Superconductivity at 5.2 K in an Electron Donor Radical Salt of Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) with the Novel Polyfluorinated Organic Anion $SF_5CH_2CF_2SO_3^-$

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The approximately 1.5 decades since the discovery of superconductivity in organic radical cation salts, in 1980,[1] have seen a steady increase in the number of new organic superconductors.[2,3] The majority of superconducting salts are based on the electron donor molecule bis(ethylenedithio)tetrathiafulvalene, commonly abbreviated BEDT-TTF or ET. The highest superconducting temperatures (T_c) reported to date in this class of materials are 11.6 K (at ambient pressure) in κ-$(ET)_2Cu[N(CN)_2]Br$[4] and 12.8 K (at 0.3 kbar applied pressure) in κ-$(ET)_2Cu[N(CN)_2]Cl$.[5] While these salts contain *polymeric* charge-compensating anions, we have recently shown that with the use of large *discrete* counter ions similarly high transition temperatures can be obtained, *viz.*, $T_c = 11.1$ K in κ_H-$(ET)_2Ag(CF_3)_4\cdot$(1,1,2-trichloroethane).[6] Our search for new organic superconductors has thus led us to explore the suitability of large polyfluorinated anions, in analogy to these perfluorinated *organometallic* complex anions. In these systems, the presence of H···F hydrogen bonding is the prime building principle governing the specific packing arrangement of the ET molecule conducting layers. One such anion is the recently synthesized species $SF_5CH_2CF_2SO_3^-$,[7] which contains the novel hypervalent SF_5 substituent. In this paper, we report the discovery of superconductivity (diamagnetic onset transition temperature of 5.2 K) at ambient pressure in β''-$(ET)_2SF_5CH_2CF_2SO_3$, along with the synthesis and the crystal and band electronic structures of this novel salt.

Small single crystals of the title compound were synthesized by the electrocrystallization method, with the use of a mixture of $LiSF_5CH_2CF_2SO_3$[8] and 12-crown-4 in 1,1,2-trichloroethane as an electrolyte.[9] An initial current density of 0.20 $\mu A/cm^2$ was applied through the platinum wire electrodes and then increased to 0.41 $\mu A/cm^2$ after 1 week, at which point crystallization commenced. The crystal growth was continued for 35 days. Inferior crystals of the same composition and crystal structure, but with lower T_c values, were formed when tetrahydrofuran was used as a solvent.

The magnetic properties of the title compound were investigated on a Lake Shore model 7000 ac susceptometer, which is capable of reaching temperatures as low as 1.2 K. The real and imaginary parts of the ac susceptibility of numerous samples (both single crystals and multiple crystals) were measured under an applied ac field of 125 Hz frequency and 80 Am^{-1} (1 Oe) amplitude in the temperature range of 1.5−10 K. All samples exhibited the signature of bulk superconductivity, i.e., a precipitous drop of the real part (χ') to a large diamagnetic signal accompanied by a maximum of the imaginary part (χ'') near the transition. For the best samples, the highest onset transition temperatures of $T_{co} = 5.2$ K were measured, while in others the onset of superconductivity was depressed to as low as 4.0 K. The majority of the crystals exhibited T_{co} between 4.8 and 5.0 K. The transition widths ranged from 0.5 to 1.2 K (range between 10 and 90% saturation of the diamagnetic signal), illustrating the variation in sample quality.

Superconductivity was also recorded by the four-probe resistivity method. The electrical resistivity along an arbitrary direction within the *ab*-plane of a single crystal of β''-$(ET)_2SF_5CH_2CF_2SO_3$ (magnetic $T_{co} = 5.1$ K) upon cooling from room temperature increased as that in a semiconductor, went through a broad maximum around 100 K ($\rho_{100}/\rho_{298} \approx 10$), and then decreased in metallic fashion upon further cooling to ca. 6 K, where the resistivity was approximately the same as that at room temperature. Below 6 K, the resistivity started to drop (steepest slope at 5.1 K) to reach zero resistance at 4.4 K.

The crystal structure of β''-$(ET)_2SF_5CH_2CF_2SO_3$[10] contains conducting layers of radical cations alternating with anion layers, typical of most ET salts.[3] The unit cell consists of one layer of each. Four ET molecules (two crystallographically independent molecules and their centrosymmetrically related equivalents) make up the repeat unit within the layers, as shown in Figure 1. All ET molecules are oriented approximately parallel to each other, forming loose stacks along the *a*-direction. The short intermolecular contacts, representative of the orbital overlaps responsible for the delocalization of the valence electrons into

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[8] $Na(SF_5CH_2CF_2SO_3)$ was prepared according to ref 7. A solution of the Na salt was passed through an Amberlite IR-120 ion exchange column. The filtrate which contained the $SF_5CH_2CF_2SO_3H$ acid was neutralized with LiOH (MCB: ACS grade) to pH 8.8. This solution was reduced in volume and transferred to a round-bottomed flask where it was freeze dried to yield $Li(SF_5CH_2CF_2SO_3)$ as light brownish-white powder. The sample was further dried for 10 days over P_2O_5. Anal. Calcd: C, 8.64; H, 0.72; F, 47.8; S, 23.06. Found: C, 8.79; H, 0.98; F, 46.4; S, 22.36 (Ullrich, S. A., M.S. Thesis, Portland State University, 1994).

[9] ET (synthesized from the literature and recrystallized from chloroform; ∼7 mg, 18 mmol) was added to the anode chamber of a standard electrochemical H-cell. The $Li(SF_5CH_2CF_2SO_3)$ electrolyte (∼75 mg, 270 mmol), 12-crown-4 (3 drops), and 1,1,2-trichloroethane (∼7.5 mL, Aldrich, distilled from P_2O_5 and filtered through Al_2O_3) were added to each of the two chambers of the H-cell in an argon filled drybox.

[10] $(C_{10}H_8S_8)_2^{+}\cdot(C_2H_2F_7O_3S_2)^-$, fw 1040.45, $a = 9.1536(6)$ Å, $b = 11.4395(8)$ Å, $c = 17.4905(12)$ Å, $\alpha = 94.316(1)°$, $\beta = 91.129(1)°$, $\gamma = 102.764(1)°$, $V = 1779.9(2)$ Å^3, $Z = 2$, space group $P\bar{1}$, $T = 123$ K, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.941$ g cm^{-3}, $\mu = 11.136$ cm^{-1}, transmission coeff = 0.763−0.920, $R(F_o) = 0.046$, $R_w(F_o) = 0.045$. At 298 K, $a = 9.260(2)$ Å, $b = 11.635(2)$ Å, $c = 17.572(5)$ Å, $\alpha = 94.69(3)°$, $\beta = 91.70(1)°$, $\gamma = 103.10(2)°$, $V = 1835.5(9)$ Å^3.

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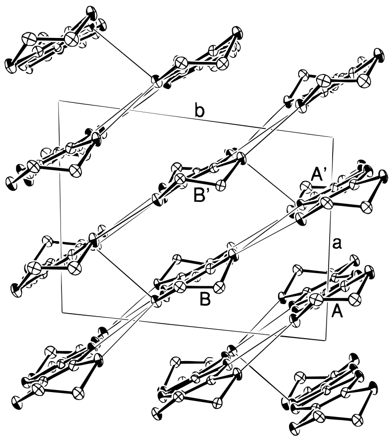

Figure 1. Projection of the conducting ET electron donor molecule layer in β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ approximately along the long axis of the ET molecule. Hydrogen atoms are omitted, and intermolecular S···S contacts shorter than 3.65 Å are indicated by thin lines. The letters A and B denote the two crystallographically independent ET molecules.

a conduction band, however, are primarily between molecules located on adjacent stacks (see Figure 1). The donor molecule packing motif is essentially the same as that found in β''-(ET)$_2$AuBr$_2$,[11−13] except for the doubling of the *b*-axis (caused by the larger size of the anion), thus we have adopted the same prefix (β''). Superconducting β''-(ET)$_4$[(H$_2$O)Fe(C$_2$O$_4$)]·C$_6$H$_5$-CN[14] also contains ET molecule layers of the β'' type, but it differs from the title compound in the number of conducting layers per unit cell. No crystal structure containing the SF$_5$CH$_2$CF$_2$SO$_3^-$ anion has been previously reported. The S−C−C−S backbone of the anion is in an essentially planar *trans*-conformation, with the substituents of the tetrahedrally coordinated atoms in the expected staggered conformations. A plane through the apical F-atom and two opposing equatorial F-atoms of the SF$_5$ group forms an angle of 12° with the plane of the backbone. Short contacts (less than the sum of the van der Waals radii) are formed by the BEDT-TTF hydrogen atoms and the anion: four to SF$_5$ fluorine atoms and six to SO$_3$ oxygen atoms. The larger number to the latter is due to the localization of the negative charge on the SO$_3$ group of the anion. These H···O and H···F contacts are likely responsible for the specific molecular packing of the crystal structure.

The ESR spectrum at room temperature of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ crystals consisted of a single resonance with line widths between 23 G ($g = 2.004$) and 34 G ($g = 2.012$), depending upon the orientation of the crystal within the magnetic field. The coincidence of line width maximum with the *g*-value maximum is typical of a β-like phase.[15,16] The variable temperature measurements showed a monotonic decrease in line width from 30 G at 300 K to 0.26 G at 5 K, while the spin susceptibility, in agreement with the electrical resistivity, decreased by about 40% between 300 and 100 K (semiconducting regime), was nearly constant from 100 to 10 K (metallic regime), and dropped precipitously below 10 K (onset of superconducting fluctuations, then bulk superconductivity).

The electronic band structure of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ was calculated by performing extended Hückel tight-binding calculations,[17,18] which show that the two highest bands are partially filled. The Fermi surfaces associated with these bands (Figure 2) consist of a hole pocket centered at *X* and a pair of wavy lines straddling along the *YM* line, thus β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ has both one-dimensional (1D) and two-dimensional (2D) Fermi surfaces. The 2D hole pocket should give rise to Shubnikov−de Haas oscillations (corresponding to 25.4% of the first Brillouin zone area) in magnetoresistance measurements. Figure 2 shows that adjacent hole pockets nearly touch, as do hole pockets and the 1D Fermi surface. Therefore, magnetoresistance measurements are also expected to exhibit an interesting breakdown phenomenon at high magnetic fields (see refs 19 and 20 for examples).

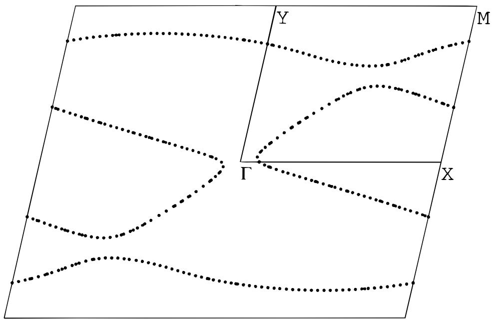

Figure 2. Fermi surfaces of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$. The closed pockets located at *X* and equivalent points are hole surfaces, whereas the wavy lines along the *YM* direction are electron surfaces ($\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $Y = (0, b^*/2)$, $M = (a^*/2, b^*/2)$).

β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ is the first example of an organic superconductor where not only the radical cation but also the charge-compensating anion consists of an organic molecule. The vast majority of organic superconductors contain diamagnetic metal complex anions, while the remainder of the previously reported superconducting salts contain small inorganic anions such as polyhalides.[3] Furthermore, the β''-structure type has only once been found to lead to superconductivity.[14] Both of these findings open up new avenues for the synthesis of new organic superconductors, possibly with higher transition temperatures.

Supporting Information Available: Figures showing the atomic labeling of both the cations and the anion; details of the crystal structure determination, positional and thermal parameters, bond lengths and angles (in the form of a CIF file) (12 pages). See any current masthead page for ordering and Internet access instructions.

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