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Rational Design of Organic Superconductors Through the Use of the Large, Discrete Molecular Anions $M(\text{CF}_3)_4^-$ ($M = \text{Cu}, \text{Ag}, \text{Au}$) and $\text{SO}_3\text{CF}_2\text{CH}_2\text{SF}_5^-$

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Abstract

A new approach to the synthesis of organic superconductors has recently been pioneered which involves the use of large, *discrete*, molecular anions as the charge-compensating entities in these charge transfer salts. The organic electron-donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) has been electrocrystallized with the novel organometallic $M(\text{CF}_3)_4^-$ ($M = \text{Cu}, \text{Ag}, \text{and Au}$) anions in a variety of 1,1,2-trihaloethane solvents. Over twenty organic superconductors have been synthesized which can be described by the general formula $(\text{ET})_2M(\text{CF}_3)_4(1,1,2\text{-trihaloethane})$. These solvated salts are shown to have highly anisotropic physical properties which can be tuned via modifications of each of their three molecular components: ET electron donor molecule, $M(\text{CF}_3)_4^-$ anion, and neutral 1,1,2-trihaloethane solvent molecule. Superconductivity has also been observed in an ET salt containing the discrete $\text{SF}_3\text{CH}_2\text{CF}_2\text{SO}_3^-$ anion with an onset temperature near 5.2 K.

Keywords: Electrocrystallization, organic superconductors

1. Introduction

The first organic superconductors, $(\text{TMTSF})_2\text{PF}_6$ ($T_c = 0.9$ K, 12 kbar) [1] and $(\text{TMTSF})_2\text{ClO}_4$ ($T_c = 1.4$ K, ambient pressure) [2] (TMTSF = tetramethyltetraselenafulvalene) contained small discrete anions. Subsequently, higher T_c s were achieved through the use of the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) electron donor molecule [3] with larger, discrete anions: $\beta\text{-(ET)}_2\text{I}_3$ ($T_c = 1.5$ K) [4], $\beta\text{-(ET)}_2\text{IBr}_2$ ($T_c = 2.8$ K) [5], and $\beta\text{-(ET)}_2\text{AuI}_2$ ($T_c = 5.0$ K) [6]. More recently, it has been discovered that when the ET electron-donor molecule is combined with large, complex, polymeric anions, organic superconductors with

significantly higher T_c s could be obtained: $\kappa\text{-(ET)}_2\text{Cu}(\text{SCN})_2$ ($T_c = 10.4$ K) [7], $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ ($T_c = 11.8$ K) [8], and $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ ($T_c = 12.8$ K, 0.3 kbar) [9].

Polymeric anions such as $\text{Cu}(\text{SCN})_2^-$ and $\text{Cu}[\text{N}(\text{CN})_2]X^-$ ($X = \text{Cl}^-, \text{Br}^-$) are formed *in situ* by a poorly understood mechanism during the electrocrystallization process. This greatly hinders the rational synthesis of salts containing polymeric anions. We have therefore pioneered an effort to prepare superconducting charge transfer salts through the use of large, discrete anions which can be rationally synthesized and modified prior to the electrocrystallization process. Because a myriad of large anions exist, initial studies have focussed on salts of monovalent anions which are stable toward oxidation, are capable of delocalizing electrical charge, and have an ability to interact with the hydrogen atoms of the ET molecule.

Following this methodology, we have recently reported the synthesis of a new family of ambient pressure organic superconductors containing over twenty members [10-14]. These salts, represented by the general formula: $(\text{ET})_2M(\text{CF}_3)_4(1,1,2\text{-trihaloethane})$ ($M = \text{Cu}, \text{Ag}, \text{Au}$), crystallize in two distinct crystallographic phases. Hexagonal plate-like crystals typical of

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the lower T_c phase (κ_L) have superconducting transition temperatures in the 2–6 K range. Crystals with a striated, needle-like morphology are characteristic of the higher T_c phase (κ_H) and have T_c s in the 9–11 K range. We report the first single crystal determinations of the T_c s of four κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1,1,2-trihaloethane) salts determined via ac susceptibility with the magnetic field aligned perpendicular to the conductive ac -plane.

Herein, we also report an extension of this research to include the electrocrystallization of the large, discrete SF $_5$ CH $_2$ CF $_2$ SO $_3^-$ anion with ET to form the new organic superconductor (T_c = 4.9 K) β'' -(ET) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$.

2. Synthesis and Characterization

Crystals of the (ET) $_2$ M(CF $_3$) $_4$ (1,1,2-trihaloethane) salts were grown in on platinum electrodes at ambient temperature for a period of two to four weeks according to a standard electrocrystallization procedure as previously described [13]. Crystals of β'' -(ET) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$ were prepared with a similar electrocrystallization procedure with the use of 1,1,2-trichloroethane or tetrahydrofuran as the crystallization solvent and a mixture of LiSF $_5$ CH $_2$ CF $_2$ SO $_3$ and 12-crown-4 as the supporting electrolyte [15].

Superconductivity was observed in both the (ET) $_2$ M(CF $_3$) $_4$ (1,1,2-trihaloethane) and β'' -(ET) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$ salts through the use of a prototype commercial ac susceptometer (Lake Shore Cryotronics, Inc.) equipped with a low temperature helium subpot option under an applied ac field of 125 Hz frequency and 80 Am $^{-1}$ (1 Oe) amplitude. Single crystal samples of the κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1,1,2-trihaloethane) salts were supported in a Delrin container with the magnetic field aligned perpendicular to the plate face ($H \perp ac$). Samples were cooled in zero field over a time period of 15 minutes. Magnetic susceptibility data were recorded while warming the samples in 0.05 K increments.

Unit cell parameters of the κ_L -(ET) $_2$ M(CF $_3$) $_4$ (1,1,2-trihaloethane) salts were determined by single crystal x-ray diffraction at ambient temperature by use of the novel CCD-area detector-based SMART X-ray diffractometer (Siemens Industrial Automation, Inc.)

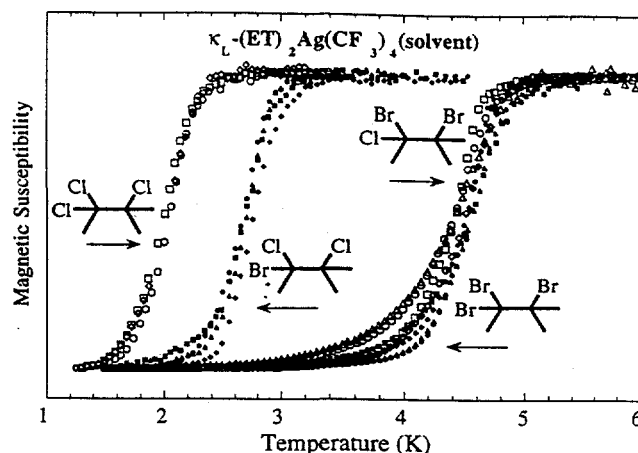


Fig. 1. Volume ac susceptibility data for single crystals of κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1,1,2-trichloroethane), κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1-bromo-1,2-dichloroethane), κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1,2-dibromo-1-chloroethane), and κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1,1,2-tribromoethane) measured with the field perpendicular to the conductive ac -plane. Susceptibility data has been normalized to account for demagnetization effects.

3. Discussion

It is clear from the superconducting transition temperatures of the κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1,1,2-trihaloethane) salts listed in Table 1 that the T_c s increase as the size of the cocrystallized 1,1,2-trihaloethane increases. This trend is also readily visible in Figure 1. This is consistent with experimental results involving the β -(ET) $_2$ X ($X = I_3^-$, IBr_2^- , AuI_2^-) and κ -(ET) $_2$ Cu[N(CN) $_2$]X ($X = Cl^-$, Br^-) families of superconductors which indicate that higher T_c s can be obtained by increasing the density of states at the Fermi level through the use of larger anions which forces the ET molecules further apart, reducing the lattice pressure.

As previously described [16], the 1,1,2-trihaloethane solvent molecule in κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1,1,2-trihaloethane) salts is disordered across a mirror plane with one halogen atom lying on the mirror plane, and a second on a general position.

Table 1.

Superconducting transition temperatures (T_c) at ambient pressure for four κ_L -(ET) $_2$ Ag(CF $_3$) $_4$ (1,1,2-trihaloethane) superconducting salts. Superconducting transition temperatures were determined on ac susceptibility data, uncorrected for demagnetization effects, according to the following definitions: T_{co} is the diamagnetic onset temperature, T_{cl} is the linear extrapolated mean-field T_c , T_{cm} is the temperature of the transition midpoint, T_{cz} is the temperature at the maximum in the imaginary component of the ac susceptibility. The 10–90% transition width, $\Delta T_{c(10-90\%)}$, is also tabulated.

1,1,2-trihaloethane	T_{co} (K)	T_{cl} (K)	T_{cm} (K)	T_{cz} (K)	$\Delta T_{c(10-90\%)}$
1,1,2-trichloroethane	2.31	2.14	1.88	1.68	0.54
1-bromo-1,2-dichloroethane	3.12	2.90	2.60	2.54	0.58
1,2-dibromo-1-chloroethane	4.90	4.42	3.70	3.77	1.52
1,1,2-tribromoethane	4.86	4.61	4.16	4.18	1.27

Thus, the three halogen atoms form the corners of an isosceles triangle. For the 1,1,2-trichloroethane and 1,1,2-tribromoethane, the corners of this triangle are fully occupied with chlorine and bromine atoms, respectively. The solvent disorder in these salts is essentially a result of the two orientations of the carbon and hydrogen positions. However, the salts which contain cocrystallized 1-bromo-1,2-dichloroethane or 1,2-dibromo-1-chloroethane have additional disorder as a result of the halogen positions. Provided that the disorder is completely random, for these two solvent molecules which have the monosubstituted halogen on the 1-position, the monosubstituted halogen resides on the mirror plane site 50% of the time and 25% of the time on both of the symmetry related sites. Because the 2-position of the 1,1,2-trihaloethane lies on the general site in the crystal structure, a solvent molecule with the monosubstituted halogen on the 2-position, such as 2-bromo-1,1-dichloroethane, will have the monosubstituted halogen on the symmetry related sites 50% of the time and never on the mirror plane site.

A slight increase in T_c is observed when one of the chlorine atoms in the disubstituted position is replaced with bromine. However, a more significant increase in T_c occurs when a second bromine atom is added to the 1,1,2-trihaloethane. A very small difference in T_c is observed between the 1,2-dibromo-1-chloroethane and 1,1,2-tribromoethane. Because the symmetry related site points more directly at the conducting ET sheets than the mirror plane site does, it is not surprising that bromine substitution on the general position will have a greater impact on the charge transport properties than substitution on the mirror plane site (which points parallel to the conducting sheets).

In general, disorder in charge transfer salts destroys superconductivity. For example, the β -(ET)₂I₂Br salt would be expected to be a superconductor similar to the isostructural β -(ET)₂X (X = I₃⁻, AuI₂⁻, IBr₂⁻) salts, except that the asymmetric I₂Br⁻ anion causes random potentials within the crystal which are detrimental to superconductivity [17]. Similarly, superconductivity is destroyed in (TMTSF)₂ClO₄ if the sample is cooled too quickly, thus locking the ClO₄⁻ anion into a disordered configuration [18]. It is remarkable that the κ_L -(ET)₂M(CF₃)₄(1,1,2-trihaloethane) (M = Cu, Ag, Au) salts superconduct even though they possess considerable disorder in both the anion and cocrystallized solvent. Here we have shown that further increasing the disorder on the solvent site by mixing

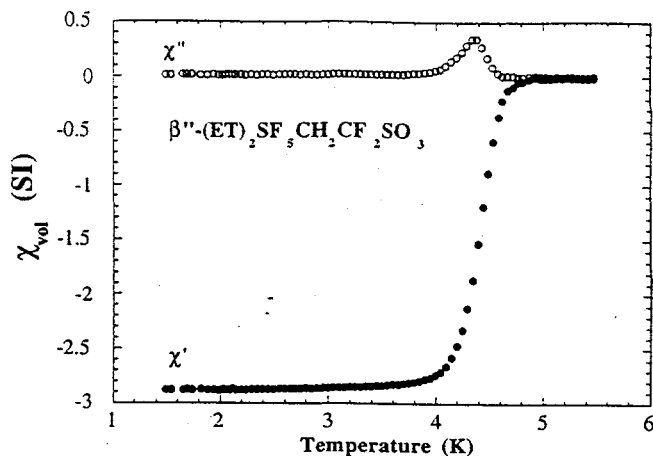


Fig. 2. Volume ac susceptibility χ_{vol} (SI units) of β'' -(ET)₂SF₅CH₂CF₂SO₃ as a function of temperature with the real (in-phase) component denoted as χ' and the imaginary (out-of-phase) component denoted as χ'' . The superconducting onset appears at 4.9 K.

the halogen atoms (bromine and chlorine) does not hinder the formation of the superconducting state substantially. Consequently, the superconducting transition temperatures increase as the size of the solvent molecule is increased, regardless of the increased disorder, following the trend observed in the uniformly substituted 1,1,2-trichloroethane and 1,1,2-tribromoethane salts.

The unit cell parameters for four κ_L -(ET)₂Ag(CF₃)₄(1,1,2-trihaloethane) salts, determined by x-ray diffraction at ambient temperature, are listed in Table 2. The length of the *a*- and *b*-axes and the unit cell volume increase with the size of the cocrystallized solvent molecule. However, the maximum in the *c*-axis length occurs in the κ_L -(ET)₂Ag(CF₃)₄(1-bromo-1,2-dichloroethane) salt, which contains a cocrystallized solvent of intermediate volume. Thus, modification of the 1,1,2-trihaloethane molecule through halogen atom substitution affects the solid state packing of these salts in a complex manner. A more quantitative understanding of the effect of solvent and anion substitution on the superconducting transition temperature will require additional x-ray structural characterization of each of the fifteen κ_L -(ET)₂M(CF₃)₄(1,1,2-trihaloethane) salts in order to determine subtle changes of intermolecular contacts.

Table 2.

Unit cell parameters at ambient temperature for four isostructural κ_L -(ET)₂Ag(CF₃)₄(1,1,2-trihaloethane) superconducting salts.

1,1,2-trihaloethane	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
1,1,2-trichloroethane	13.159(11)	38.11(4)	8.591(2)	4308(9)
1-bromo-1,2-dichloroethane	13.207(4)	38.122(6)	8.598(6)	4329(4)
1,2-dibromo-1-chloroethane	13.228(2)	38.227(5)	8.579(2)	4338(1)
1,1,2-tribromoethane	13.270(6)	38.284(12)	8.588(4)	4363(4)

We have extended our search for new organic superconductors to include charge transfer salts of other large, discrete, monovalent anions. Again, our efforts have been rewarded with the discovery of superconductivity in β'' -(ET) $_2\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3$, which contains the novel $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3^-$ anion. As illustrated in Figure 2, the ac susceptibility of this salt shows the magnetic onset of superconductivity at 4.9 ± 0.3 K. Similar to the case of the highly successful (ET) $_2\text{M}(\text{CF}_3)_4(1,1,2\text{-trihaloethane})$ series of superconductors, the $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3^-$ anion can be easily modified through chemical methods to yield related anions which will likely yield additional superconducting salts.

4. Conclusions

We have demonstrated that the crystallization of large, discrete anions with electron donor molecules, such as ET, is a viable route to the synthesis of new organic superconductors. Two distinct superconducting phases have been prepared through the use of the $\text{M}(\text{CF}_3)_4^-$ anions, κ_L - and κ_H -(ET) $_2\text{M}(\text{CF}_3)_4(1,1,2\text{-trihaloethane})$, yielding twenty-one superconducting salts with superconducting transition temperatures ranging from 2.1 to 11.1 K. Additional superconducting salts based on this system will likely be prepared in the future. Surprisingly, the disordered anion and solvent molecules in the κ_L -(ET) $_2\text{M}(\text{CF}_3)_4(1,1,2\text{-trihaloethane})$ salts does not destroy the superconducting state. It is likely that the synthesis of related salts with ordered anions or solvent molecules would result in materials with higher T_c s.

Preparation of the superconducting β'' -(ET) $_2\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3$ salt illustrates that the above methodology is not specific to the $\text{M}(\text{CF}_3)_4^-$ anions, but can be expanded to include a large variety of novel anions. Such systems are easily modifiable through chemical techniques and have the potential to form isostructural series of salts. Development of structure/property relationships in such series of materials will provide a key to understanding the superconducting mechanisms in these molecular metals.

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