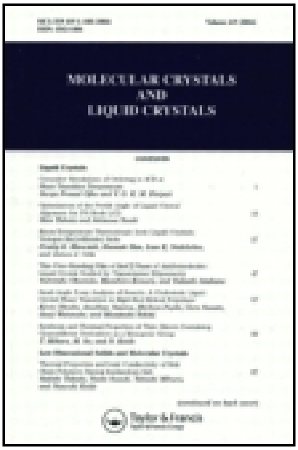

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Chemical modification of the superconducting β′-(ET) 2 SF 5 CH 2 CF 2 SO 3 structure through use of CF 3 C RR ″SO 3 - ANIONS

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CHEMICAL MODIFICATION OF THE SUPERCONDUCTING β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ STRUCTURE THROUGH USE OF CF$_3$C*RR*′SO$_3{}^-$ ANIONS

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Discrete, organic anions provide an attractive alternative for the synthesis of molecular superconductors. We have previously prepared the first completely organic superconductor, β''-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ [BEDT-TTF, hereafter abbreviated ET, is bis(ethylenedithio)tetrathiofulvalene]. Molecular metals which contain organic anions are essentially free of the magnetic impurities (i.e. Cu^{+2}) that often plague the physical property studies of organic superconductors such as κ-(ET)$_2$Cu[N(CN)$_2$]Br. We have undertaken a research effort aimed at the crystallization of conducting charge transfer salts which possess fluorinated alkylsulfonate anions as the charge compensating entities. Herein we report the extension of this work to include the synthesis and characterization of ET salts of the trifluoromethylsulfonate anions, CF$_3$CRR′SO$_3{}^-$ (R, R′ = F, H).

Keywords: organic superconductors; trifluoroethylsulfonate anions; bis(ethylenedithio)tetrathiafulvalene; crystal structure

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INTRODUCTION

We have previously crystallized the first ***truly organic*** superconductor, β''-$(ET)_2SF_5CH_2CF_2SO_3$, which has a T_c of 4.4 K [1]. These single-phase, stoichiometric crystals are indefinitely stable in air and essentially free of magnetic impurities, such as Cu^{+2}, that plague precise physical measurements of the more common κ-$(ET)_2Cu(SCN)_2$ and κ-$(ET)_2Cu[N(CN)_2]X$ ($X = Cl$, Br) superconductors. Thus, the β''-$(ET)_2SF_5CH_2CF_2SO_3$ salt is ideal for detailed physical property measurements.

In the search for new superconductors, the most significant feature of the β''-$(ET)_2SF_5CH_2CF_2SO_3$ salt is that it contains an anion with substantial modification potential: 1) The hydrogen and fluorine atoms on the carbon backbone can be exchanged in ten distinct configurations. 2) The carbon backbone can be lengthened or shortened, allowing even more H/F substitution patterns. 3) The SF_5 moiety can be replaced with groups such as CF_3, CH_3, CCl_3, etc. 4) the SO_3 moiety can be replaced with groups such as PO_3H, SeO_3, CO_2, etc. Through crystallization and characterization of ET salts containing these related anions, we have shown that minor structural changes result in significant physical property variations. As an example of the type 1 modification, we have crystallized the closely related β''-$(ET)_2SF_5CHFCF_2SO_3$ salt and explained the observed metal to insulator transition near 200 K with structural data and electronic band structure calculations [2]. We have studied type 2 modifications through the crystallization and characterization of the β''-$(ET)_2SF_5CH_2SO_3$, β'-$(ET)_2SF_5CF_2SO_3$, and β''-$(ET)_2SF_5CHFSO_3$ salts[3]. At 5 K, these compounds exhibit insulating, antiferromagnetic, and metallic states, respectively. Herein, we report initial results involving ET salts containing anions derived through a combination of modification types 2 and 3. Specifically, we describe the crystallization and preliminary characterization of β''-$(ET)_2CF_3CH_2SO_3$ (**I**), $(ET)_2Li(CF_3CHFSO_3)_2$ (**II**), and δ'-$(ET)_2CF_3CF_2SO_3$ (**III**).

TABLE I Unit Cell Constants for $(ET)_2CF_3CRR'SO_3^-$ (R, $R' = F$, H) Salts

	I	**II**	**III**
Sp. Grp.	$P\bar{1}$	$P\bar{1}$	$Pca2_1$
a (Å)	8.8777(5)	8.6403(3)	14.497(2)
b (Å)	11.7241(6)	11.4978(4)	6.6092(10)
c (Å)	17.2225(9)	20.3438(9)	35.169(6)
α (°)	77.295(2)	82.007(2)	90
β (°)	86.947(3)	80.055(2)	90
γ (°)	77.244(3)	80.639(2)	90
V (Å^3)	1705.5(2)	1951.3(1)	3369.8(1.4)
T (K)	298	150	150

SYNTHESIS

Crystals were grown by standard electrocrystallization techniques with 1,1,2-trichloroethane as the solvent [4]. Crystals of δ′-$(ET)_2CF_3CF_2SO_3$, $(ET)_2Li(CF_3CHFSO_3)_2$ and β″-$(ET)_2CF_3CH_2SO_3$ were grown from solutions of $PPN(CF_3CF_2SO_3)$ (metathesized from $LiCF_3CF_2SO_3$ [5]), 12-crown-4/$LiCF_3CHFSO_3$ and $PPN(CF_3CH_2SO_3)$, respectively.

CRYSTAL STRUCTURES

As with most ET-based salts, the crystal structures of **I**, **II**, and **III** consist of sheets of ET molecules separated by layers of charge compensating anions. Within the electron-donor sheets, short S···S contacts (< 3.6 Å) are observed between ET molecules in adjacent stacks. The hydrogen atoms on the ethylene end-groups of ET form hydrogen-bonding interactions with the anion layers.

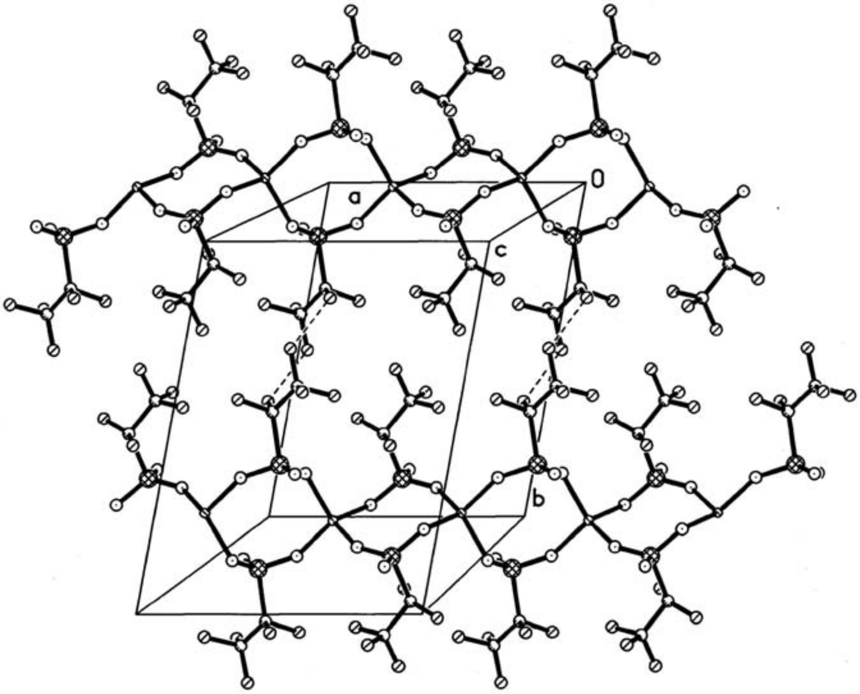

FIGURE 1 The anion layer in the $(ET)_2Li(CF_3CHFSO_3)_2$ strucure.

The ET molecules in β''-$(ET)_2CF_3CH_2SO_3$ pack in a motif isostructural to β''-$(ET)_2SF_5CH_2SO_3$, and similar to the β''-$(ET)_2SF_5CH_2CF_2SO_3$ superconductor. Two crystallographically independent ET molecules (A and B) are observed in each of these structures. The ET sheet in the β''-motif is characterized by tilted stacks of ET molecules. In the β''-$(ET)_2CF_3CH_2SO_3$ and β''-$(ET)_2SF_5CH_2SO_3$ structures, ET molecules A and B have different oxidation states and alternate along the stacking axis. The molecular tilt along the stacking axis is such that ET molecules in adjacent stacks are essentially coplanar. Thus, ribbons of ET molecules are observed, with alternating ribbons having different oxidation states.

When $LiCF_3CHFSO_3$ is used as an electrolyte for the electrocrystallization process with ET, a novel salt forms that contains a polymeric $Li(CF_3CHFSO_3)_2^-$ anion (Figure 2). The ET molecules in the $(ET)_2Li(CF_3CHFSO_3)_2$ structure pack in an arrangement that has a modified β''-motif in which the ET molecules within a stack are dimerized.

When crystallized with the $CF_3CF_2SO_3^-$ anion, ET packs in a rather uncommon δ'-motif [6] in which dimerized ET molecules are twisted with respect to the stacking axis.

PHYSICAL PROPERTIES

Similar to β''-$(ET)_2SF_5CH_2SO_3$, β''-$(ET)_2CF_3CH_2SO_3$ behaves as a semiconductor. Raman spectroscopic data show that the two crystal-

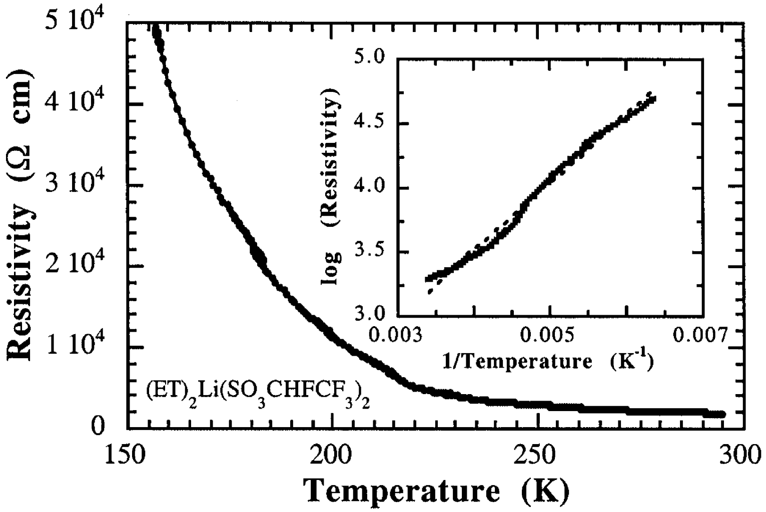

FIGURE 2 Resistivity of $(ET)_2Li(CF_3CHFSO_3)_2$ as a function of temperature. Inset shows an Arrhenius-type plot.

lographically independent molecules have different oxidation states, thus leading to charge localization. Four-probe electrical conductivity measurements indicate that single crystals of $(ET)_2Li(CF_3CHFSO_3)_2$ show semiconductive properties. (Figure 2) The data fit an Arrhenius-type model with an activation energy of 0.10 eV (Inset of Figure 2). Variable temperature ESR measurements reveal that the spin susceptibility of δ'-$(ET)_2CF_3CF_2SO_3$ decreases significantly below 50 K, typical of an antiferromagnetic phase transition.

CONCLUSIONS

Fluorinated alkyl sulfonate anions are shown to be versatile components of ET-based salts. Derivatives of the superconducting β''-$(ET)_2SF_5CH_2CF_2SO_3$ structure have been prepared through chemical modification of the organic anion. However, seemingly subtle alterations of the anion identity have resulted in drastic changes in the salt's physical properties. The observed properties have been explained on the basis of the packing motif of the ET molecules and the hydrogen bonding interactions between the ET molecules and the cocrystallized anions. We are currently investigating the use of various $CF_3CHFSO_3^-$ electrolytes in an attempt to grow crystals of $(ET)_2CF_3CHFSO_3$, which do not incorporate the Li^+ cation. Further extensions of this work to include additional alkyl sulfonate derivatives are also in progress.

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