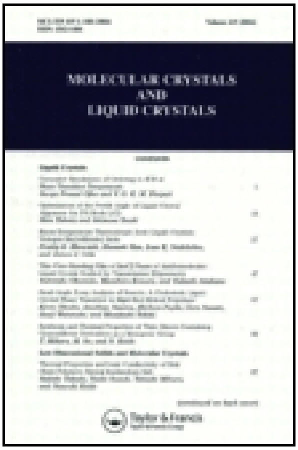

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Synthesis and Physical Properties of a Novel, Highly Tunable Family of Organic Superconductors: $(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) (M = Cu, Ag, Au)

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SYNTHESIS AND PHYSICAL PROPERTIES OF A NOVEL, HIGHLY TUNABLE FAMILY OF ORGANIC SUPERCONDUCTORS: $(ET)_2M(CF_3)_4$(1,1,2-TRIHALOETHANE) (M = CU, AG, AU)

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Abstract Electrocrystallization of the bis(ethylenedithio)tetrathiafulvalene (ET) electron donor molecule with the novel $M(CF_3)_4^-$ (M = Cu, Ag, and Au) anions in a variety of 1,1,2-trihaloethane solvents has led to the discovery of a remarkable series of 21 organic superconductors. These $(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) salts occur in two structural modifications of the κ-type packing motif. Crystals of the plate-like morphology have superconducting transition temperatures in the range 2 - 5.8 K (low T_c phase, κ_L), while the transitions of the needle-like morphology are in the range 9.2 - 11.1 K (high T_c phase, κ_H).

INTRODUCTION

Currently, the cation-radical organic superconductors with the highest superconducting transition temperatures are comprised of sheets of dimerized bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF, or ET) electron-donor molecules, arranged in a parquet motif, separated by layers of polymeric anions. Materials containing this type of packing arrangement of ET molecules have been designated as κ-phase salts. The charge transfer salts with the highest T_cs are κ-$(ET)_2Cu(SCN)_2$[1] and members of the κ-$(ET)_2Cu[N(CN)_2]X$ (X = Cl, Br, CN) series.[2-4] All of these superconductors contain polymeric anions which are prepared *in situ* during the electrocrystallization process via a poorly understood "self-assembly" process.

In an attempt to provide greater control over the synthesis of new organic superconductors, we have recently pioneered a new approach for the preparation of κ-phase molecular superconductors. This approach involves the electrocrystallization of large, discrete anions with the electron donor molecules. Since a vast quantity of such anions exist, prudent choices must be made in selecting the most promising ones. Criteria which we feel are important include: symmetry, ability to delocallize charge over a large region of space, and the ability to form hydrogen bonds with the ethylene group hydrogen atoms of ET. The novel $M(CF_3)_4^-$ (M = Cu, Ag, and Au) anions met these criteria, and upon electrocrystallization with ET have yielded a plethora of new superconductors.

To date, we have identified two superconducting phases which contain $M(CF_3)_4^-$ anions. One phase, which typically crystallizes with a plate-like morphology, and has T_cs below 6 K, and has been designated as the κ_L-phase (L signifies the lower T_c phase). A second phase, which crystallizes in a filamentary needle-like morphology, has superconducting transition temperatures in the range 7-11 K and has been named the κ_H-phase (where the subscript H signifies the higher T_c phase). Both of these phases contain molecules of the crystallization solvent in the solid state structure. Thus, not only can these two phases be modified via exchange of the anion's metal atom, but also by replacement of the crystallization solvent. To date, we have discovered five 1,1,2-trihaloethane solvents which produce superconducting salts, resulting in 21 distinct organic superconductors. The tunability of this system is unprecedented among molecular superconductors, and many more members of this family are certain to be discovered.

SYNTHESIS AND CHARACTERIZATION

Crystals of $(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) were grown according to a standard electrocrystallization procedure, as previously described.[5] ET (10 mg, 0.026 mol, Strem Chemicals, recrystallized from chloroform) was added to the anode chamber of an H-cell. About 25 mg of PPN[$M(CF_3)_4$] [PPN = bis(triphenyl-phosphoranylidene)ammonium, M = Cu, Ag, Au], prepared via the literature method,[6, 7] was added to both chambers of the cell. The H-cell was then filled with 15 ml of 1,1,2-trihaloethane solvent (1,1,2-trichloroethane, 1,1,2-tribromoethane, 1,2-dibromo-1-chloroethane, 1-bromo-1,2-dichloroethane or 2-bromo-1,1-dichloroethane), prepared and purified as previously reported.[5] Crystals were grown on platinum electrodes at 25 °C with a current density of 0.2 $\mu A/cm^2$. In 1,1,2-trihaloethane, needle-like crystals of the κ_H-phase began to grow within a day. After about a week, chains of plate-like crystals of the κ_L-phase began to grow along the κ_H-needles. When brominated solvents were used, the initial growth was in the form of κ_L-plates, but sometimes small amounts of κ_H-needles were observed, intergrown with the plate-like morphology. All crystals were stored on dry ice after harvesting as a precautionary measure to prevent decomposition via solvent loss.

Superconductivity was detected in both the κ_H- and κ_L-phases with the use of an ac susceptometer (Lake Shore Cryotronics, Inc.) operating with a 1 G modulation field and a frequency of 125 Hz. Samples were cooled from room temperature over a time period of 15 minutes and magnetic susceptibility data were recorded while warming. The ESR measurements were performed with the use of an IBM ER-200 X-Band spectrometer with a TE_{102} rectangular cavity.

RESULTS AND DISCUSSION

It has been shown that the onset superconducting transition temperatures of randomly oriented, multiple crystal samples of the κ_L-$(ET)_2M(CF_3)_4$(1,1,2-trichloroethane) (M = Cu, Ag, Au) series are 4.0, 2.4, and 2.1 K, respectively.[8-10] Additional superconducting κ_L-$(ET)_2M(CF_3)_4(CHX_2CH_2X)$ (X = Cl, Br) salts have been prepared by selectively exchanging the chlorine atoms of the cocrystallized 1,1,2-trichloroethane solvent molecule with bromine.[5] By electrocrystallizing the three $M(CF_3)_4^-$ anions in five different 1,1,2-trihaloethane solvents a total of fifteen superconducting salts have been prepared with superconducting transition temperatures in the range 2.1 to 5.8 K. The T_cs of these superconducting salts are listed in Table I.

Crystals of κ_H-$(ET)_2M(CF_3)_4$(1,1,2-trichloroethane) (M = Cu, Ag, Au) typically begin to grow shortly after electrocrystallization commences. These needle-like crystals grow for only a few days before plates of the corresponding κ_L-phase begin growing along the needle axis. The way that the κ_H-phase often acts as a seed for growth of the κ_L-phase suggests that these phases may be structurally related. The very filamentary nature of the κ_H-needles has impeded initial characterization efforts. When 1,1,2-trichloroethane is chosen as the crystallization solvent, thick black plates of the κ_L-phase can easily be grown and characterized. When brominated solvents are used, the κ_L-phase grows as thinner, sometimes flaky, black plates. Growth of the κ_H-phase is hindered by the use of brominated 1,1,2-trihaloethanes. The majority of crystals grown from these brominated solvents are thus of the κ_L-phase. Quite often large, shiny black rod-shaped crystals of the non-solvated $(ET)_2M(CF_3)_4$ salt cocrystallize in the same electrocrystallization cell as the κ_H- and κ_L-phases.[11] This is the only phase which has crystallized when solvents other than 1,1,2-trihaloethanes have been used.

ESR is a very useful tool for identifying the three different phases of crystals which often grow simultaneously in the same electrocrystallization cell. The ambient

TABLE I Summary of onset superconducting transition temperatures in the κ-(ET)$_2M$(CF$_3$)$_4$(1,1,2-trihaloethane) (M = Cu, Ag, Au) family. These $T_{\rm co}$s were determined via ac susceptibility measurements on bulk crystals.

Compound	$T_{\rm co}$ (K)
κ_H-(ET)$_2$Ag(CF$_3$)$_4$(1,1,2-trichloroethane)	11.1
κ_H-(ET)$_2$Au(CF$_3$)$_4$(1,1,2-trichloroethane)	10.5
κ_H-(ET)$_2$Ag(CF$_3$)$_4$(2-bromo-1,1-dichloroethane)	10.2
κ_H-(ET)$_2$Cu(CF$_3$)$_4$(1,1,2-trichloroethane)	9.2
κ_H-(ET)$_2$Ag(CF$_3$)$_4$(1-bromo-1,2-dichloroethane)	7.3
κ_H-(ET)$_2$Ag(CF$_3$)$_4$(1,1,2-tribromoethane)	7.2
κ_L-(ET)$_2$Au(CF$_3$)$_4$(1,1,2-tribromoethane)	5.8
κ_L-(ET)$_2$Cu(CF$_3$)$_4$(1,2-dibromo-1-chloroethane)	5.5
κ_L-(ET)$_2$Cu(CF$_3$)$_4$(1,1,2-tribromoethane)	5.2
κ_L-(ET)$_2$Au(CF$_3$)$_4$(2-bromo-1,1-dichloroethane)	5.0
κ_L-(ET)$_2$Au(CF$_3$)$_4$(1,2-dibromo-1-chloroethane)	5.0
κ_L-(ET)$_2$Cu(CF$_3$)$_4$(2-bromo-1,1-dichloroethane)	4.9
κ_L-(ET)$_2$Ag(CF$_3$)$_4$(1,1,2-tribromoethane)	4.8
κ_L-(ET)$_2$Ag(CF$_3$)$_4$(1,2-dibromo-1-chloroethane)	4.5
κ_L-(ET)$_2$Ag(CF$_3$)$_4$(2-bromo-1,1-dichloroethane)	4.1
κ_L-(ET)$_2$Cu(CF$_3$)$_4$(1,1,2-trichloroethane)	4.0
κ_L-(ET)$_2$Ag(CF$_3$)$_4$(1-bromo-1,2-dichloroethane)	3.8
κ_L-(ET)$_2$Cu(CF$_3$)$_4$(1-bromo-1,2-dichloroethane)	3.5
κ_L-(ET)$_2$Au(CF$_3$)$_4$(1-bromo-1,2-dichloroethane)	3.2
κ_L-(ET)$_2$Ag(CF$_3$)$_4$(1,1,2-trichloroethane)	2.4
κ_L-(ET)$_2$Au(CF$_3$)$_4$(1,1,2-trichloroethane)	2.1

temperature line widths of the κ_H- and κ_L-$(ET)_2Cu(CF_3)_4$(1,1,2-trichloroethane) phases are 6.3-6.7 G and 70-84 G, respectively.[12] The non-solvated, $(ET)_2Cu(CF_3)_4$, phase has an intermediate, but distinct line width of 35-40 G. The angular dependence of the ESR signal suggests that both the κ_L- and κ_H-phases contain a κ-type structure. The line width of the κ_L-phase is typical for κ-phase salts while the line width of the κ_H-phase is substantially narrower than is normally observed for this phase, suggesting a significant structural difference between these two phases.

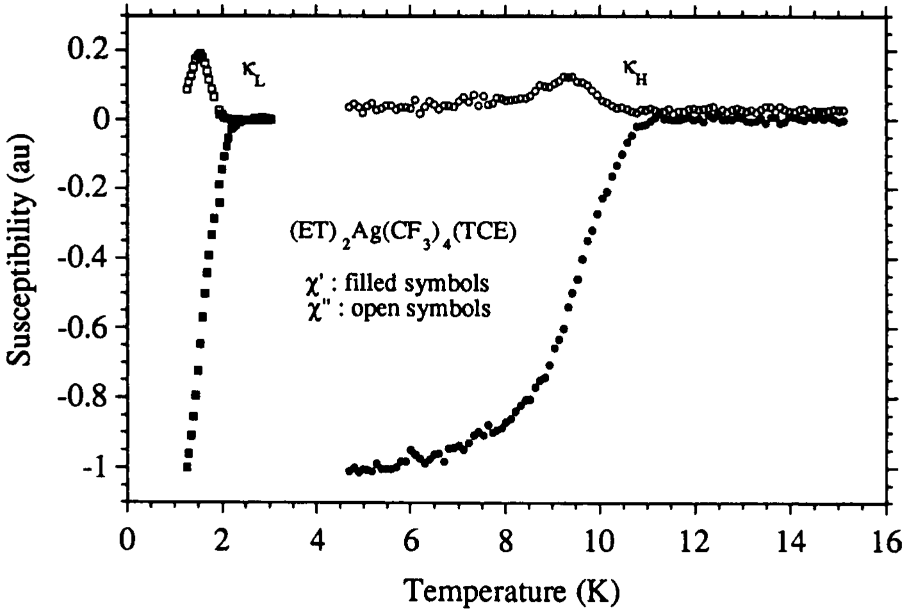

FIGURE 1 Ac susceptibility as a function of temperature for both superconducting phases of $(ET)_2Ag(CF_3)_4$(TCE). Onset T_c = 2.4 K (κ_L-phase) and 11.1 K (κ_H-phase).

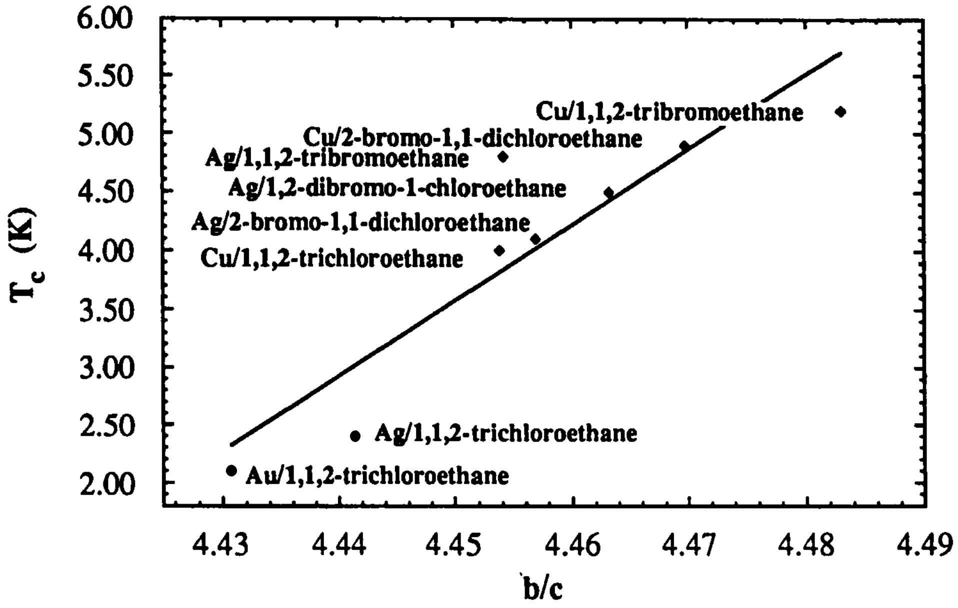

FIGURE 2 Superconducting transition temperatures, as determined from ac susceptibility data collected on randomly oriented multiple crystal samples of various members of the κ_L-$(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) family.

We report an initial attempt to correlate structural and physical properties of the κ_L-$(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) superconductors. Unit cell parameters for several members of this family have been determined via X-ray diffraction at ambient temperature. The relationship between the superconducting transition temperature and any single unit cell length or the cell volume failed to show any discernible correlation. More complex combinations of these parameters revealed that the T_cs of these salts depend simultaneously on one of the intralayer repeat units (c, negative correlation) and the interlayer spacing (b, positive correlation). Over the restricted numeric range of b and c, it is convenient to make the b/c ratio the dependent variable. This correlation is illustrated in figure 2.

CONCLUSION

The use of large discrete anions provides an attractive route to the synthesis of new ET-based κ-phase organic superconductors. Fifteen charge-transfer salts of the κ_L-phase containing the $M(CF_3)_4^-$ anions and 1,1,2-trihaloethanes have been synthesized to date. In addition, these same components have so far yielded six superconductors of the κ_H-phase. It is likely that additional superconductors in the κ-$(ET)_2M(CF_3)_4$(solvent) will be synthesized in the future. As more accurate values for T_c are determined from single crystal studies, trends which relate the physical and structural properties of these salts will become more evident. After complete X-ray crystal structures are determined on these salts, it will be possible to have a much deeper understanding of how minor structural variations affect the charge transport properties of these fascinating materials.

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