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CONF-900528-3

STRUCTURE-PROPERTY RELATIONSHIPS FOR ß- AND κ-PHASE BEDT-TTF SALTS AND THEIR USE IN THE SYNTHESIS OF κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br: A SALT HAVING THE HIGHEST-T_c (INDUCTIVE ONSET = 11.6 K, RESISTIVE ONSET = 12.5 K) YET OBSERVED IN AN ORGANIC SUPERCONDUCTOR

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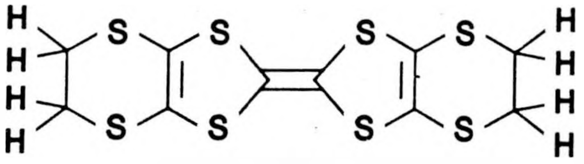
INTRODUCTION

The electron-donor molecule BEDT-TTF (or ET, **1**) and its salts have yielded the highest number of ambient pressure organic superconductors and also the highest T_c's reported to date compared to any other electron-donor molecule. The most highly developed structure-property correlations for ET salts are for the isostructural ß-(ET)$_2$X, X = mono-valent linear anion, superconductors.[1,2] In these salts both the S···S distances in the corrugated-sheet[3] networks, and T_c, increase concomitantly with the linear anion length, i.e., T_c of I_3^- (0.5 kbar), 8 K > AuI_2^-, 4.98 K > IBr_2^-, 2.8 K.[2] The synthesis of these materials has been summarized in detail in the literature.[2]



BEDT-TTF (ET)

1

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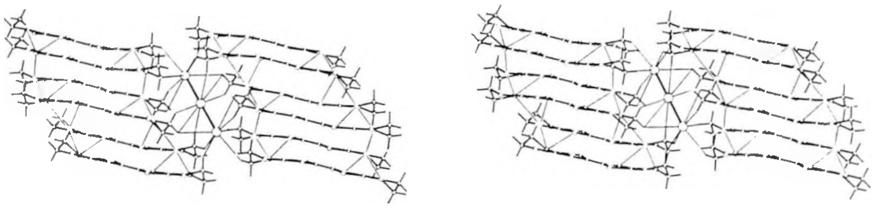
ß-Phase (ET)$_2$X, X = Anion, Superconductors

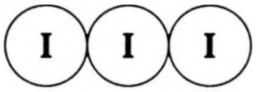
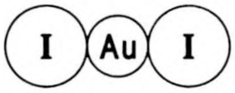
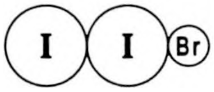
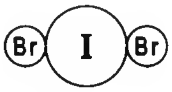
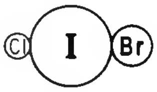
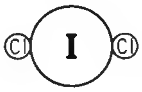
In the isostructural ß-phase materials, the anions reside within a cavity of ethylene-group hydrogen atoms formed by the corrugated-sheet[3] layers of ET molecules as shown in the stereodiagram, **2**.



2

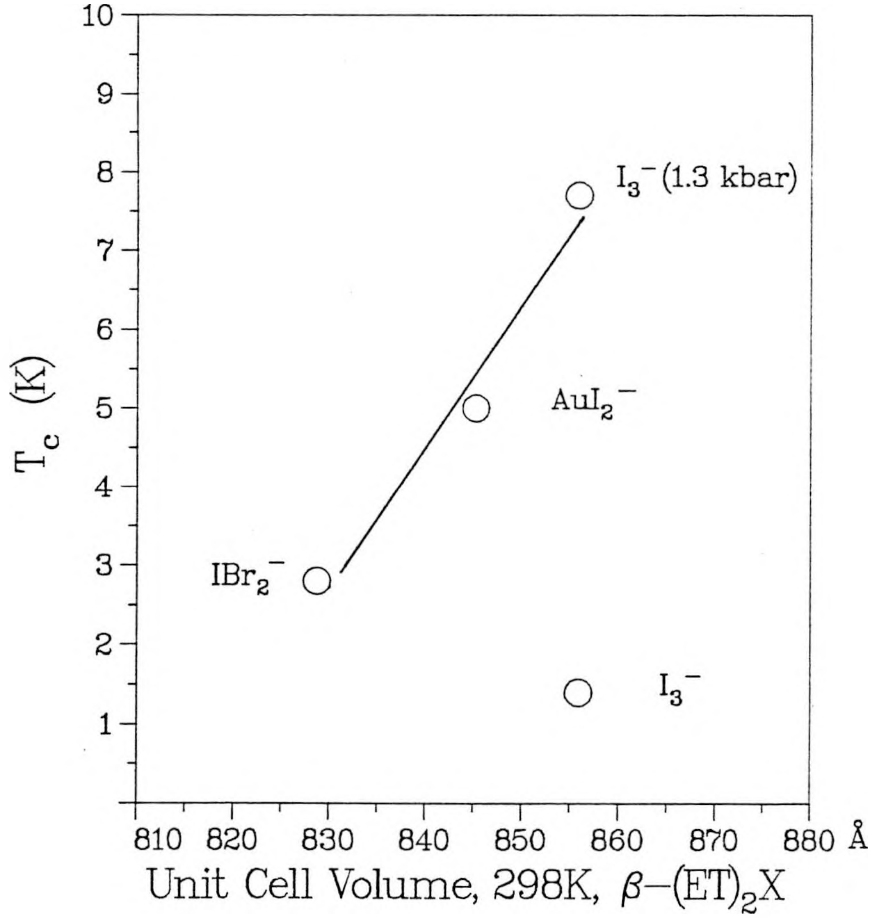
The effect of varying the anion length is to change the unit cell volume in a like fashion and at the same time alter the system of intra- and interstack S···S contact distances between ET molecues. The linear anions that yield ß or ß-like structures are shown in **3** where anion length, unit cell volume, and T_C (where appropriate) are given. Thus, over the range of anions given in **3**, the electrical properties range from that of metals with metal-insulator

ß-(ET)$_2$X

X		V_c (Å^3/298 K)	T_c (K)
I_3^-		855.9	1.5
AuI_2^-		845.2	5
I_2Br^-		842.3	none
IBr_2^-		828.7	2.80
$ClIBr^-$		821.3	?
ICl_2^-		814.3	T_{MI}=22.1

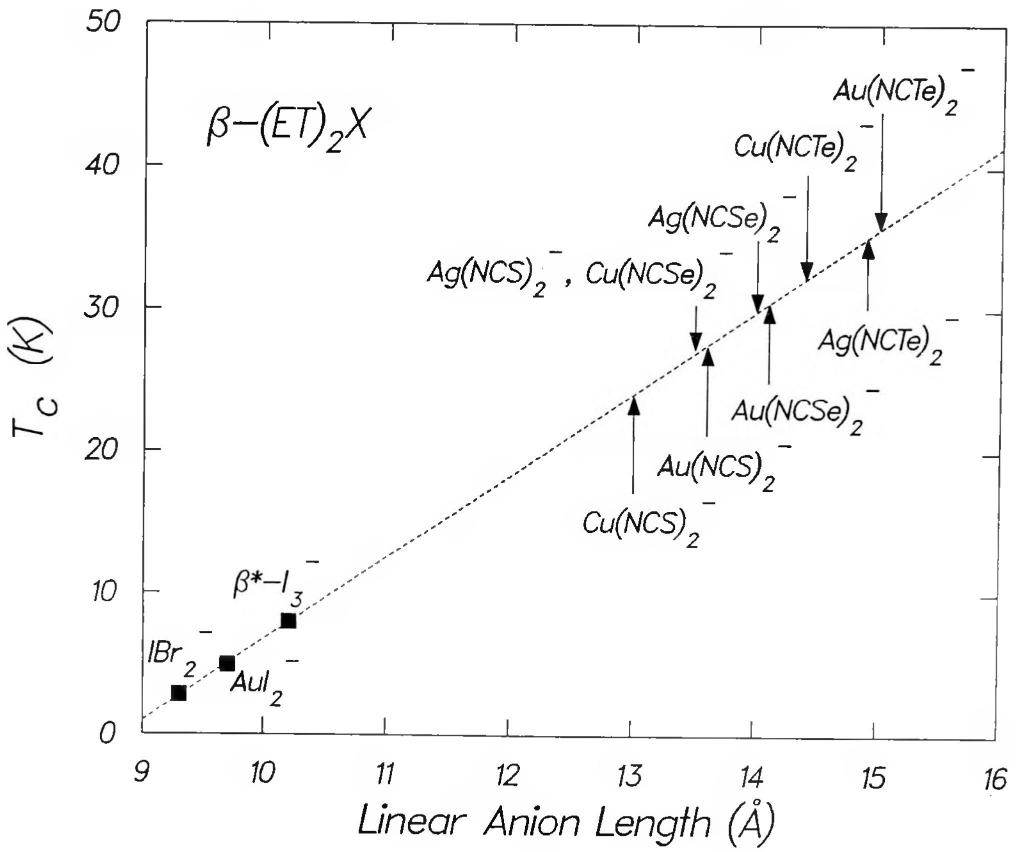
3

transitions in the shortest anions to ambient pressure superconductivity in the longer anions (IBr_2^-, AuI_2^- and I_3^-). ß-$(ET)_2I_3$ is unique because a modest pressure of only 0.5 kbar is sufficient to convert it to a new structure[4] [ß*-$(ET)_2I_3$] with T_c = 8 K, which is the maximum found to date in ß-$(ET)_2X$ type superconductors. These observations (unit cell volume and T_c) formed the basis of a useful structure-property correlation[1,2] for the isostructural salts as shown in **4**. From **4** we can see that anions longer than I_3^- might give new ß-$(ET)_2X$ superconductors with $T_c > 8$ K!



4

Since triatomic anions containing terminal halide atoms that are longer than I_3^- are presently unknown, new anionic species[2] such as $(NCS\text{-}M\text{-}SCN)^-$ and $(NC\text{-}M\text{-}CN)^-$, M = metal, have been investigated as the source of potential ß-$(ET)_2X$ superconductors. A conjectured correlation similar to that vein in **4**, but based on anion length, is shown in **5**.



5

An inspection of **5** reveals that T_c's as high as ~40 K might be achieved in ß-$(ET)_2X$ phase materials if the linear anions depicted in **5** could be prepared and incorporated in the ß-$(ET)_2X$ structure. In an attempt to prepare longer anions that I_3^-, candidate species such as $(NC\text{-}Ag\text{-}CN)^-$, $(I\text{-}Ag\text{-}I)^-$and $(NCS\text{-}Au\text{-}SCN)^-$ were suggested,[2] which, coupled with the introduction of the in situ crown ether-anion preparatory route,[5] led to the synthesis of the first polymeric anion ET conductors[5,6] viz., $(ET)Ag_4(CN)_5$ and $(ET)_3Ag_{6.4}I_8$, respectively.

κ-Phase $(ET)_2X$, X = Anion, Superconductors

These findings vide supra were necessary precursors to the discovery[7] of ambient pressure superconductivity in the first polymeric anion superconductor, κ-$(ET)_2Cu(NCS)_2$, with the highest T_c (10.4 K, resistive midpoint) in an organic superconductor, at that time.[7-9] However, this salt belongs to an entirely different structural class than the ß-phase salts, viz., the so-called "κ-type" containing orthogonally arranged molecular dimers rather than a corrugated-sheet network.[8,9b] Thus, complex polymeric anions offered a new route to the synthesis of ET superconductors. However, our previous structure-property correlations[2] for ß-phase systems do not apply to κ-phase salts because of their different structural features.

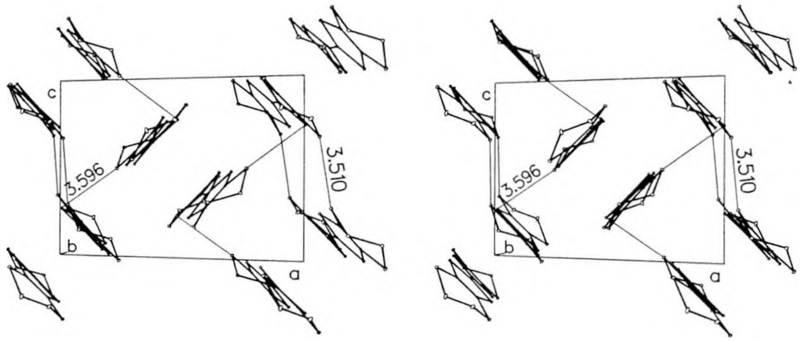
The negative pressure derivative of T_c for κ-$(ET)_2Cu(NCS)_2$, is larger than that for ß-$(ET)_2X$ salts, and, in fact, is the largest known (–3 to –3.6 K/kbar) for any superconductor.[10,11] These findings, and the recent analyses of structural features of other known κ-phase salts,[12-14] again suggest 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 "effective volume" of ET have also been put forward by Saito et al.[15] Although no precise structure-property correlations of the type determined for ß-phase materials exist for κ-phase systems, the main predictors of superconductivity[12-14] in the latter materials are (1) "bond over ring" intradimer molecular overlap and (2) relatively short (~3.35 Å) intradimer separations.

κ-$(ET)_2Cu[N(CN)_2]Br$, A New Organic Superconductor

Our investigations based on the above guidelines led us to consider bis(pseudohalide)cuprate(I) type of anions larger than $Cu(NCS)_2^-$, in particular, the substitution of dicyanamide ion, $(NC\text{-}N\text{-}CN)^-$, for thiocyanate. We also considered substitution reactions on the trigonal copper atom site that eventually resulted in the synthesis of a new superconducting cation-radical salt, κ-$(ET)_2Cu[N(CN)_2]Br$. The dicyanamide ion, $[N(CN)_2]^-$, although bent, is larger than the thiocyanate, $(SCN)^-$, anion. The new salt is an ambient pressure superconductor with an inductive onset $T_c = 11.6$ K (resistive onset = 12.5 K), which represents a new high for an organic superconductor.[20]

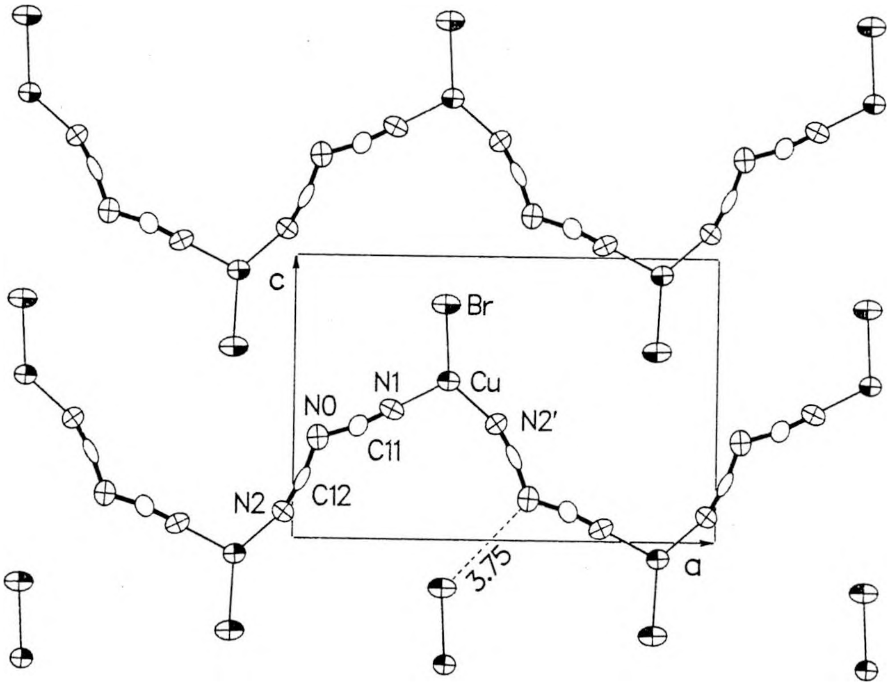
Preliminary ESR measurements on a single crystal of κ-$(ET)_2Cu[N(CN)_2]Br$ indicated a single absorption line spectrum with a peak-to-peak linewidth at room temperature in the range of 60-85 G, depending on crystal orientation. Low temperature studies revealed an estimated relative spin susceptibility that was approximately constant (300 K-100 K) indicative of a metallic sample. Both, the magnitude of the peak-to-peak linewidth, and its temperature dependence are similar to those of previously known κ-phase compounds, e.g., κ-$(ET)_2Cu(NCS)_2$[16,17] and κ-$(ET)_4Hg_{2.89}Br_8$.[18]

The crystal structure of κ-$(ET)_2Cu[N(CN)_2]Br$ was determined by use of single crystal X-ray diffraction data. 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. The structure contains alternating layers (perpendicular to the b axis) of ET donor-molecules and polymeric $\{Cu[N(CN)_2]Br\}_\infty^-$ anions. The overall arrangement with respect to symmetry elements and unit cell directions is the same as that in κ-$(MDT\text{-}TTF)_2AuI_2$.[19] The ET donor-molecule network (see stereodiagram **6**) contains centrosymmetric face-to-face dimers arranged in a typical κ-fashion,[12] i.e., adjacent dimers are approximately perpendicular to each other (74.5°). The central C=C bond of one molecule, if projected along the normal to the molecular plane, is on top of one of the 5-membered rings of the other molecule within the dimer ("bond-over-ring") arrangement. This feature is common to all known κ-phase superconductors.[12,13] All S···S intramolecular contacts within a dimer exceed the sum of the van der Waals radii (3.6 Å), but shorter contacts exist between dimers, as shown in **6**. The topology of the S···S contacts in this salt is different from that found in κ-(ET)$_2$Cu(NCS)$_2$[9b]



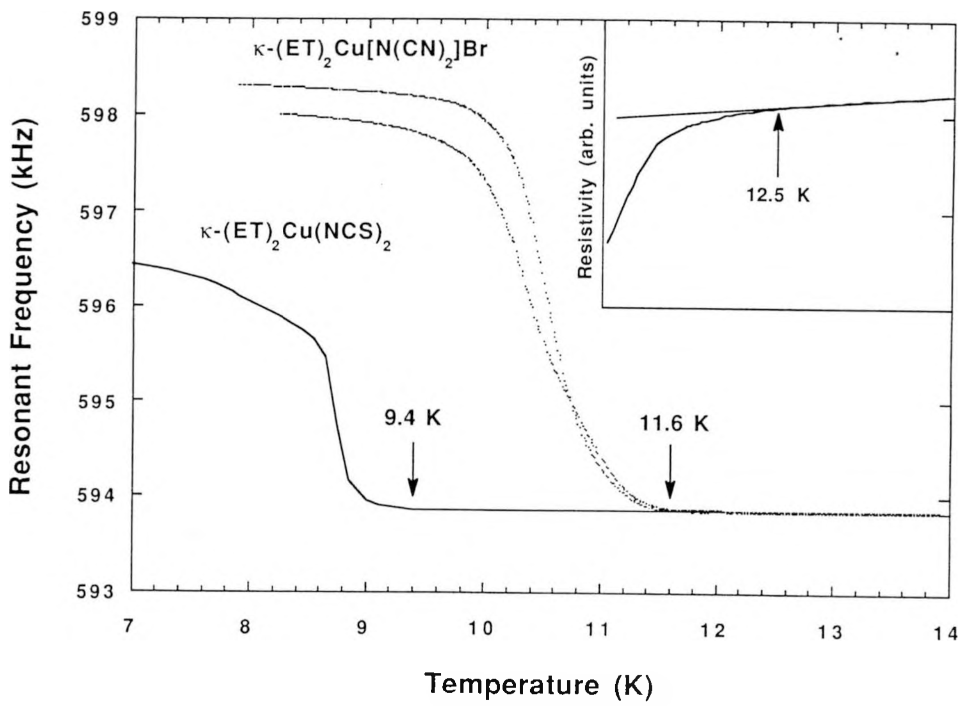
6

The polymeric anion, which resides on a mirror plane, is shown in **7**. 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.



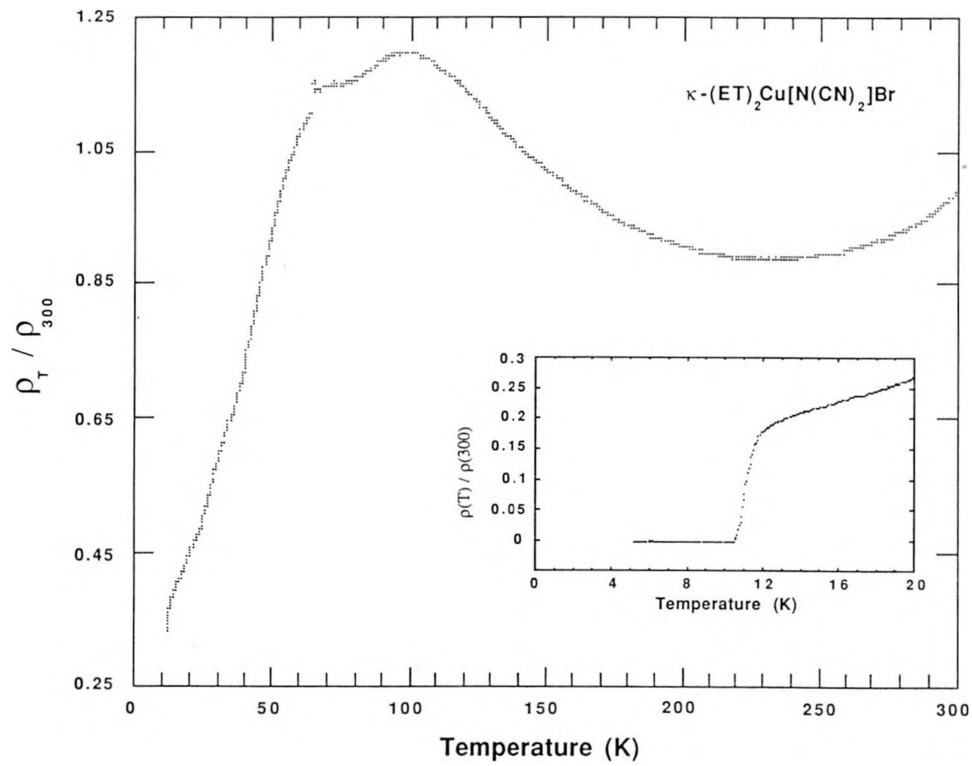
7

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. Superconducting transition curves determined by the rf method are illustrated in **8** for two single-crystal specimens of ~200 μg mass each. This figure includes, for comparison, the transition curve previously determined[9b] for κ-(ET)$_2$Cu(NCS)$_2$ by the same technique, apparatus, and thermometry. In these 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 K to ~8 K, a temperature below signal saturation.



8

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[9b] 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 the Figure). Magnetization experiments were carried out by use of a SQUID magnetometer, and for cooling in a magnetic field H of 1 Oe, with $H \parallel b$, the onset of the diamagnetic susceptibility occurred at the same temperature, 11.6 ± 0.1 K. 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. Clearly the salt is a volume superconductor with a T_c substantially higher (~1-2 K) than that of κ-$(ET)_2Cu(NCS)_2$. Four-probe resistivity measurements of a single crystal specimen of κ-$(ET)_2Cu[N(CN)_2]Br$ gave a resistive onset T_c of 12.5 ± 0.1 K (see inset in **8**) in two different experiments (with the same crystal specimen) in which a different apparatus, with different thermometry, was utilized. A complete 4-probe resistivity curve is given in **9** indicating (see inset) again, an onset of 12.5 ± 0.1 K, a midpoint of 11.2 ±0.1 K, and completion at 10.5 ± 0.1 K. The linearly extrapolated resistive onset, i.e., the intersection of lines extrapolated from the normal state resistivity and from the linear drop of the resistance in the superconducting state, is 11.6 ± 0.1 K, in perfect agreement with the inductive onset of 11.60 ± 0.05 K. 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. It is also noteworthy that κ-$(ET)_2Cu[N(CN)_2]Br$ displays a broad resisitivity maximum at ~90-100 K, a feature previously observed in other κ-phase salts, κ-$(ET)_2Cu(NCS)_2$[7,9,11] and κ-$(DMET)_2AuBr_2$.[23]



9

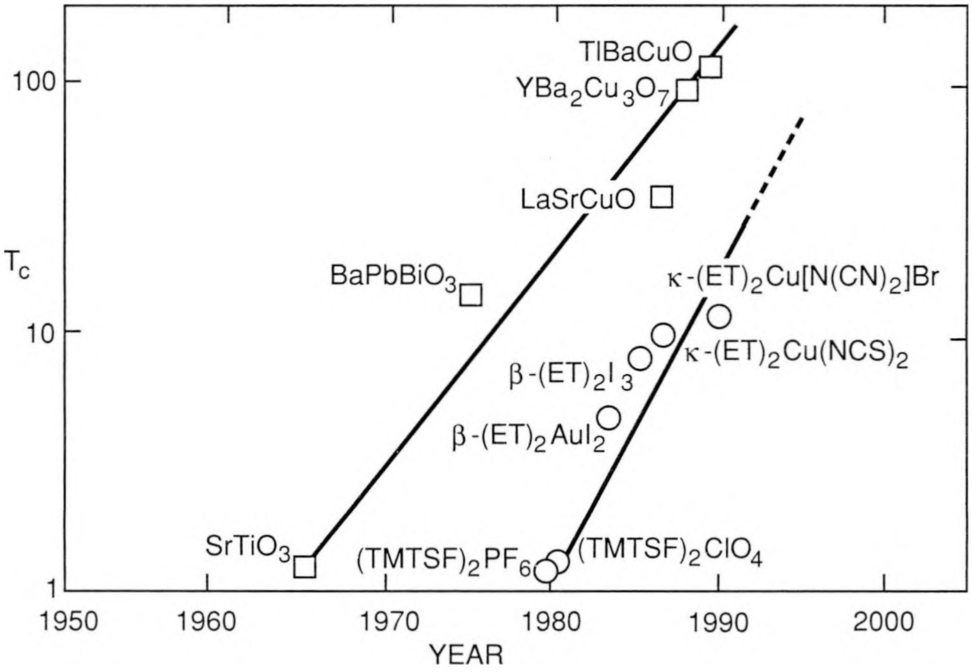
In order to put the above cited new developments into proper perspective, the T_c increment (~1-2 K) of κ-$(ET)_2Cu[N(CN)_2]Br$ over κ-$(ET)_2Cu(NCS)_2$ is approximately the same as the increment observed of κ-$(ET)_2Cu(NCS)_2$ over the previous highest-T_c organic superconductor ß*-$(ET)_2I_3$ ($T_c = 8$ K).

The calculated dispersion relations and Fermi surface (two highest-occupied bands based on a tight-binding band electronic structure calculation)[21] reveals that with the formal oxidation of $(ET)_2^+$, the highest occupied band of κ-$(ET)_2Cu[N(CN)_2]Br$ is half-filled, and its Fermi surface consists of overlapping distorted circles centered at Γ and its equivalent points in reciprocal space. Therefore, κ-$(ET)_2Cu[N(CN)_2]Br$ is expected to be a two-dimensional metal. The band dispersion relations and the Fermi surface of κ-$(ET)_2Cu[N(CN)_2]Br$ are very similar to those of other κ-phase salts.[9b,12,14,15,22]

CONCLUSION

A new ambient pressure organic superconductor, κ-$(ET)_2Cu[N(CN)_2]Br$, has been discovered with an inductive onset $T_c = 11.6 \pm 0.1$ K (resistive onset = 12.5 ± 0.1 K). The anion in the new salt consists of a polymeric mixed (halide)(pseudohalide)cuprate(I) species. Because of the large number of metal/halide/pseudohalide substitutions that can be made in this anionic species, it opens up an entirely new conceptual approach to the design of additional conducting and superconducting (with even higher T_c's) cation-radical salts by use of planar polymeric anions. Studies along theses lines are currently under way in our laboratory.

Finally, some perspective on the present status and future prospects of organic superconductors in relation to the high-T_c oxide superconductors can be gained from an inspection of **10**. It is also becoming increasingly clear that in terms of structure (both are layered superconductors) and the physics (both are type II-superconductors with anisotropic coherence lengths, anisotropic H_{c2}, and in which superconductivity is competing with magnetic ground states, etc.), the organic superconductors are more similar to the high-T_c oxide superconductors than to other classes of superconductors. Thus, the prospects for discovering high-T_c in organic systems appear very bright!



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ACKNOWLEDGMENT

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