generate a substantial amount of ROOR′. On the other hand, $[Fe^{III}(NTB)Cl_2](ClO_4)$ (**3**) and $[Fe^{III}(NTB)Br_2](ClO_4)$ (**4**) are much slower catalysts but produce smaller proportions of ROOR′ compared to the $Fe^{III}(TPA)$ species. Finally, the catalyst $Fe^{III}\cdot(BPG)Br_2$ (**5**) proved to be the slowest and forms the smallest proportion of ROOR′. The rate of catalysis slows as the tripodal ligand used becomes more electron-donating; however the catalyst becomes more selective for peroxide heterolysis. The greater basicity of the latter ligands may help stabilize the putative $Fe^V{=}O$ intermediate and provide the opportunity for characterizing this intermediate. Such efforts as well as investigations of the effect of catalyst nuclearity on the course of alkane functionalization are in progress.

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A New Ambient-Pressure Organic Superconductor, κ-$(ET)_2Cu[N(CN)_2]Br$, with the Highest Transition Temperature Yet Observed (Inductive Onset T_c = 11.6 K, Resistive Onset = 12.5 K)

In this communication, we report the discovery of a new ambient-pressure organic superconductor κ-$(ET)_2Cu[N(CN)_2]Br$, with the highest inductive onset transition temperature, T_c = 11.6 K (resistive onset = 12.5 K), reported to date in such systems. Cation-radical salts derived from the electron-donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or "ET", $C_{10}H_8S_8$) are of great interest because of the subtle interplay between a rich variety of structural types and the varied solid-state properties, most notably superconductivity, that they exhibit. The only structure–property correlations for ET materials that have been developed are those for the β-$(ET)_2X$, X = monovalent linear anion, superconductors.[1] In these salts, both the S⋯S distances in the corrugated-sheet[2] networks and T_c increase concomitantly with linear anion length, i.e., T_c of I_3^- (0.5 kbar), 8 K > T_c of AuI_2^-, 4.98 K > T_c of IBr_2^-, 2.8 K.[1] These findings, combined with the negative pressure dependence of T_c (ca. −1 K/kbar) in these materials,[3,4] led to the suggestion that β-$(ET)_2X$ superconductors with even higher T_c's might be realized by further increasing the conducting S⋯S contact distances inside the donor molecule lattice if isostructural salts with anions longer than I_3^- could be prepared.[1,5] Thus, candidate anions such as $(NC{-}Ag{-}CN)^-$, $(I{-}Ag{-}I)^-$, and $(NCS{-}Au{-}SCN)^-$ were suggested,[1] which, coupled with the introduction of the in situ crown ether–anion preparatory route,[6] led to the synthesis of the first *polymeric* anion ET conductors,[6,7] viz., $(ET)Ag_4(CN)_5$, and $(ET)_3Ag_{6.4}I_8$, respectively. These findings were necessary precursors to the discovery[8] of ambient-pressure superconductivity in the first *polymeric* anion superconductor, κ-$(ET)_2Cu(NCS)_2$, with the highest resistive T_c (10.4 K) in an organic superconductor at that time.[8-10] However, this salt belongs to an entirely different structural class than the β-phase salts, viz., the so-called "κ-type" containing orthogonally arranged molecular dimers as opposed to a corrugated-sheet network.[9,10a] Thus, complex polymeric anions offered a new route to the synthesis of ET superconductors.

The negative pressure derivative of T_c for κ-$(ET)_2Cu(NCS)_2$ is even larger than that for β-$(ET)_2X$ salts, and, in fact, is the largest known (−3 to −3.6 K/kbar) for any superconductor.[11,12] These results, and the recent analyses of structural features of other known κ-phase salts,[13,14,25] again suggest that the expansion of the ET donor molecule network, perhaps attainable through the incorporation of even larger polymeric anions, is a viable approach to further raise T_c's in κ-phase materials. Similar arguments based on the "effective volume" of ET have also been put forward by Saito et al.[15]

Our investigations based on these guidelines have now resulted in the discovery of a new superconducting cation-radical salt, κ-$(ET)_2Cu[N(CN)_2]Br$, where $[N(CN)_2]^-$ is the dicyanamide ion, which, although bent, is larger than the thiocyanate anion. The material is an ambient-pressure superconductor with T_c = 11.6 K (resistive onset = 12.5 K), which represents a new high for an organic superconductor. In this communication, we present its preparation, crystallographic and band electronic structure, ESR characteristics, and its superconducting transition.

Synthesis and ESR Study. Our interest in synthesizing cation-radical salts of ET with other bis(pseudohalo)cuprate(I) type of anions larger than $Cu(NCS)_2^-$ prompted us to consider the dicyanamide ion, $(NC{-}N{-}CN)^-$, as a possible pseudohalide. While there is no literature precedent for an anionic bis(dicyanamido)cuprate(I) species, we set out to synthesize it by analogy to the bis(thiocyanato)cuprate(I) salt.[16] During the course of our initial synthetic studies, in addition to the desired bis(dicyanamido)cuprate(I) salt, we also prepared another complex $\{Cu_2[N(CN)_2]_3Br\}^{2-}$, isolated as the tetraphenylphosphonium salt.[17] Electrocrystallization of ET by use of this latter salt in 1,1,2-trichloroethane (TCE) under galvanostatic conditions (current

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(17) Reaction of CuBr with 2 equiv of $Ph_4PN(CN)_2$ in refluxing acetonitrile resulted in a clear solution, which when cooled, yielded colorless crystals, mp 135–136 °C. Anal. Calcd for $(Ph_4P)_2[Cu_2(C_2N_3)_3Br]\cdot CH_3CN$: C, 59.79; H, 3.83; N, 12.45; P, 5.52; Br, 7.12. Found: C, 59.85; H, 3.81; N, 12.55; P, 5.30; Br, 6.52.

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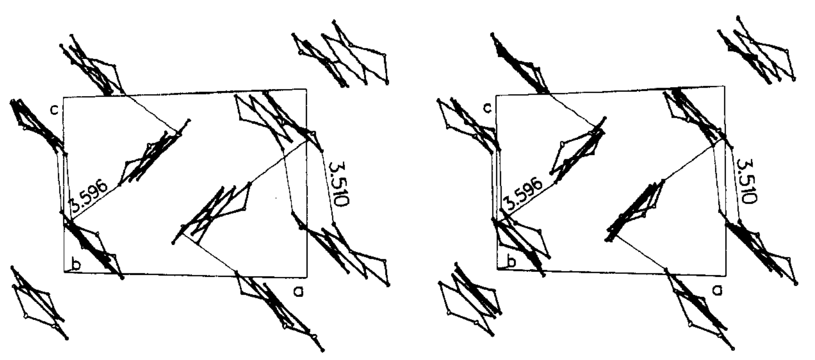

Figure 1. Stereoview of the ET donor molecular layer in κ-$(ET)_2Cu[N(CN)_2]Br$ showing the typical κ-type arrangement of mutually perpendicular face-to-face dimers. S···S contacts shorter than 3.60 Å (the sum of the van der Waals radii) are indicated with thin lines, and the two crystallographically independent such contacts are labeled. The atoms are drawn with arbitrarily small ellipsoids for clarity.

density ca. 0.2 $\mu A/cm^2$) yielded black shiny platelike crystals. Crystal structure analysis (vide infra) revealed the composition to be κ-$(ET)_2Cu[N(CN)_2]Br$. Subsequently, we have also prepared the same κ-phase salt by carrying out the in situ electrocrystallization of ET (10 mg, 0.026 mmol) by use of a 1:1 mixture of CuBr (59 mg, 0.41 mmol) and tetraphenylphosphonium dicyanamide (156 mg, 0.38 mmol) in 15 mL of TCE.

Preliminary ESR measurements on a κ-$(ET)_2Cu[N(CN)_2]Br$ crystal indicated a single absorption line spectrum with a peak-to-peak line width at room temperature in the range 60–85 G, depending on the crystal orientation. Low-temperature measurements revealed that the line width increased with decreasing temperature from 56 G (300 K) to 74 G (100 K). The estimated relative spin susceptibility was approximately constant in the temperature range measured, which is indicative of a metallic sample. Both the magnitude of the peak-to-peak line width and its temperature dependence are similar to those of previously known κ-phase compounds, e.g., κ-$(ET)_2Cu(NCS)_2$[18,19] and κ-$(ET)_4Hg_{2.89}Br_8$.[20]

Structure. The crystal structure of κ-$(ET)_2Cu[N(CN)_2]Br$ was determined from single-crystal X-ray diffraction data.[21] It contains alternating layers (perpendicular to the *b* axis) of ET donor molecules and polymeric $\{Cu[N(CN)_2]Br\}_\infty^-$ anions, and the overall arrangement with respect to symmetry elements and unit cell directions is the same as that in κ-$(MDT\text{-}TTF)_2AuI_2$.[22] The ET donor molecule network (see Figure 1) contains centrosymmetric face-to-face dimers in a typical κ-fashion;[13] i.e., adjacent dimers are approximately perpendicular to each other (74.5°). If projected along the normal to the molecular plane, the central C=C bond of one molecule is on top of one of the five-membered rings of the other molecule within the dimer ("bond-over-ring" arrangement), which appears to be common to all known κ-phase superconductors.[13,14] All S···S intermolecular contacts within a dimer are longer than the sum of the van der Waals radii (3.6 Å), but shorter contacts exist between dimers, as shown in Figure 1. The topology of the S···S contacts in this salt is different from that found in κ-$(ET)_2Cu(NCS)_2$.[10a] Large thermal parameters and an artificially short C–C bond length indicate disorder in one of the ethylene end groups, although the conformation parallel to the other ethylene end group ("eclipsed") seems to be prefer-

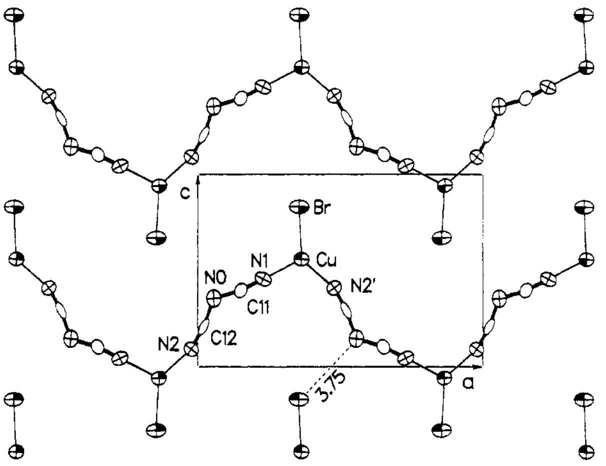

Figure 2. Polymeric anion layer in κ-$(ET)_2Cu[N(CN)_2]Br$ consisting of zigzag copper dicyanamide chains with an extra bromide ligand on each copper(I) atom. All atoms shown are located on a mirror plane, and they are drawn with 50% probability ellipsoids.

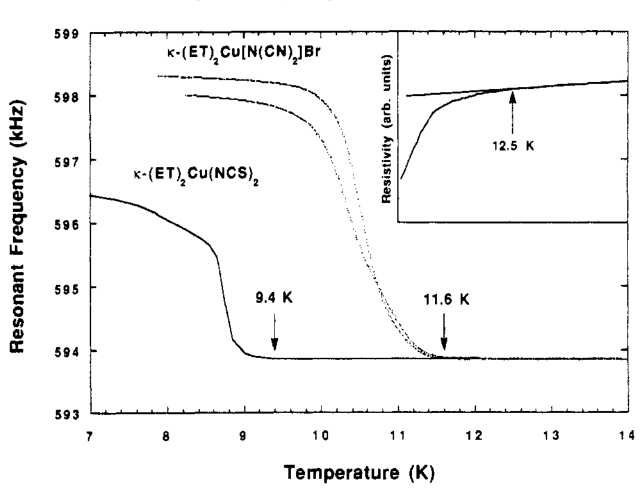

Figure 3. Resonant frequency as a function of temperature in zero applied magnetic field as determined by rf penetration depth measurements of two single-crystal specimens of κ-$(ET)_2Cu[N(CN)_2]Br$ (inset shows resistive onset). For comparison, a similarly determined curve is shown for κ-$(ET)_2Cu(NCS)_2$, with the frequencies offset to the same normal-state base line.

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(21) X-ray data were collected on a Syntex $P2_1$ diffractometer, and the orthorhombic unit cell data (space group *Pnma*, $Z = 4$) are as follows (298 K): $a = 12.942$ (3) Å, $b = 30.016$ (4) Å, $c = 8.539$ (3) Å, $V = 3317$ (1) $Å^3$. Diffraction data were collected (ω-scans, 1.4°, 1.5–6° min^{-1}) at 298 K in the range $4° \leq 2\theta \leq 45°$, and 3925 reflections were averaged ($R_{ave}(F) = 0.025$) to 2171 unique, allowed reflections, which were corrected for absorption ($\mu = 28.5\ cm^{-1}$, $T_{min} = 0.720$, $T_{max} = 0.773$). Full-matrix least-squares refinement of a model (206 variables) obtained by direct methods by use of 1713 reflections, with $F_o > 3\sigma$ yielded $R(F) = 0.075$ and $R_w(F) = 0.054$ (GOF = 1.85). 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, 1978 and 1986.

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red.[23] The polymeric anion, which resides on a mirror plane, is shown in Figure 2. It contains infinite zig-zag chains of ...Cu-dicyanamide-Cu... units, and the copper atoms complete their coordination spheres with the bromine atom. Trigonal coordination around Cu$^+$ is occasionally observed, most notably in κ-(ET)$_2$Cu(NCS)$_2$, where similar chains exist. One notable difference between the two salts is that in κ-(ET)$_2$Cu[N(CN)$_2$]Br the chains run along the longer of the two unit cell axes within the layer (i.e., *a*), whereas in κ-(ET)$_2$Cu(NCS)$_2$ they run along the shorter direction. The bromine atom forms one long contact (3.75 Å) to the central nitrogen atom of a dicyanamide ion located on an adjacent chain.

Superconducting Transition. Superconductivity in κ-(ET)$_2$Cu[N(CN)$_2$]Br was established by the use of rf penetration depth measurements, low-field dc magnetization measurements, and resistivity measurements. In the first method,[26] superconductivity is detected by an increase in the resonant frequency of an rf coil (500–600 kHz) in an inductance-capacitance circuit caused by the exclusion of the rf field (<1 mOe) in the sample due to the occurrence of diamagnetic shielding currents. Superconducting transition curves determined by this method are illustrated in Figure 3 for two single-crystal specimens of ~200 μg mass each. This figure includes, for comparison, the transition curve previously determined[10a] for κ-(ET)$_2$Cu(NCS)$_2$ by the same technique, apparatus, and thermometry. In our present measurements, the crystals were cooled overnight from room temperature to 60 K and further cooled to ~25 K at a rate of ~0.5 K/min to avoid possible problems with frozen-in crystallographic disorder that often lowers T_c in organic superconductors. The transition curves were determined by measurements of the frequency at intervals of 0.01 K with comparably slow cooling from 25 to ~8 K, a temperature below signal saturation. Preliminary studies indicate that T_c can be depressed by rapid cooling rates.

The curves for both crystal specimens of κ-(ET)$_2$Cu[N(CN)$_2$]Br exhibit a weak superconducting onset temperature of 11.60 ± 0.05 K, a strong increase in the resonant frequency beginning near 11.4 K, and saturation of the increased resonant frequency beginning near 9.6 K. In contrast, the transition curve for κ-(ET)$_2$Cu(NCS)$_2$ exhibits[10a] an onset of 9.4 K, a strong increase in the resonant frequency beginning near 8.9 K, and saturation near 6 K (not shown in Figure 3). Magnetization experiments were carried out by use of a SQUID magnetometer on the crystal specimen having the largest rf signal at saturation. For cooling in a magnetic field *H* of 1 Oe, with $H \| b$, the onset of the diamagnetic susceptibility occurred at the same temperature, 11.6 ± 0.1 K, and the susceptibility curve had essentially the same shape and saturation temperature as that of the rf transition curve. We estimate ~30% bulk superconductivity at 4 K from our measurements of both dc-field cooled and zero-field cooled magnetization. Thus, there exists some degree of inhomogeneity in the T_c and considerable flux pinning, but clearly the salt is a volume superconductor with a T_c substantially higher than that of κ-(ET)$_2$Cu(NCS)$_2$. The highest onset T_c for an inductive determination reported for κ-(ET)$_2$Cu(NCS)$_2$ is an ac susceptibility measurement yielding 10.3 ± 0.4 K.[27] Resistivity measurements of a single-crystal specimen of κ-(ET)$_2$Cu[N(CN)$_2$]Br gave a resistive onset T_c of 12.5 ± 0.1 K, a rapid acceleration of the superconducting transition beginning near 11.6 K, a transition midpoint of 11.2 K, and completion of the transition (zero resistance) at 10.5 K. The room-temperature conductivity was estimated to be σ(300 K) = 48 (Ω cm)$^{-1}$. All thermometers used in the several measurements reported here have been calibrated by Lake Shore Cryotronics, Inc., against standards calibrated by the U.S. National Institute of Standards and Technology. A determination of the superconducting transition of Nb as a check of the thermometry yielded a sharp transition with onset of 9.47 K compared with 9.50 K for very pure Nb. In a separate experiment, the magnetization curves were determined simultaneously with the use of a SQUID magnetometer for new single-crystal specimens of κ-(ET)$_2$Cu[N(CN)$_2$]Br and κ-(ET)$_2$Cu(NCS)$_2$. The dimagnetic onsets were 11.0 K for the former salt and 9.3 K for the latter, indicating an increase in T_c of 1.7 K for the κ-(ET)$_2$Cu[N(CN)$_2$]Br salt over that of the κ-(ET)$_2$Cu(NCS)$_2$ salt.

Band Electronic Structure. The dispersion relations of the two highest occupied bands and the associated Fermi surface calculated for κ-(ET)$_2$Cu[N(CN)$_2$]Br on the basis of tight-binding band electronic structure calculation[24] are shown in Figure S1 in the supplementary material. With the formal oxidation of (ET)$_2$$^+$, the highest occupied band of κ-(ET)$_2$Cu[N(CN)$_2$]Br is half-filled, and its Fermi surface consists of overlapping distorted circles centered at Γ and its equivalent points in reciprocal space. Thus, κ-(ET)$_2$Cu[N(CN)$_2$]Br is a two-dimensional metal. The band dispersion relations and the Fermi surface of κ-(ET)$_2$Cu[N(CN)$_2$]Br are very similar to those of other κ-phase salts.[13,25,28]

Conclusion. We have established that κ-(ET)$_2$Cu[N(CN)$_2$]Br is the organic superconductor with the highest transition temperature found to date. Since the anion of this salt consists of a polymeric mixed (halo)(pseudohalo)cuprate(I) species, rather than a bis(pseudohalo)cuprate(I) species, and because of the large number of metal/halide/pseudohalide substitutions that can be made in the former species, it opens up an entirely new conceptual approach for the design of more conducting and superconducting (with even higher T_c's) cation-radical salts by use of such planar, polymeric anions. These studies are currently underway in our laboratory. Our results indicate promising prospects for ever rising T_c's in new organic superconductors!

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Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table S1) and final atom positional parameters (Table S2) and a depiction of the dispersion relations and Fermi surface (Figure S1) for κ-(ET)$_2$Cu[N(CN)$_2$]Br (4 pages). Ordering information is given on any current masthead page.

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