The First Organic Cation-radical Salt Superconductor (T_c = 4 K) with an Organometallic Anion: Superconductivity, Synthesis and Structure of κ_L-(BEDT-TTF)$_2$Cu(CF$_3$)$_4$·TCE

John A. Schlueter,[a] Urs Geiser,*[a] Jack M. Williams,*[a] H. Hau Wang,*[a] Wai-Kwong Kwok,[a] John A. Fendrich,[a] K. Douglas Carlson,*[a] Crystal A. Achenbach,[a] James D. Dudek,[a] Dieter Naumann,*[b] Thomas Roy,[b] J. E. Schirber*[c] and W. R. Bayless[c]

[a] *Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[b] *Institut für Anorganische Chemie, Universität Köln, Greinstrasse 6, D-50939 Köln, Germany*
[c] *Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

Superconductivity at ambient pressure with onset T_c = 4.00 ± 0.05 K is reported in a unique organic cation-radical salt κ_L-(ET)$_2$Cu(CF$_3$)$_4$·TCE, [ET = bis(ethylenedithio)tetrathiafulvalene, TCE = 1,1,2-trichloroethane] with the Cu(CF$_3$)$_4^-$ species being the first Cu^{3+} and F containing *organometallic* anion in an organic superconductor.

Over 50 organic superconductors exist with the majority derived from the electron-donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET).[1,2] The ET-based superconductors comprise two major structural types: (*i*) the 'β-phase'-type, with triclinic unit cell, all donor molecules parallel in a honeycomb fashion, max. $T_c \approx$ 8 K; and (*ii*) the 'κ-phase'-type with dimerized ET molecules, dimers rotated by *ca.*90° in a parquet fashion, max. $T_c \approx$ 13 K. Well-defined structure-property correlations exist only for the β-phases.[2] The highest-T_c κ-phase systems are κ-(ET)$_2$Cu(NCS)$_2$, $T_c \approx$ 10 K,[3] and two isostructural salts κ-(ET)$_2$Cu[N(CN)$_2$]X, where X = Br, T_c = 11.6 K (ambient pressure),[4] and X = Cl, T_c = 12.8 K (at 0.3 kbar pressure).[5] The Cu[N(CN)$_2$]X$^-$ salts are unique in possessing a novel structural feature: an 'anion hole'[6] in the polymeric anion layers through which ET-molecules on *opposite* sides of the mirror-symmetric anion layer are linked by short C–H···H–C contacts. We speculated[6] that these linkages influence the T_c values either through improved phonon mediation of superconducting pairs, an increase in the density of states at the Fermi level, or by providing Josephson coupling across the diamagnetic anion layer, thereby accounting for the higher T_c values in the Cu[N(CN)$_2$](Br,Cl)$^-$ salts than in the Cu(NCS)$_2^-$ salt. Thus, if new salts with the same crystallographic space group as that of the Cu[N(CN)$_2$](Br,Cl)$^-$ superconductors could be found, variations in the interlayer separations might substantially influence T_c thereby leading to initial structure-property correlations for κ-phase systems. Consequently, we have searched for new anions that provide such a change in interlayer distance. We report here our first success with this approach by the use of the recently discovered[7] discrete organometallic anion Cu(CF$_3$)$_4^-$, which yielded a κ-phase superconductor isomorphous to κ-(ET)$_2$Cu[N(CN)$_2$]X, but with an *expanded* anion layer thickness.

ET (Strem Chemicals) was recrystallized from chloroform, and TCE (Aldrich, 98%) was freshly distilled from P$_2$O$_5$, then passed through an alumina column prior to use. Bis(triphenylphosphoranylidene)ammonium tetrakis(trifluoromethyl)cuprate(III), [N(PPh$_3$)$_2$]Cu(CF$_3$)$_4$, was prepared *via* the published method.[7] Plate-like single crystals were grown by the use of the electrocrystallization† technique.[8] Poorly crystallized needles§ (too small to be presently characterized by X-ray diffraction) formed after 4 days, and within a week, black plates of κ_L-(ET)$_2$Cu(CF$_3$)$_4$·TCE began growing among the needles. The crystals were characterized (at 260 K) by their ESR peak-to-peak line widths of 68 G (field $H\|$ plate, $g_\|$ = 2.0070) and 54 G ($H\perp$ plate, $g_\perp$ = 2.0107), respectively, in complete agreement with κ-(ET)$_2$Cu[N(CN)$_2$]Br.[9]

The crystal structure‡ of κ_L-(ET)$_2$Cu(CF$_3$)$_4$·TCE consists of alternating layers of ET molecules (see Fig. 1) and layers of Cu(CF$_3$)$_4^-$ anions and TCE solvent molecules. The donor molecules form a typical κ-type arrangement, *i.e.* the molecules are arranged in approximately face-to-face dimers, whereas neighbouring dimers are rotated by *ca.* 90° with respect to each other. The disordered anions and TCE solvent molecules occupy mirror planes between the ET layers. The CuC$_4$-core of the anion is almost planar, with the mirror plane bisecting the C–Cu–C angles. Thus, the anion molecular plane is at right angles to the mirror plane, resulting in the thickest anion layer observed in any κ-phase structure and all ET-based superconductors. The resulting separation between the conducting ET molecular layers should result in extremely two-dimensional electronic properties.

Superconductivity was detected by rf penetration depth measurements[10–12] (cryostat cooled by pumped liquid ^{4}He). With this method, superconductivity is detected by an increase in the resonant frequency (≈580 kHz) of an rf coil in an inductance–capacitance circuit caused by the exclusion of the rf field from the sample by the development of persistent shielding currents. The superconducting transition of the sample (several crystals of total mass 350 μg) is illustrated in Fig. 2. The onset T_c is 4.00 ± 0.05 K, with a strong increase in the resonant frequency beginning near 3.5 K, and saturation of the transition slightly above 2 K. Superconductivity was also observed by use of an ac susceptometer (Lake Shore Cryotronics) and T_c was found to be independent of cooling rate (23–43 K min^{-1}).

The pressure dependence (to 1 kbar) of T_c was studied by use of solid He as the pressure transmitting medium.[13] The onset of diamagnetism was detected with an rf technique[14] which requires no leads on the crystals and can be used with extremely small samples. The onset T_c at 0.15 bar was 3.7 K, which extrapolates to a T_c of 4.0 K at ambient pressure. With increasing pressure p, T_c decreased with dT_c/dp = −2.5 ± 0.2 K kbar.$^{-1}$ A gradual decrease of the superconducting signal

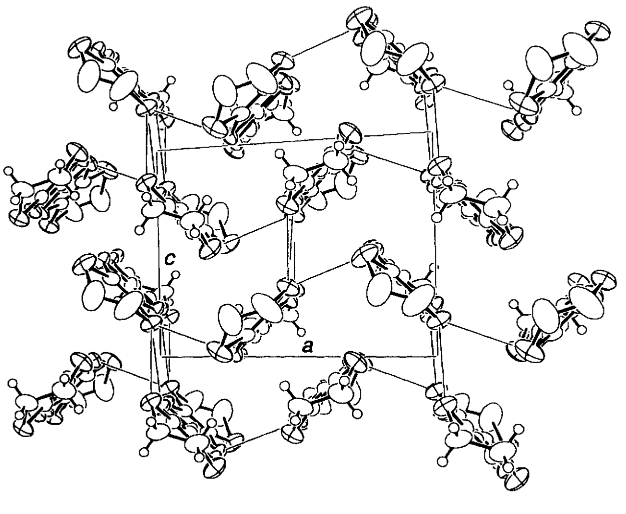

Fig. 1 Perspective view of the ET donor molecule layer in κ_L-(ET)$_2$Cu(CF$_3$)$_4$·TCE. The view is approximately along the central C=C bond direction, and the atoms (except for hydrogen) are drawn with 50% probability ellipsoids. Short intermolecular S···S contacts shorter than 3.65 Å are drawn with thin lines.

with time was found. After two weeks, the signals decreased by an order of magnitude, although the observed values of T_c did *not* change discernibly at any given pressure. The large negative pressure derivative of -2.5 K kbar^{-1} is similar to that of most κ-phase $(ET)_2X$ materials regardless of composition, unit cell size and T_c.[2]

Our findings place us a step closer to the development of structure-property correlations for κ-phase superconductors because, for the first time, three isomorphous salts can be compared. We observe a decrease in T_c from ≈12 to ≈4 K, concomitant with an increase in the spacing, from ≈15 to ≈19 Å, between the centres of adjacent donor molecular layers, when comparing the *isomorphous* salts κ-$(ET)_2Cu[N(CN)_2]X$, (X = Br, Cl) and κ_L-$(ET)_2Cu(CF_3)_4$·TCE. If, for simplicity, we assume an r^{-q} dependence of T_c with distance r, these values lead to an exponent $q \approx 4.7$. However, we would expect a *positive* value of dT_c/dp if applied pressure were to *decrease* the *interlayer* distances, and a different explanation for the variations in T_c may be needed. It is possible that the intrinsic T_c of all these isomorphous salts is ≈12 K, but T_c in the title compound is depressed because of the disorder of both the anion and solvent molecule. It has been found repeatedly in the past that crystallographic disorder can depress T_c or even suppress superconductivity altogether.[2,15]

It is surprising that the use of a large, *monomeric* anion such as $[Cu(CF_3)_4]^-$ leads to a new superconducting κ-phase material isomorphous with the κ-$(ET)_2Cu[N(CN)_2]X$ (X = Br, Cl), because the latter salts all contain large infinite-array polymeric anions formed by self-assembly in solution. Thus, it appears that large and discrete monovalent anions should also be sought in the search for new superconducting κ-phase ET salts. Finally, we believe that it may be possible to further modify the κ-$(ET)_2Cu(CF_3)_4$·TCE salt by varying the solvent molecule incorporated in the anion layer, and thereby produce new superconducting salts with differing T_c values.

We thank Mr Brad Dodrill (Lake Shore Cryotronics) for guidance in achieving temperatures down to 2 K with the ac susceptometer. Work at Argonne National Laboratory 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-138 and DE-AC04-94AL85000, respectively. C.A.A. is a student undergraduate research participant, sponsored by the Argonne Division of Educational Programs, from the University of Wisconsin/Richland Center. Research at the University of Cologne was supported by the Fonds der Chemischen Industrie and the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen (Arbeitsgemeinschaft Fluorchemie).

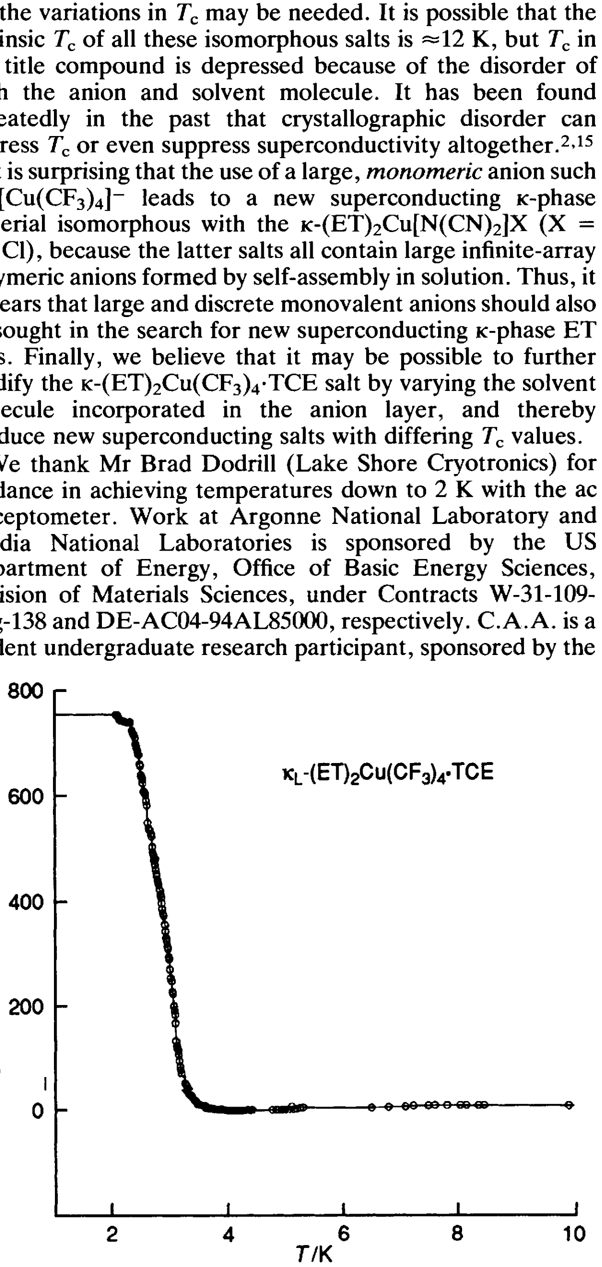

Fig. 2 Change in resonant frequency of an rf inductance-capacitance circuit as a function of temperature for a small sample of κ_L-$(ET)_2$-$Cu(CF_3)_4$·TCE inserted in the coil. The pronounced change in frequency indicates a superconducting transition with onset T_c = 4.00(5)K and saturation slightly above 2 K.

Received, 6th April 1994; Com. 4/02060J

Footnotes

† Electrochemical cell assembled in an argon-filled dry box (296 K). Electrolyte: 6 mmol dm^{-3} PPN·$Cu(CF_3)_4$ in TCE (a mixture of TCE with 10% ethanol yielded identical results). Saturated solution of ET in TCE added to anode chamber. Current density: 0.45 μA cm^{-2}; platinum electrodes.

‡ At 298 K: orthorhombic, space group *Pnma*, a = 13.169(2), b = 38.031(3), c = 8.5388(11), V = 4276.4(9) Å^3, Z = 4. R = 0.073 (R_w = 0.052) with 307 varied parameters and 2260 unique, observed ($I > 2\sigma$) reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *Added in proof*: The needles are also superconducting (T_c = 9 K) and possibly a κ-phase.[16] We have therefore denoted the plate phase herein as κ_L (L : low T_c).

References

1 T. Ishiguro and K. Yamaji, *Organic Superconductors*, Springer-Verlag, Berlin, Heidelberg, 1990.
2 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, *Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory,* Prentice Hall, NJ, 1992.
3 H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto and J. Tanaka, *Chem. Lett.*, 1988, 55.
4 A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung and M.-H. Whangbo, *Inorg. Chem.*, 1990, **29**, 2555.
5 J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung and M.-H. Whangbo, *Inorg. Chem.*, 1990, **29**, 3262.
6 Presented at the International Conference on Materials and Mechanisms of Superconductivity of High T_c Superconductors, Kanazawa, Japan (July, 1991): J. M. Williams, H. H. Wang, K. D. Carlson, A. M. Kini, U. Geiser, A. J. Schultz, W. K. Kwok, U. Welp, G. W. Crabtree, S. Fleshler, M.-H. Whangbo and J. E. Schirber, *Physica (Amsterdam)*, 1991, **C185–189**, 355.
7 D. Naumann, T. Roy, K.-F. Tebbe and W. Crump, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1482.
8 T. J. Emge, H. H. Wang, M. A. Beno, J. M. Williams, M.-H. Whangbo and M. Evain, *J. Am. Chem. Soc.*, 1986, **108**, 8215.
9 H. H. Wang, M. A. Beno, K. D. Carlson, U. Geiser, A. M. Kini, L. K. Montgomery, J. E. Thompson and J. M. Williams; in *Organic Superconductivity*, ed. V. Kreshin and W. L. Little, Plenum, New York, 1990, p. 51.
10 A. L. Schawlow and G. E. Devlin, *Phys. Rev.*, 1959, **113**, 120.
11 F. Behroozi, M. P. Garfunkel, F. H. Rogan and G. A. Wilkinson, *Phys. Rev. B: Solid State*, 1974, **10**, 2756.
12 G. W. Crabtree, K. D. Carlson, L. N. Hall, P. T. Copps, H. H. Wang, T. J. Emge, M. A. Beno and J. M. Williams, *Phys. Rev. B: Condens. Matter*, 1984, **30**, 2958.
13 J. E. Schirber, *Cryogenics*, 1970, **10**, 418.
14 L. J. Azevedo, J. E. Schirber, J. M. Williams, M. A. Beno and D. R. Stephens, *Phys. Rev. B: Condens. Matter*, 1984, **30**, 1570.
15 U. Geiser, A. J. Schultz, H. H. Wang, D. M. Watkins, D. L. Stupka, J. M. Williams, J. E. Schriber, D. L. Overmyer, D. Jung, J. J. Novoa and M.-H. Whangbo, *Physica C (Amsterdam)*, 1991, **174**, 475.
16 J. A. Schlueter, K. D. Carlson, J. M. Williams, U. Geiser, H. H. Wang, U. Welp, W.-K. Kwok, J. A. Fendrich, J. D. Dudek, C. A. Achenbach, P. M. Keane, A. S. Komosa, D. Naumann, T. Roy, J. E. Schirber and W. R. Bayless, submitted for publication to *Physica (Amsterdam) C*.