J. CHEM. SOC., CHEM. COMMUN., 1995

Synthesis and Characterization of Two New Organic Superconductors, κ_L- and κ_H-[Bis(ethylenedisulfanyl)tetrathiafulvalene]$_2$Au(CF$_3$)$_4$·(1,1,2-Trichloroethane) *via* Microelectrocrystallization

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A novel microelectrocrystallization (MEC) procedure (ten-fold decrease in halogenated solvent use, micromolar quantities of electron donor molecule and supporting electrolyte, and Hg free electrodes), necessitated by the very small available quantities of the novel organometallic Au(CF$_3$)$_4^-$ anion, has been developed to prepare two distinct phases of κ-(ET)$_2$Au(CF$_3$)$_4$·(TCE) [ET = bis(ethylenedisulfanyl)tetrathiafulvalene, TCE = 1,1,2-trichloroethane] which exhibit ambient pressure superconductivity with onset temperatures of 2.1 and 10.5 K.

A key to determining the important structural features and characteristic properties of organic superconductors, and ultimately the mechanism of superconductivity in these unusual systems, is the development of an isostructural series of materials in which subtle alterations of the molecular interactions result in significant property changes associated with the superconducting state. Preservation of a superconducting ground state in the previously known series of isostructural organic superconductors [*e.g.* β-(ET)$_2$X, X$^-$ = I$_3^-$, IBr$_2^-$ and AuI$_2^-$][1,2] can be achieved only *via* substitution of the anion moiety. In contrast, donor modification results in unrelated structures with nonsuperconducting ground states. We recently reported the electrocrystallization of an unique series of organic superconductors,[3–5] κ-(ET)$_2$M(CF$_3$)$_4$·(1,1,2-trihaloethane), (M = Cu and Ag), which are the first ambient pressure superconductors that contain a cocrystallized organic solvent molecule, thus allowing possible modification *via* both anion and solvent substitution. Remarkably, many members of this family crystallize in two superconducting phases with distinct T_cs and morphologies, κ_L and κ_H (where the subscripts L and H denote the lower and higher T_c salts, respectively), and exhibit a large range of superconducting transition temperatures (2–11 K). We have extended this research to include the previously unknown and difficult to prepare Au(CF$_3$)$_4^-$ anion,[6] and we now report the preparation of two new superconducting salts in this family, κ_L- and κ_H-(ET)$_2$Au(CF$_3$)$_4$·(TCE) (TCE = 1,1,2-trichloroethane), with onset superconducting transition temperatures of 2.1 and 10.5 K, respectively.

Ordinarily, the synthesis and crystal growth of organic conductors and superconductors is performed by use of a technique broadly known as 'electrocrystallization' which occurs at a controlled rate in an organic solvent by anodic oxidation of an electron donor molecule (such as ET) in combination with an anion.[1] With the advent of very sensitive modern instrumentation and the world-wide impetus to reduce the use of halogenated organic solvents, it is now possible to prepare and study very small quantities in the search for new conducting materials. This approach is especially useful for 'screening' runs, when electron donor molecules [*e.g.* isotopically (^{13}C, ^{34}S) substituted ET] or anions [*e.g.* Au(CF$_3$)$_4^-$] can only be prepared in small quantities due to chemical or economic considerations.

A micro H-cell was fabricated by connecting two 1 cm^3 volumetric flasks (equipped with female size 9 ground glass joints) with an 8 mm ultra fine fritted sealing tube (Andrews Glass). The electrodes were constructed of 1 mm diameter platinum wire inserted through an Ace-Thred (Ace Glass) adjustable electrode adapter modified with a male size 9 ground glass joint.

Commonly used H-cells[7] require nearly an order of magnitude more solvent, electrolyte, and donor molecule than the MEC cell, the majority of which must be disposed of at the conclusion of the electrocrystallization process. Additionally, electrodes are frequently constructed with the use of mercury as a conductive medium between the platinum electrode and copper wiring connected to the power source. These practices are economically and environmentally unsound, and have been significantly improved upon through the use of the MEC procedure described herein.

Bis(triphenylphosphoranylidene)ammonium tetrakis(trifluoromethyl)aurate(III),[6] [N(PPh$_3$)$_2$]Au(CF$_3$)$_4$, electrolyte (13 mg, 13 μmol) was divided between the two compartments of the MEC cell, ET (5 mg, 13 μmol, Strem Chemicals, recrystallized from chloroform) was placed in the anode chamber, and a total of 2 cm^3 of TCE (Fluka, freshly distilled from P$_2$O$_5$ and passed through a column containing alumina) was added. This dilute electrolyte solution (6 mmol dm^{-3}) was necessitated by the very small quantity of electrolyte obtained during synthesis. It is doubtful that crystallization would have occurred in a standard 15 cm^3 H-cell because of the very low [N(PPh$_3$)$_2$]Au(CF$_3$)$_4$ concentration that would have resulted from further dilution of the available electrolyte. Shiny black crystals of both the plate-like (1.234 mg) and needle-like (0.423 mg) morphologies grew simultaneously on the platinum anode under an applied current density of 0.20 μA cm^{-2}.

Single crystal X-ray diffraction studies established that the plate-like phase of κ_L-(ET)$_2$Au(CF$_3$)$_4$·(TCE) is isostructural to the κ_L-(ET)$_2$M(CF$_3$)$_4$·(TCE) (M = Cu and Ag) superconducting salts.[8] The unit cell parameters† of the Au(CF$_3$)$_4^-$ and Ag(CF$_3$)$_4^-$ salts[8] [V_c = 4322(2) and 4322.8(8) Å^3, respectively] are essentially identical. A structural investigation of the needle-like κ_H-(ET)$_2$Au(CF$_3$)$_4$·(TCE) crystals has been hindered by the filamentary nature of crystals of this phase.

Superconductivity was detected by rf penetration depth measurements[9–11] in both the plate-like, κ_L, and needle-like, κ_H, morphologies. Data from crystals of κ_L-(ET)$_2$Au(CF$_3$)$_4$·(TCE), shown in Fig. 1, exhibit a small change in resonant frequency at 2.8 K, with a strong superconducting signal beginning near 2.1 K. A similar two stage transition has been observed in κ_H-(ET)$_2$Ag(CF$_3$)$_4$·(TCE),[5] and may be the result of two possible orientations of the cocrystallized and crystallographically disordered TCE solvent molecule. Crystals of κ_H-(ET)$_2$Au(CF$_3$)$_4$·(TCE) show a sharp change in resonant frequency near 10.5 K.

AC susceptibility measurements were performed with use of a Lake Shore Cryotronics 7221 AC susceptometer operating with a 1 G modulation field and a frequency of 125 Hz. Samples were slow cooled in zero-field over a time period of 15 min. Magnetic susceptibility data were recorded while warming in 0.1 K increments. The real (χ', in-phase) and imaginary (χ'', out-of-phase) components were measured on a 3.014 mg sample of randomly oriented needle-like crystals of κ_H-(ET)$_2$Au(CF$_3$)$_4$·TCE. The temperature dependence of the volume susceptibility, uncorrected for demagnetization, is illustrated in Fig. 2. The onset of superconductivity is observed in the real component at 10.4 ± 0.1 K. The transition width, defined at 10–90% completion of the transition, is 1.5 K. A sharper transition would be expected for oriented single crystals. The large value of the diamagnetic signal suggests that this sample is a high quality bulk superconductor. Typical of type II superconductors, a maximum in the out-of-phase component is observed near the transition midpoint.

The pressure dependence[12,13] of the superconducting onset temperature of κ_H-(ET)$_2$Au(CF$_3$)$_4$·TCE, revealed a large negative presure derivative (-2.6 K kbar^{-1}) similar to that observed for κ_H-(ET)$_2$Cu(CF$_3$)$_4$·TCE (-2.2 to -3.0 K kbar^{-1})[4] and κ_H-(ET)$_2$Ag(CF$_3$)$_4$·TCE (-1.9 K kbar^{-1})[5] and reminiscent of κ-(ET)$_2$X superconductors in general.[14,15] This pressure dependence suggests that by use of even larger, discrete (nonpolymeric) monoanions, it may be possible to prepare other superconducting κ-phase charge transfer salts with even higher superconducting transition temperatures.

The microelectrocrystallization technique described herein is a powerful new means for preparing charge transfer salts with the use of small quantities of ordinary or novel anions and donor molecules in an economically efficient and environmentally sound manner. This approach has been utilized to electrocrystallize two superconducting phases containing the difficult to prepare Au(CF$_3$)$_4^-$ anion. These findings confirm that all three members of the (ET)$_2$M(CF$_3$)$_4$·TCE (M = Cu, Ag and Au) family form at least two superconducting phases each. An extensive crystallographic study is currently in progress to correlate the minor structural changes in members of the κ-(ET)$_2$M(CF$_3$)$_4$·(1,1,2-trihaloethane) family with their superconducting properties. We speculate that new isostructural members of the (ET)$_2$Au(CF$_3$)$_4$·(solvent) family will be prepared *via* solvent substitution.

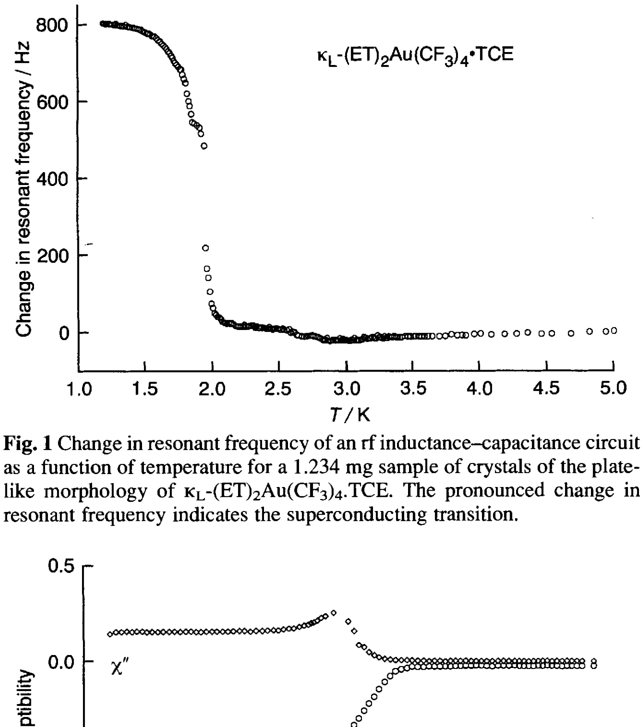

Fig. 1 Change in resonant frequency of an rf inductance–capacitance circuit as a function of temperature for a 1.234 mg sample of crystals of the plate-like morphology of κ_L-(ET)$_2$Au(CF$_3$)$_4$.TCE. The pronounced change in resonant frequency indicates the superconducting transition.

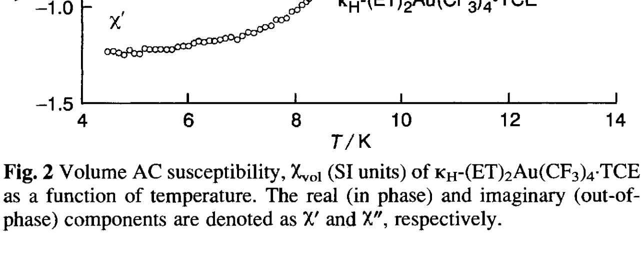

Fig. 2 Volume AC susceptibility, χ_{vol} (SI units) of κ_H-(ET)$_2$Au(CF$_3$)$_4$·TCE as a function of temperature. The real (in phase) and imaginary (out-of-phase) components are denoted as χ' and χ'', respectively.

We thank Mr Brad Dodrill (Lake Shore Cryotronics) for continuing technical advice. Work at Argonne and Sandia National Laboratories is sponsored by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contracts W-31-109-Eng-38 and DE-AC04-94AL85000, respectively. Research at the University of Cologne was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. S. A. S. and M. E. K. are undergraduate research participants from Mansfield University (Mansfield, PA) and Hope College (Holland, MI), respectively, sponsored by the Argonne Division of Educational Programs.

Received, 15th March 1995; Com. 5/01670C

Footnote

† a = 13.221(3), b = 38.057(8), c = 8.590(2) Å, $\alpha = \beta = \gamma = 90°$, T = 295 K; obtained from the carefully centred setting angles of 50 reflections with $21° < 2\theta < 33°$ (λ = 0.7101 Å).

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