structure was resolved by using SHELX-97 programs. Crystal data: $\text{C}_{11.5}\text{H}_{11.5}\text{O}_2\text{S}_{8.5}$, $M_r = 454.22$, orthorhombic crystal system, $Pma2$ space group, $a = 32.772(3) \text{ \AA}$, $b = 7.9604(7) \text{ \AA}$, $c = 6.6868(7) \text{ \AA}$, $V = 1744.5(3) \text{ \AA}^3$, $Z = 4$ and $R = 0.0541$.

Figure 1 Packing diagram viewed along the c -axis of the unit cell



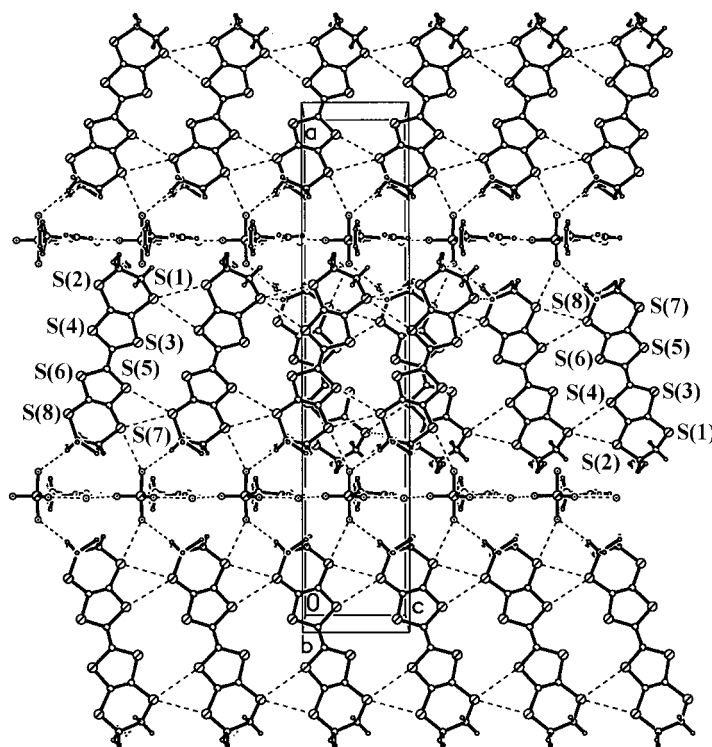
The dashed lines indicate S...S distances less than 3.7 Å.

Crystal structure is shown in **Figure 1** and **Figure 2**. A unit cell contains four crystallographically independent ET molecules, two allylsulfonate anions and two water molecules. The crystal arrangement of the title compound consists of slabs of cationic radicals, separated by thin layers of anions. Dimerised $\text{ET}^{0.5+}$ radicals are piled up in stacks forming staggered face-to-face type in the b -axis direction. $\text{ET}^{0.5+}$ radicals also form another kind of side-by-side uniform one-dimensional chains along the c -axis direction, which clearly indicates the absence of interstack definite dimmers. Comparison between close intrastack and interstack S...S distances, we can conclude that close S...S interactions of side-by-side type (parallel to the c -axis direction) are

much stronger than those of face-to-face type (parallel to b -axis direction). So $(\text{ET})_2(\text{CH}_2=\text{CH}-\text{CH}_2-\text{SO}_3)\cdot\text{H}_2\text{O}$ can be classified into one-dimensional molecular conductors.

The anion array consists of linear chains of allylsulfonate linked by hydrogen bonds of $\text{H12A}\dots\text{O1} = 2.5770 \text{ \AA}$ and $\text{H12A}\dots\text{O2} = 2.5594 \text{ \AA}$ to form thin layers parallel to the cationic layers, with which they form alternating stacks parallel to the a -axis. Water molecules are attached to linear chains of allylsulfonate by short contact $\text{O2}\dots\text{OW1} = 2.54(2) \text{ \AA}$. Furthermore, proximity interactions between anions and ET cationic radicals also appear, involving short contacts $\text{O3}\dots\text{S7} = 3.106(14) \text{ \AA}$ and $\text{O3}\dots\text{H10A} = 3.106(14) \text{ \AA}$, by means of which crystal maintains the stability of thin walls of anions.

Figure 2 Packing diagram viewed along the b -axis of the unit cell

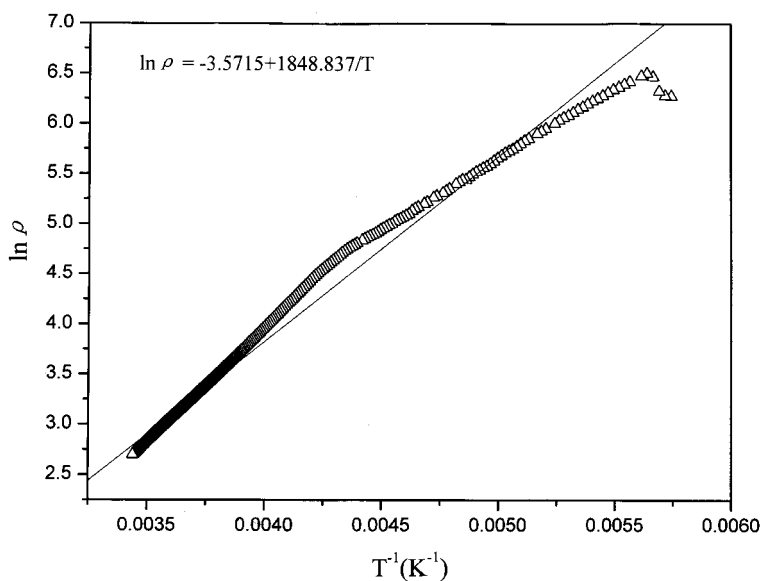


Conductivity

The conductivity measurements were made in the temperature range of 170-291K on the (100) plane of a single crystal along the [001] direction. The single crystal of the title compound has a room-temperature electrical conductivity of $0.0489 \text{ } \Omega^{-1}\cdot\text{m}^{-1}$. Varien-temperature resistance measurements show that the conductivity of the title

crystal is thermally activated.

Figure 3 plot of $\ln\rho$ vs. T^{-1} for $(\text{ET})_2(\text{CH}_2=\text{CH}-\text{CH}_2-\text{SO}_3)\cdot\text{H}_2\text{O}$



A plot of the the natural logarithm resistivity *versus* reciprocal temperature in the warming process is shown in **Figure 3**, which demonstrates a semiconductive behavior of the title compound (the resistivity data in warming process are more accurate in our experimental set-up). Calculated from the plot of the $\ln\rho$ *versus* T^{-1} in warming process, the activation energy of the crystal is 0.319 eV.

Acknowledgments

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