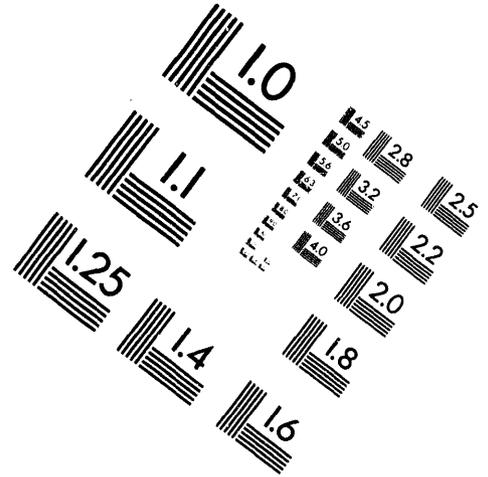
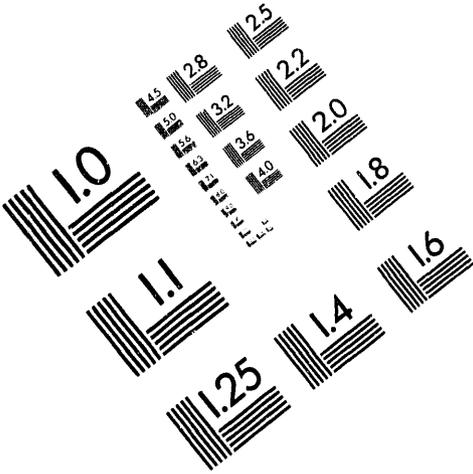




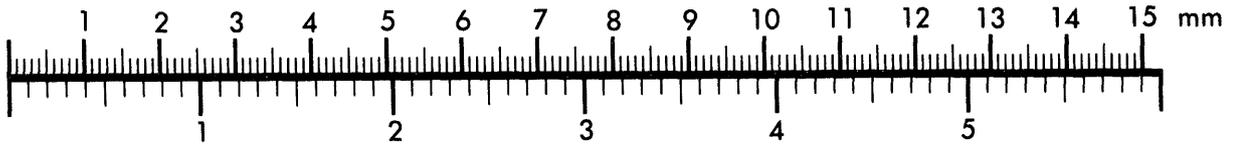
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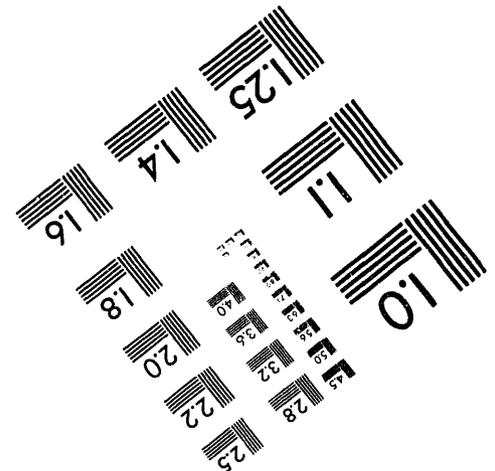
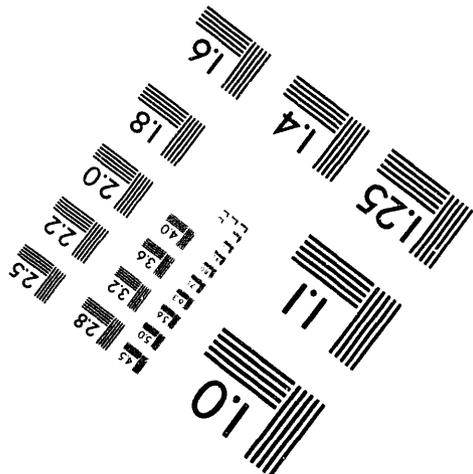
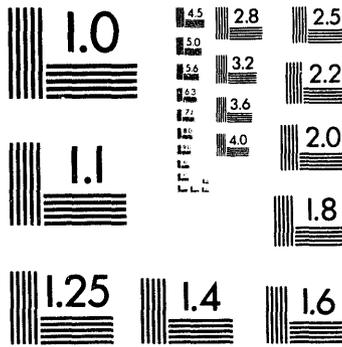
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New ET-based organic superconductors with the organometallic anion $\text{Cu}(\text{CF}_3)_4^-$

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Abstract

Electrocrystallization of bis(ethylenedithio)tetrathiafulvalene (ET) with $(\text{PNP})\text{Cu}(\text{CF}_3)_4$ in 1,1,2-trichloroethane (TCE) results in two new superconductors, $\kappa_{\text{L}}\text{-(ET)}_2\text{Cu}(\text{CF}_3)_4(\text{TCE})$, **1**, with $T_c = 4.0$ K, and $\kappa_{\text{H}}\text{-(ET)}_2\text{Cu}(\text{CF}_3)_4(\text{TCE})_x$, **2**, with $T_c = 9.2$ K. **1** forms well-developed plate-like crystals whose structure was determined by X-ray crystallography. Its band electronic structure is reported. The κ_{H} -phase forms long, thin needle bundles.

1. INTRODUCTION

Whereas the first organic superconductors, i.e., $(\text{TMTSF})_2\text{PF}_6$ ($T_c = 0.9$ K at 12 kbar pressure) [1] and $(\text{TMTSF})_2\text{ClO}_4$ ($T_c = 1.4$ K at ambient pressure) [2] in the tetramethyltetraselenafulvalene (TMTSF) series, and subsequently, $\beta\text{-(ET)}_2\text{I}_3$ ($T_c = 1.5$ K in the absence of special pressure treatment) [3] in the bis(ethylenedithio)tetrathiafulvalene (ET) series, were composed of electron-donor radical cations and *simple* inorganic anions, the more recently discovered salts with much higher T_c s contain much more *complex* and in many cases, *polymeric* anions. The best known examples are $\kappa\text{-(ET)}_2\text{Cu}(\text{NCS})_2$ ($T_c = 10$ K, ambient pressure) [4], and the

record holders $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ ($T_c = 11.8$ K, ambient pressure) [5] and $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ ($T_c = 12.8$ K, 0.3 kbar pressure) [6]. All organic superconductors (excluding fullerenes) with T_c greater than 10 K contain polymeric anion chains built of planar copper(I) complexes with bridging and terminal halide or pseudohalide anions.

Our search for new superconductors has not been restricted to polymeric anions. As the case of the crystallographically ordered $\beta^*\text{-(ET)}_2\text{I}_3$ (after pressure treatment, $T_c = 7\text{--}8$ K) [7, 8, 9] proved, relatively high transition temperatures could also be obtained with the use of *large, monovalent, monomeric* anions. When a salt of the new air-stable organometallic cation $\text{Cu}(\text{CF}_3)_4^-$ [10] became available, we immediately

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synthesized the corresponding ET salts [11, 12] in the hope of producing a new superconductor. The immense success of this endeavor is reported in this paper.

2. SYNTHESIS AND CHARACTERIZATION

A standard electrocrystallization procedure [13] was used to grow crystals. The electrolyte consisted of a solution of ET (Strem Chemicals, recrystallized from chloroform) and bis(triphenylphosphoranylidene)-ammonium tetrakis(trifluoromethyl)cuprate(III), $[N(PPh_3)_2]Cu(CF_3)_4$ [10], in TCE (Aldrich, 98%, freshly distilled over P_2O_5). The addition of 10% ethanol to the solvent yielded identical results. After four days, thin dark needles started to grow, whereas after a week the main growth was in the form of black plates. Once the plates started to form, very little further growth of the needle phase was observed. After harvesting, the crystals were separated under the microscope and stored over dry ice whenever they were not in use. These precautions were necessary since we observed severe deterioration of the optical transmission and loss of sharp extinctions between crossed polarizers in thin crystals, especially of the needle phase, over a span of a few days.

The crystal structure [11] of the plate phase, κ_L -(ET) $_2Cu(CF_3)_4 \cdot (TCE)$, **1**, was determined by use of single crystal X-ray diffraction. At 298 K, the unit cell was found to be orthorhombic, $a = 13.169(2)$ Å, $b = 38.031(3)$ Å, $c = 8.5388(11)$ Å, $V = 4276.4(9)$ Å 3 , $Z = 4$, space group $Pnma$. As in most ET-based cation radical salts [14, 15], the structure consists of alternating layers of ET molecules and layers of anions (see Figure 1). The latter also incorporate one solvent molecule per formula unit. The layer normal corresponds to the b -axis.

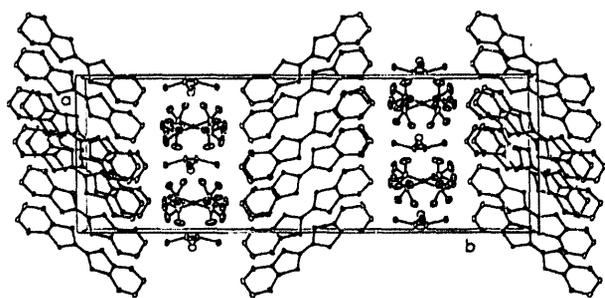


Figure 1. Perspective projection of the unit cell of κ_L -(ET) $_2Cu(CF_3)_4 \cdot (TCE)$ along the c -axis.

The packing arrangement of the ET molecules within the conducting layer is of the κ -type commonly found in many other superconducting ET salts, e.g., κ -(ET) $_2Cu(NCS)_2$ and the κ -(ET) $_2Cu[N(CN)_2]X$ ($X = Cl, Br$)

series. The κ -phase packing is characterized by the presence of face-to-face dimers (often centrosymmetric, as in the present case). The dimers are tilted by approximately 45° with respect to a unit cell axis, and surrounding dimers are tilted by the same amount in the opposite direction. Intermolecular S...S contacts shorter than the sum of the van der Waals radii (3.6 Å) connect molecules of adjacent dimers, but not within the dimer. These short contacts are frequently indicative of electronic orbital overlap and thus provide electron conduction pathways. In **1**, the S...S contacts form a network of two-dimensional topology, and the band electronic structure calculation (*vide infra*) corroborates the observed geometry.

The anion and the solvent molecule are both located on a crystallographic mirror plane. The orientation of the anion, which contains an approximately square-planar CuC_4 core as in the corresponding PNP^+ salt [10], is such that the trifluoromethyl groups are disordered around the $Cu-C$ bond in order to avoid unusually short non-bonded $F...F$ contacts. Similarly, the carbon atoms of the TCE molecule were found in disordered positions.

Overall, there are two ET molecular layers and two anion/solvent layers per unit cell. The space group and the overall arrangement of the molecular components is the same as in the "high- T_c " κ -(ET) $_2Cu[N(CN)_2]X$ salts.

The needle phase, **2**, did not yield crystals suitable for single crystal X-ray diffraction [12]. A few needles exhibited very weak, broad diffraction maxima which could be tentatively indexed with the same cell as **1**, either due to the inclusion of some κ_L -phase inside the needle bundles or because the structures of the two phases are very closely related. Other needle crystallites did not exhibit a discernible diffraction pattern at all. The composition of **2** was determined by use of energy dispersive X-ray spectroscopy inside a scanning electron microscope. Several crystals of **2** consistently showed an S:Cu molar ratio of 16:1, indicating an ET:anion ratio of 2:1. However, the chlorine content varied from 0.6 to 3 Cl atoms per Cu atom, indicating a variable solvent content (assuming no other source of chlorine) between 0.2 and 1 molecule of TCE per formula unit.

The ESR peak-to-peak linewidths (at room temperature) are: **1**: 50 G, **2**: 16 G. However, the ESR spectra of most of the needles exhibit a sizeable admixture of the 50 G component, again indicating that some κ_L -phase may be included inside the needle bundles. The narrow 16 G linewidth resembles that found in the β -(ET) $_2X$ salts, where X is a linear, triatomic anion [14].

The electrical resistivity of both modifications, **1** and **2**, initially increased upon cooling, then reached a maximum ($T_{max} = 150$ K for **1**, 100 K for **2**), and finally decreased in metallic fashion below the maximum. We were not able to cool the crystals to sufficiently low temperatures to observe the superconducting transitions

resistively. A resistivity maximum is characteristic of κ -phase materials, and this trait led us to tentatively label the needle phase 2 as κ_H (H for high T_c).

The band electronic structure of κ_L -(ET)₂Cu(CF₃)₄·(TCE) was calculated by performing extended Hückel tight binding computations [16, 17] for a single donor-molecule layer of the salt, based on the room temperature crystal structure. Figure 2a shows the dispersion relations of the four highest occupied bands of 1. With the oxidation state (ET)₂⁺, there are six electrons to fill the four bands, thus the highest two bands are partially filled. The Fermi surfaces associated with these bands, shown in Figure 2b, are described by overlapping circles centered at Γ and its equivalent positions. Consequently, 2 is expected to have two-dimensional metallic properties. The band structure is virtually the same as that found in the κ -(ET)₂Cu[N(CN)₂]X (X = Cl, Br) salts [5, 18].

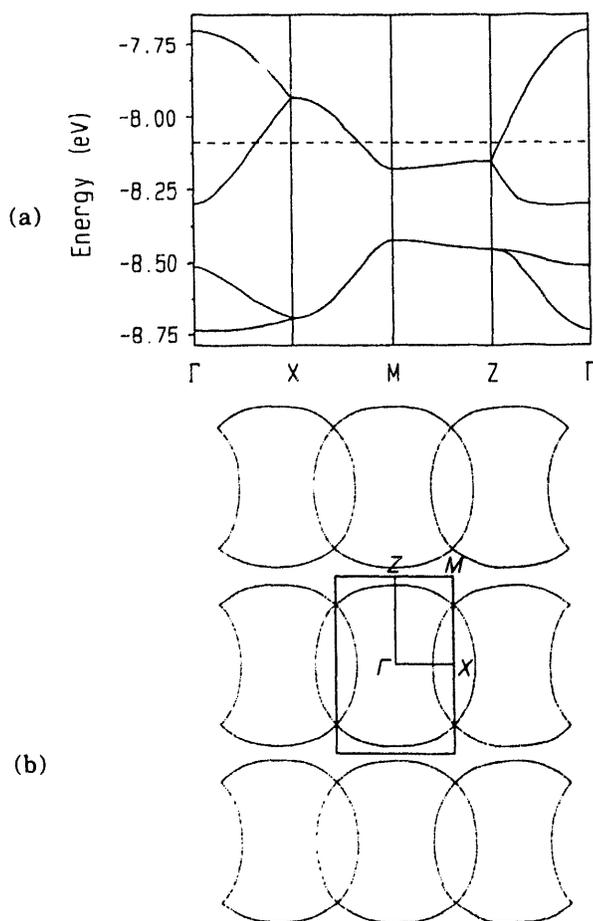


Figure 2. (a) Dispersion relations of the four highest occupied bands calculated for a single donor-molecule layer of κ_L -(ET)₂Cu(CF₃)₄·(TCE). The Fermi level is represented by a dashed line. $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $M = (a^*/2, c^*/2)$, and $Z = (0, c^*/2)$. (b) Corresponding Fermi surfaces in an extended zone.

3. SUPERCONDUCTIVITY

Superconductivity in both phases 1 and 2 was detected inductively with the use of an rf resonance circuit or an ac susceptometer (Lake Shore Cryotronics, Inc.) and explored further in dc magnetization studies and rf techniques applied to crystals under pressure. For the plate phase 1 in an rf circuit, we observed the onset of superconductivity at 4.00 ± 0.05 K (independent of cooling rate). The resonance frequency underwent its strongest increase near 3.5 K and saturated slightly above 2 K. A slightly lower superconducting onset temperature (3.5 K) was observed in the ac susceptibility (Figure 3), probably due to temperature gradients in the pumped helium cryostat.

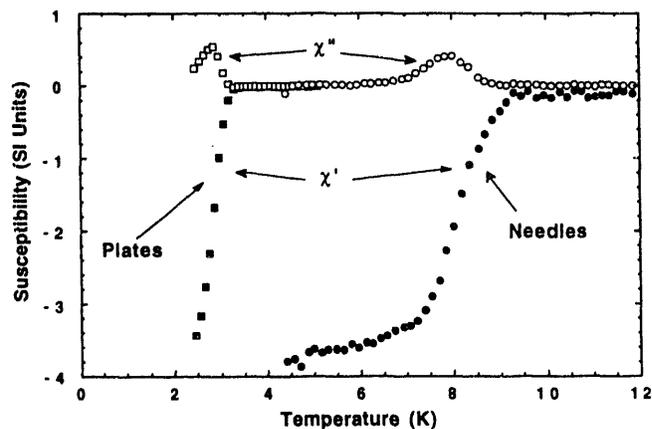


Figure 3. Ac susceptibility (filled symbols: real part χ' ; open symbols: imaginary part χ'') as a function of temperature for both superconducting phases of ET :Cu(CF₃)₄ salts. Onset $T_c = 4.0$ K (κ_L phase 1) and 9.2 K (κ_H phase 2).

In the needle phase 2, the diamagnetic susceptibility (Figure 3) showed an onset T_c of 9.2 ± 0.1 K and a rather broad transition (10%-90% width: 1.4 K), possibly due to impurities, but more likely because of the random orientation of microdomains within the needles with respect to the magnetic field.

With an applied hydrostatic pressure, the superconducting transition temperatures in both modifications decreased with increasing pressure. In κ_L -(ET)₂Cu(CF₃)₄·(TCE), the decrease was approximately linear with $dT_c/dp = -2.5 \pm 0.2$ K/kbar, whereas in κ_H -(ET)₂Cu(CF₃)₄·(TCE), the initial decrease was $dT_c/dp = -3.0 \pm 0.2$ K/kbar, tapering off to -2.2 ± 0.3 K/kbar above ca. 1–1.5 kbar.

4. CONCLUSIONS

With the use of a large (compared to the previously employed, simple inorganic anions) organometallic anion, $\text{Cu}(\text{CF}_3)_4^-$, we have discovered not one, but two new organic superconductors in the ET family. The better characterized of the two, $\kappa_L\text{-(ET)}_2\text{Cu}(\text{CF}_3)_4\cdot(\text{TCE})$, is isostructural with the "high- T_c " $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) salts. However, the anion layer in the present compounds has much more spatial extent in the direction normal to the anion layer, thus forcing the conducting ET molecular layers apart by an additional $\sim 4 \text{ \AA}$. This increased distance, and the disorder in the CF_3 -groups of the anion and in the solvent molecule, lead to a lower T_c compared to the dicyanamide salts (4 K vs. 12 K). The superconducting needle phase 2 has a much higher T_c (9 K), but its detailed characterization awaits the advent of larger crystals. The resistivity data suggest a κ -type structure for the needle phase. In summary, monomeric organometallic anions have proven suitable for the synthesis of new organic superconductors. Further studies on related materials, e.g., the corresponding silver complexes, are under way.

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