The structure of **3**, as demonstrated by X-ray analysis,[16] showed the unit cell composed of discrete monomeric units with two carboxylate groups occupying the axial positions of the ideal octahedron centered on vanadium [O1-V-N1 = 88.28 (9)°, O1-V-N2 = 87.6 (1)°, N1-V-N2 = 91.6 (1)°] (Figure 2). The nitrogen atoms of the four pyridine molecules occupy the equatorial plane forming V-N distances [V-N1 = 2.220 (3) Å] comparable to those of $VCl_2(py)_4$.[17] The two carboxylate ligands work as a simple monodentate group forming V-O distances [V-O1 = 2.087 (2) Å], which fall in the range of those formed by the bridging carboxylates in complex **1**.

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Supplementary Material Available: A full ORTEP drawing for **1** and labeling schemes for **1** and **3**, listings of crystallographic data, atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **1** and **3**, and listings of least-squares planes and dihedral angles for **3** (27 pages); listings of observed and calculated structure factors for **1** and **3** (69 pages). Ordering information is given on any current masthead page.

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[16] Crystal data for $C_{48}H_{42}N_4O_4V$ (**3**) at room temperature: monoclinic, space group $P2_1/n$ with $a = 9.999$ (2) Å, $b = 18.333$ (7) Å, $c = 11.500$ (1) Å, $\beta = 105.53$ (1)°, $V = 2031.1$ (9) $Å^3$, $Z = 2$, $d_{calcd} = 1.291$ g cm^{-3}, $\mu = 0.26$ mm^{-1}. Of 3009 unique reflections collected by using Mo (λ = 0.709 30 Å) radiation ($2\theta_{max} = 46.9°$), 1933 with $I > 2.5\sigma(I)$ were used in the final refinement. $R = 0.045$ ($R_w = 0.017$) for 316 parameters. The highest residual peak in the final difference Fourier map was 0.200 e/$Å^3$.

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Superconductivity at 2.8 K and 1.5 kbar in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: The First Organic Superconductor Containing a Polymeric Copper Cyanide Anion

Recently we have reported the organic superconductors with the highest superconducting transition temperatures (T_c) at ambient pressure, viz., κ-(ET)$_2$Cu[N(CN)$_2$]Br (T_c = 11.6 K inductively),[1] as well as at a slight elevated pressure, viz., κ-(ET)$_2$Cu[N(CN)$_2$]Cl (T_c = 12.8 K at 0.3 kbar, inductively),[2] where ET (or BEDT-TTF) is bis(ethylenedithio)tetrathiafulvalene. These record-high T_c's clearly established the κ-type structural family as the most prominent group of ET-based superconductors. The κ-structural type is characterized by *conducting* organic layers, sandwiched between essentially *insulating* anion layers, of face-to-face dimers of ET donor molecules, which themselves are rotated by about 90° with respect to neighboring dimers. Furthermore, the long axes of all ET molecules are inclined ca. 30° with respect to the layer normal. Thus, the ET molecule layers have a rectangular intralayer repeat unit of typically 9 Å × 13 Å for κ-phases. However, not all κ-phase salts are isostructural, as they differ in the relative arrangement of the layers and in the symmetry of the anion (the organic layers are always virtually centrosymmetric, even if not so required by the space group symmetry). κ-(ET)$_2$Cu[N(CN)$_2$]X (X = Cl, Br) and the nonsuperconducting iodide analogue[3,4] are orthorhombic two-layer systems, whereas κ-(ET)$_2$Cu(NCS)$_2$ (T_c = 10.4 K),[5] κ-(ET)$_2$Ag(CN)$_2$·H$_2$O (T_c = 5.0 K),[6] and κ-(ET)$_2$I$_3$ (T_c = 3.6 K)[7] are monoclinic single-layer systems.

In our attempt to synthesize new κ-phase superconductors, we have concentrated on ET salts with complex anions composed of Cu(I) or Ag(I) metal ions and pseudohalide anions. The Cu^+-CN^- system is an obvious candidate, but synthesis attempts in the past starting from anhydrous (n-Bu)$_4$NCu(CN)$_2$[8] failed to yield any characterizable product. However, the "targeted anion approach", by use of a *preformed* anion as found in KCu$_2$(CN)$_3$·H$_2$O, and the presence of trace amounts of water, led to the discovery of the first copper-cyanide containing superconductor, κ-(ET)$_2$Cu$_2$(CN)$_3$, whose synthesis, crystal structure, superconducting properties, and band electronic structure we describe herein.

Synthesis. The title compound was synthesized by two different electrocrystallization routes: In method 1 we used a solution of 8.5 mg of ET (Strem Chemical Co., Inc.), 17.1 mg of CuCN (8 equiv), 12.3 mg of KCN (8 equiv), and 18-crown-6 (~8 equiv) in a solvent mixture containing 1,1,2-trichloroethane (TCE), 9.9% (vol) absolute ethanol, and 0.1% (vol) water, whereas method 2 started from a solution of 8 mg of ET, 41.3 mg of KCu$_2$(CN)$_3$·H$_2$O[9] (8 equiv) containing the "preformed" anion (vide infra), and 18-crown-6 (~8 equiv) in TCE and 10% (vol) absolute ethanol. In the absence of small amounts of water, either deliberately mixed into the solution or as crystal water in the case of KCu$_2$(CN)$_3$·H$_2$O, no characterizable product was formed. The electrocrystallization cells were prepared inside a glovebox, and crystal growth on a Pt anode at a current density of 0.1-0.2 μA cm^{-2} was carried out for about 30 days. The product (black rhomboid-shaped platelets) appears to be a single phase, as judged by visual inspection and the room-temperature ESR line width, $\Delta H_{pp} \approx 60$ G, of several crystal specimens.

Crystal Structure. All crystals examined to date were twinned. However, a small crystal containing a single crystal domain of at least two-thirds of the crystal volume, as estimated from X-ray diffraction photographs, was used for a structure determination.[10] Since the twinning law could not be determined, all reflections

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[10] X-ray data were collected on a Syntex P2$_1$ diffractometer, and the monoclinic unit cell data (space group $P2_1/c$, $Z = 2$) are as follows (298 K): $a = 16.117$ (5) Å, $b = 8.5858$ (9) Å, $c = 13.397$ (3) Å, $\beta = 113.42$ (2)°, $V = 1701.2$ (7) $Å^3$. A total of 4696 diffraction data were collected (ω scans, 1.2°, 1.5-6° min^{-1}) in the range $4° \leq 2\theta \leq 50°$ (all h, $k \geq -1$, $l \geq -2$). A total of 43 reflections were eliminated a priori as severely affected by twinning, and the remainder were corrected for absorption ($\mu = 22.25$ cm^{-1}, $T_{min} = 0.679$, $T_{max} = 0.957$) and averaged ($R_{av} = 0.046$) to 2964 unique, allowed reflections. The structure was solved by direct methods, with 188 variables refined by full-matrix least-squares methods to 2043 observed reflections ($F_o > 4\sigma$), with $R(F) = 0.118$, $R_w(F) = 0.116$, and GOF = 4.02. The programs used in the analysis of the diffraction data were modified versions of: Strouse, C. *UCLA Crystallographic Program Package*; University of California: Los Angeles, CA, 1986.

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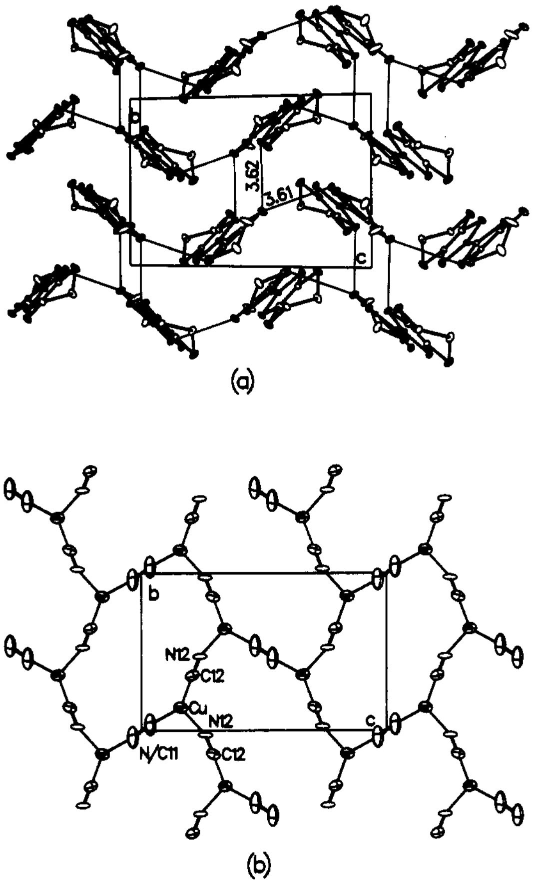

Figure 1. (a) Perspective view of the conductive ET molecule layer in κ-$(ET)_2Cu_2(CN)_3$, projected approximately along the long ET molecular axis. The thin lines represent S···S contacts less than 3.65 Å (all of them are longer than the van der Waals distance, $2r_{vdw}$ = 3.60 Å; esd's $\leq$ 0.01 Å). The atoms are drawn with 10% probability ellipsoids. (b) Polymeric $Cu_2(CN)_3^-$ anion layer in κ-$(ET)_2Cu_2(CN)_3$. The atoms are drawn with 50% probability ellipsoids, and the disordered cyanide group is labeled "N/C11".

stemming from the other twin components had to be ignored. Many of these overlapped with the reflections of the main domain, resulting in poor agreement factors. The structure as reported here certainly shows correct connectivity and molecular arrangement, but bond lengths and angles exhibit somewhat higher standard deviations (0.02 Å and 1.4° for a C–C bond and a C–C–S angle, respectively) than those typically obtained from high-quality single crystals of comparable materials, viz. 0.01 Å and 0.7° in κ-$(ET)_2Cu[N(CN)_2]Br$.[1]

The crystal structure contains alternating layers (parallel to the *bc* plane) of ET donor molecules and polymeric $Cu_2(CN)_3^-$ anions, both shown in Figure 1. The ET molecule layer, Figure 1a, exhibits typical κ-packing; i.e., it contains face-to-face dimers of ET molecules (intradimer separation = 3.34 Å), that are rotated about 46° with respect to the unit cell axes and are orthogonal (91.5° dihedral angle) to adjacent dimers. Furthermore, the long molecular axis of all ET molecules is tilted about 30° with respect to the layer normal. The intermolecular S···S contact distances are longer than those in most ET salts; surprisingly, none of them is shorter than the van der Waals distance, $2r_{vdw}$ = 3.60 Å,[11] unlike all other existing κ-phase ET salts. The absence of short intermolecular S···S contacts is correlated to the fact that the area *bc* = 115.0 $Å^3$ is larger than the corresponding area in most other κ-salts; viz., *ac* = 110.5 $Å^2$ in κ-$(ET)_2Cu[N(CN)_2]Br$[1] and *bc* = 110.8 $Å^2$ in κ-$(ET)_2Cu(NCS)_2$.[5] The anion layer, Figure 1b, consists of an essentially planar, polymeric network of triangularly coordinated copper(I) ions and bridging cyanide groups. One of the cyanide ions is located on an inversion center and thus must be crystallographically disordered. The anion network is a more planar variation of that found in $KCu_2(CN)_3{\cdot}H_2O$,[9] where the potassium ions and the water molecules are found in the interstices formed by the 18-membered copper cyanide rings. Other ET salts with polymeric macrocyclic anions have been found, e.g., $(ET)Cu_2(SCN)_3$[12] and $(ET)Ag_4(CN)_5$,[13] but the present compound is the first one containing $ET^{1/2+}$ and the first superconductor in this category. The only superconductor based on the oxygen-containing derivative bis(ethylenedioxo)tetrathiafulvalene, β_m-$(BEDO\text{-}TTF)_3Cu_2(SCN)_3$ with T_c = 1.06 K,[14] contains an analogous anion, thiocyanate substituting for cyanide groups.

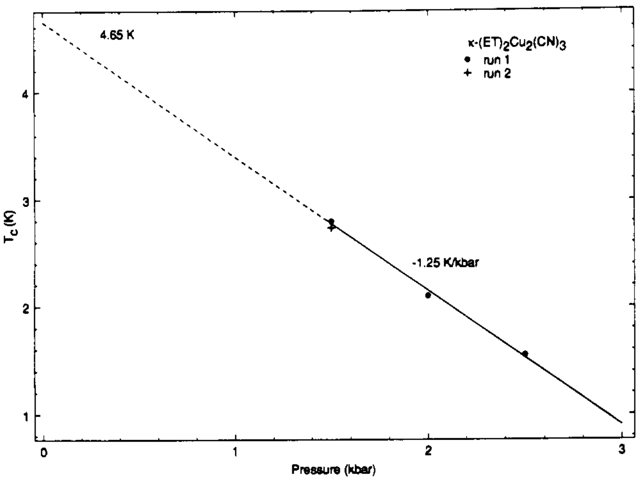

Figure 2. Superconducting transition temperature, T_c, as a function of applied pressure in κ-$(ET)_2Cu_2(CN)_3$. No bulk superconductivity was observed below 1.5 kbar. "Run 1" and "run 2" denote measurements on two separate crystals.

Superconductivity. Whereas at ambient pressure, κ-$(ET)_2Cu_2(CN)_3$ was determined by use of a four-probe resistivity apparatus to be a semiconductor with ρ(298 K) $\approx$ 0.1 Ω cm and $E_a \approx$ 48 meV, superconductivity was detected inductively at pressures above 1.5 kbar. The apparatus was the same as that used in previous studies (e.g. in κ-$(ET)_2Cu[N(CN)_2]Cl$[2]), in which careful isobaric freezing[15] of He about the sample generates the required pressure, and superconducting onset temperatures are detected by use of an rf impedance method described earlier.[16] Temperatures were measured with a carbon-glass thermometer attached to the exterior of the pressure vessel in the immediate vicinity of the sample. By attaching a small chip of Nb together with the sample inside the measuring coil, together with the negligibly small pressure dependence of T_c of Nb, $dT_c/dp = -2 \times 10^{-3}$ K/kbar, it was possible to measure and to correct for the small temperature gradient inside the pressure vessel, which is significant only at pressures below ~0.5 kbar.

The results are shown in Figure 2. Only a very weak diamagnetic signal (less than 5%) was observed at 1.0 kbar, but at 1.5 kbar, the strong superconducting signature was observed with an onset T_c = 2.8 K. Upon further increase in pressure, the superconducting transition temperature decreased gradually with a slope $dT_c/dp \approx -1.25$ K/kbar. This decrease is smaller than in the "high-T_c" κ-phases κ-$(ET)_2Cu[N(CN)_2]Br$, κ-$(ET)_2Cu[N(CN)_2]Cl$ and κ-$(ET)_2Cu(NCS)_2$ with values of −2.4,[17] −3.4,[2] and −3 K/kbar,[18,19] respectively.

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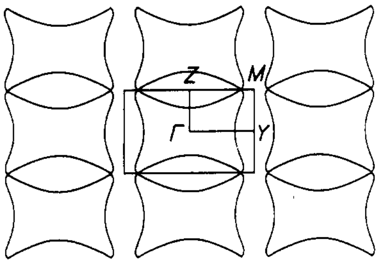

Figure 3. Fermi surface associated with the highest occupied band of κ-$(ET)_2Cu_2(CN)_3$. $\Gamma = (0, 0)$, $Y = (b^*/2, 0)$, $Z = (0, c^*/2)$, $M = (b^*/2, c^*/2)$.

Band Electronic Structure. The dispersion relations of the two highest occupied bands calculated for κ-$(ET)_2Cu_2(CN)_3$ on the basis of the extended Hückel tight-binding method[20,21] are shown in Figure S1 (supplementary material). The overall width of the two bands is ca. 0.25 eV, which is narrower than that found in other κ-phase salts[22,23] by a factor of about 4. This finding reflects the fact that the donor molecules in κ-$(ET)_2Cu_2(CN)_3$ interact weakly via the long intermolecular S···S contacts, none of which is shorter than the van der Waals distance (3.60 Å). With the formal oxidation of $(ET)_2^+$, the highest occupied band of κ-$(ET)_2Cu_2(CN)_3$ is half-filled. The Fermi surface of this band, shown in Figure 3, consists of overlapping closed loops so that κ-$(ET)_2Cu_2(CN)_3$ is predicted to be a two-dimensional metal. The observed semiconducting property of this salt at ambient pressure could well be a consequence of electron localization caused by the narrow band width.[24-26]

Concluding Remarks. κ-$(ET)_2Cu_2(CN)_3$ in many ways is similar to κ-$(ET)_2Cu[N(CN)_2]Cl$, the organic superconductor with the highest T_c reported to date.[2] Both are semiconductors at ambient pressure, even though the band electronic structure at the one-electron approximation suggests a metallic ground state, and under applied pressure, both become superconductors, κ-$(ET)_2Cu_2(CN)_3$ at 2.8 K and 1.5 kbar and κ-$(ET)_2Cu[N(CN)_2]Cl$ at 12.8 K and 0.3 kbar. The mechanism of conduction at elevated pressure is not clear at the moment, but it is very unlikely that these moderate pressures affect the electronic structures of these salts in any major way. In the β-$(ET)_2X$ family of superconductors, it was found that an increase in unit cell volume resulted in increased T_c's,[27] and one could be led to believe that in the κ-phases the salt with the most expanded ET network, i.e., κ-$(ET)_2Cu_2(CN)_3$ should have the highest T_c. However, structure-property relationships in the κ-phase salts have proven not to be so straightforward.[23] It should be noted, though, that the effect of disorder in the anion, such as the disordered cyanide group in the title compound, has always been to lower T_c or even completely suppress superconductivity, such as in β-$(ET)_2I_2Br$[28] and that there is hope that T_c might be raised substantially if the cyanide group disordering could be prevented, e.g., by substitution with a centrosymmetric bridging ligand (molecular or single-atomic) of suitable size.

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Supplementary Material Available: Tables giving the details of the X-ray diffraction data collection, atomic coordinates and isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters and a band dispersion diagram (Figure S1) (5 pages); a table of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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