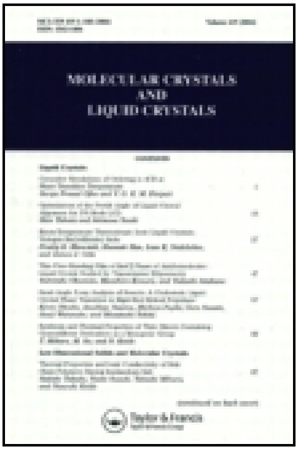

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New Organic Superconductors in the System $(ET)_2$ $M(CF_3)_4$(Solvent) (M = Cu, Ag, Au): Dramatic Effects of Organometallic Anion and Solvent Replacement

John A. Schlueter [a] , Jack M. Williams [a] , Urs Geiser [a] , Hau H. Wang [a] , Aravinda M. Kini [a] , Margaret E. Kelly [a] , James D. Dudek [a] , Dieter Naumann [b] & Thomas Roy [b]

[a] Chemistry and Materials Science Divisions, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL, 60439, USA

[b] Institut für Anorganische Chemi, Universität Köln, Greinstrasse 6, D-50939, Köln, Germany

Version of record first published: 24 Sep 2006.

To cite this article: John A. Schlueter , Jack M. Williams , Urs Geiser , Hau H. Wang , Aravinda M. Kini , Margaret E. Kelly , James D. Dudek , Dieter Naumann & Thomas Roy (1996): New Organic Superconductors in the System $(ET)_2$ $M(CF_3)_4$(Solvent) (M = Cu, Ag, Au): Dramatic Effects of Organometallic Anion and Solvent Replacement, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 285:1, 43-50

To link to this article: http://dx.doi.org/10.1080/10587259608030776

Mol. Cryst. Liq. Cryst., 1996, Vol. 285, pp. 43–50
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NEW ORGANIC SUPERCONDUCTORS IN THE SYSTEM $(ET)_2M(CF_3)_4$(SOLVENT) (M = Cu, Ag, Au): DRAMATIC EFFECTS OF ORGANOMETALLIC ANION AND SOLVENT REPLACEMENT

JOHN A. SCHLUETER, JACK M. WILLIAMS, URS GEISER, HAU H. WANG, ARAVINDA M. KINI, MARGARET E. KELLY & JAMES D. DUDEK
Chemistry and Materials Science Divisions, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

DIETER NAUMANN & THOMAS ROY
Institut für Anorganische Chemi, Universität Köln, Greinstrasse 6, D-50939 Köln, Germany

Abstract Over twenty molecular-based superconductors have been synthesized recently via electrocrystallization of the organic bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) electron donor molecule with the novel organometallic $M(CF_3)_4^-$ (M = Cu, Ag, and Au) anions in a variety of 1,1,2-trihaloethane solvents. The highly anisotropic physical properties of these solvated $(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) salts can be tuned via modifications of each of their three *discrete* molecular components. These unique salts crystallize in two distinct structural modifications of the κ-type packing motif (sheets of dimerized electron-donor molecules arranged in a parquet fashion). Crystals of the lower T_c phase (κ_L) have a plate-like morphology and superconducting transition temperatures in the 2 - 6 K range, while the transitions of the higher T_c phase (κ_H), which typically have a needle-like morphology, are in the 9 - 11 K range. The synthesis, structure, and physical properties of this new family of materials will be discussed.

INTRODUCTION

The first organic superconductors were charge transfer salts composed of the tetramethyltetraselenafulvalene (TMTSF) electron-donor molecule and small, discrete anions. Molecular metals such as $(TMTSF)_2PF_6$[1] and $(TMTSF)_2ClO_4$[2] required very low temperatures, and often external applied pressure, in order to stabilize a superconducting state. Subsequently, crystallization of the extended electron donor molecule, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) with larger charge-compensating anions resulted in higher superconducting transitions temperatures in molecular superconductors of the β-$(ET)_2X$ (X = IBr_2^-, AuI_2^- and I_3^-) family.[3-5] The search for superconductivity in salts containing even larger anions led to the discovery of κ–$(ET)_2Cu(SCN)_2$[6] and the κ–$(ET)_2Cu[N(CN)_2]X$ (X = Cl, Br, CN) series.[7-9] These latter salts were the first to possess superconducting transition temperatures above 10 K. However, each contains complex, polymeric anions which are formed *in situ* during the electrocrystallization process by a poorly understood and difficult-to-control "self-assembly" process.

We have recently pioneered a new approach to fabricating novel organic superconductors through the use of large, discrete, monovalent anions. Such anions can be synthesized rationally and modified through chemical methods and conveniently introduced into the electrochemical cell. This method provides much greater control over the identity of the anion species in final cation-radical salts, allowing minor anion modifications to be made rationally prior to the electrocrystallization step. Because an enormous selection of large, monovalent anions exists, a plethora of distinct charge transfer salts could potentially be synthesized. This necessitates a careful choice when selecting anions as components of potential new organic superconductors. Several of the criteria that we feel are important for anions to satisfy include: rigidity, symmetry, charge delocalization and hydrogen bonding capabilities.

Utilizing the above strategy, the $M(CF_3)_4^-$ (M = Cu, Ag, Au) anions were chosen as likely candidates for the preparation of superconducting charge transfer salts. We have recently electrocrystallized two distinct superconducting phases which contain the ET electron-donor molecule and these $M(CF_3)_4^-$ anions.[10-14] Both of these phases contain cocrystallized solvent molecules. Through metal atom modification of the anion and halogen substitution of the 1,1,2-trihaloethane solvent molecule, a series of superconducting salts has been synthesized. The crystal phase with lower superconducting transition temperatures typically crystallizes with a plate-type morphology and has been termed the κ_L-phase (L signifies lower T_c) because the dimerized ET electron donor molecules are arranged in a parquet pattern (κ-motif). The second phase, termed the κ_H-phase (H signifies higher T_c), typically grows as thin bundles of needle-like crystals. Although the filamentary nature of these crystals has made initial X-ray structural determination efforts difficult, preliminary diffraction patterns indicate that this phase has a similar κ-type structure. This $(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) ternary system has, in a short time, yielded the most tunable family of organic superconductors. To date, twenty one superconductors have been discovered in this family with a wide range of T_cs (κ_L-phase: fifteen superconductors, T_c = 2.1 - 5.8 K, κ_H-phase: six superconductors, T_c = 7.2 - 11.1 K).

SYNTHESIS AND CHARACTERIZATION

Crystals of the $(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) superconducting salts were grown according to a standard, previously reported, electrocrystallization procedure.[13] ET and d_8-ET were synthesized in strictly parallel syntheses according to the literature method and recrystallized from chloroform prior to use. Single crystals of κ_L-(h_8-ET)$_2$Ag(CF$_3$)$_4$(1,1,2-tribromoethane) and κ_L-(d_8-ET)$_2$Ag(CF$_3$)$_4$(1,1,2-tribromoethane) were grown in parallel experiments: about 10 mg of the electron-donor molecule was added to the anode chamber of an electrochemical H-cell. PPN[M(CF$_3$)$_4$] (~25 mg), prepared according to the method of Naumann and Roy,[15, 16] was added to both chambers. The H-cell were then filled with 2 to 15 ml of 1,1,2-trihaloethane (1,1,2-trichloroethane, 1-bromo-1,2-dichloroethane, 2-bromo-1,1-dichloroethane, 1,2-dibromo-1-chloroethane, or 1,1,2-tribromoethane) solvent, which was prepared and purified as described previously.[13] Shiny, black crystals were grown at 25 °C on platinum wire electrodes with an initial current density of 0.2 μA/cm^2. After harvesting, all crystals were stored on dry ice to prevent possible decomposition as a result of solvent loss.

Superconductivity was detected, and T_cs determined for both the κ_L- and κ_H-phases, with the use of a commercial 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 to 1.5 K over a time period of about fifteen minutes and the magnetic susceptibility data were recorded while warming. Four single plate-like crystals of both κ_L-(h_8-ET)$_2$Ag(CF$_3$)$_4$(1,1,2-tribromoethane) and κ_L-(d_8-ET)$_2$Ag(CF$_3$)$_4$(1,1,2-tribromoethane) were chosen for ac susceptibility studies. These studies were performed with the magnetic field perpendicular to the conductive *ac* plane. The T_cs of the superconducting samples were determined according to four different definitions: T_{co} is the diamagnetic onset, T_{cl} is the linearly extrapolated mean-field value, T_{cm} is the midpoint of the superconducting transition, and χ''_{max} is the maximum in the imaginary component of the ac susceptibility. 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

The electrocrystallization solvent has a strong influence on the phase and morphology of crystals formed. When 1,1,2-trichloroethane is used as a solvent, crystal growth in the form of black needle-like crystals generally begins within a day. Within a week, well formed, thick, black, plate-like crystals begin to form both directly on the platinum anode and in chains along the needle-like crystals. In brominated solvents, crystal growth is primarily in the form of thin black plates of κ_L–$(ET)_2M(CF_3)_4$(1,1,2-

TABLE I Onset superconducting transition temperatures (T_{co}) of bulk, randomly oriented crystals of κ_L-(ET)$_2M$(CF$_3$)$_4$(1,1,2-trihaloethane) salts.

Solvent	M = Cu	M = Ag	M = Au
1,1,2-trichloroethane	4.0 K	2.4 K	2.1 K
1-bromo-1,2-dichloroethane	3.5 K	3.8 K	3.2 K
2-bromo-1,1-dichloroethane	4.9 K	4.1 K	5.0 K
1,2-dibromo-1-chloroethane	5.5 K	4.5 K	5.0 K
1,1,2-tribromoethane	5.2 K	4.8 K	5.8 K

trihaloethane). In 1,1,2-tribromoethane, thin flaky plates of κ_L–(ET)$_2M$(CF$_3$)$_4$(1,1,2-tribromoethane) are predominantly formed, with very limited growth of the κ_H–(ET)$_2M$(CF$_3$)$_4$(1,1,2-tribromoethane) phase. It is possible that modification of crystallization conditions such as electrode surface, electrolyte concentration, temperature, or current density may yield a greater percentage of the higher T_c phase.

As shown in Table I, significant changes in the superconducting transition temperature of the κ_L-(ET)$_2M$(CF$_3$)$_4$(1,1,2-trihaloethane) salts can be achieved via modification of both the M(CF$_3$)$_4^-$ anion and the cocrystallized solvent molecule. The values recorded in this table were determined on bulk samples of randomly oriented crystals, and have an uncertainty of about 0.25 K. A redetermination of these T_cs based on oriented single crystals is currently in progress. For each of the three M(CF$_3$)$_4^-$ anions, the higher T_cs occur for the κ_L-(ET)$_2M$(CF$_3$)$_4$(1,1,2-trihaloethane) salts with the larger cocrystallized solvent molecules. However, the T_c is not directly related to only the size of the solvent molecule. The solvent molecules 1-bromo-1,2-dichloroethane and 2-bromo-1,1-dichloroethane are essentially the same physical size, however, the superconducting transition temperatures of the κ_L-(ET)$_2M$(CF$_3$)$_4$(1-bromo-1,2-dichloroethane) salts are consistently lower than those of κ_L-(ET)$_2M$(CF$_3$)$_4$(2-bromo-1,1-dichloroethane).

In addition to the κ_H-phases and κ_L-phases, a third crystalline phase of ET salts containing the M(CF$_3$)$_4^-$ anions has been prepared. This (ET)$_2M$(CF$_3$)$_4$ salt is non-solvated, and sometimes grows in the same electrocrystallization cell under identical conditions as κ_H- and κ_L-phases. When solvents other than 1,1,2-trihaloethanes are chosen as solvents, this non-solvated (ET)$_2M$(CF$_3$)$_4$ phase is the sole product. ESR has proven to be a very efficient tool for the non-destructive identification of these three phases. The κ_L-phases typically have ESR linewidths between 55 and 70 G, the κ_H–phases between 5.5 and 6.5 G, and the non-solvated phase in the range 30 to 40 G. The

TABLE II Superconducting transition temperatures (T_C) at ambient pressure for κ_L-$(ET)_2Ag(CF_3)_4$(1,1,2-tribromoethane) with compositions of natural isotopic abundance (h_8) and with deuterium (d_8) substitution of the hydrogen atoms in the ET electron-donor molecule.

Crystal	T_{co} (K)	T_{cl} (K)	T_{cm} (K)	$T_{c\chi''}$ (K)	$\Delta T_{c(10\text{-}90\%)}$
κ_L-$(d_8\text{-}ET)_2Ag(CF_3)_4$(1,1,2-tribromoethane)					
1	5.15	4.83	4.35	4.30	1.11
2	5.39	4.90	4.25	4.29	1.54
3	5.45	5.00	4.29	4.38	1.85
4	5.04	4.89	4.27	4.33	1.39
Mean	5.26±0.19	4.91±0.07	4.29±0.04	4.33±0.04	1.47±0.31
κ_L-$(h_8\text{-}ET)_2Ag(CF_3)_4$(1,1,2-tribromoethane)					
1	4.67	4.44	3.72	3.78	1.52
2	4.86	4.61	3.98	4.00	1.39
3	4.79	4.49	3.79	3.83	1.68
4	5.05	4.67	4.17	4.19	0.98
Mean	4.84±0.19	4.55±0.11	3.92±0.20	3.95±0.19	1.39±0.30
ΔT_C	0.42±0.27	0.36±0.13	0.37±0.20	0.38±0.19	

linewidths of the κ_L-phases are similar to other κ–phase salts. Research is in progress to determine the cause of the very sharp linewidths observed for the κ_H–phases.

In an attempt to gain insight into the superconducting properties of the κ_L-$(ET)_2M(CF_3)_4$(1,1,2-trihaloethane) salts, we decided to investigate the effect on T_c of deuterium atom substitution of the ET electron-donor molecule. The T_cs determined for these crystals are listed in Table II. For ready visual comparison, the internal susceptibility (χ_{int}) data for the four h_8 and d_8 crystals studied herein are plotted in Figure 1. This was done by linearly correcting the χ' data to a normal-state value of 0 (at 6.5 K) and calculating an experimental demagnetization factor, assuming a saturation susceptibility of -1 (at 1.5 K). Finally, χ_{int} was calculated for each data point through the use of this experimentally determined demagnetization factor.

It is clear that a sizable shift (about 0.4 K) in the superconducting transition temperature occurs upon deuteration of the ET molecule. The T_c observed upon deuteration is higher than that in crystals of natural hydrogen abundance. These values are in contrast to those calculated by use of the BCS model which predicts that the lower

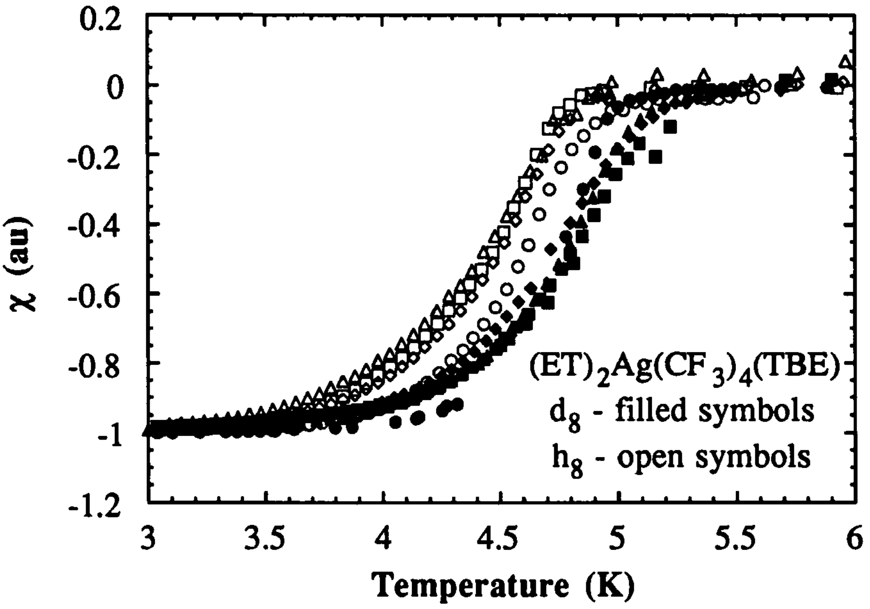

FIGURE 1 Point-by-point volume susceptibilities χ' (corrected for demagnetization) for all eight crystals of κ_L–(ET)$_2$Ag(CF$_3$)$_4$(1,1,2-tribromoethane): four with isotopes of natural abundance (open symbols) and four with deuterium labeling of the eight hydrogen atoms of ET (filled symbols).

frequency phonons obtained in the deuterated salt would cause a lower transition temperature to be observed.[17, 18] This inverse isotope effect suggests that the interaction of the hydrogen atoms of the ET donor molecule with the anion layer may play an important role in the origin of the superconducting state.

CONCLUSION

A new direction for the synthesis of organic superconductors involving the use of large discrete anions has been pioneered. This new approach has so far yielded over twenty unique superconducting salts through the use of the square-planar, organometallic M(CF$_3$)$_4^-$ anions. It is likely that additional superconductors of the κ-(ET)$_2M$(CF$_3$)$_4$(1,1,2-trihaloethane) family will be discovered through further modification of the electron-donor molecule, the anion, or the cocrystallized solvent molecule. The wide range of superconducting transition temperatures observed in this series makes this an ideal system for investigating the effects on the superconducting state of small structural changes. The inverse isotope effect observed upon deuteration of κ_L-$(ET)_2Ag(CF_3)_4$(1,1,2-tribromoethane) suggestes that hydrogen/anion interactions are important for the stabilization of the superconducting state. It is probable that other such families of superconductors will also be discovered through the use of this new synthetic strategy.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38. Research at the University of Cologne was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

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