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NEW AMBIENT PRESSURE ORGANIC SUPERCONDUCTORS: α-$(BEDT\text{-}TTF)_2(NH_4)Hg(SCN)_4$, βm-$(BEDO\text{-}TTF)_3Cu_2(NCS)_3$, and κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$

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INTRODUCTION

More than one hunderd and twenty conducting salts based on the organic donor-molecule BEDT-TTF are known, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene (abbreviated herein as ET). Several of the early salts possessed tetrahedral and octahedral anions, such as $(ET)_2ClO_4(TCE)$,[1] $(ET)_2PF_6$,[2] $(ET)_2ReO_4$,[3] and $(ET)_2BrO_4$.[4] The perchlorate salt is metallic to 1.4 K,[1] and the perrenate derivative was the first ET based organic superconductor (T_c 2 K, 4.5 kbar).[3] Since the discovery of ambient pressure superconductivity in β-$(ET)_2I_3$ (T_c 1.4 K),[5] other isostructural β-$(ET)_2X$ salts have been prepared with higher T_c's. These salts are β-$(ET)_2IBr_2$ (T_c 2.8 K),[6] β-$(ET)_2AuI_2$ (T_c 4.98 K),[7] and β^*-$(ET)_2I_3$ (T_c 8 K).[8] A structure-property correlation for the β-type salts has been reviewed in this volume;[9] it predicts that T_c's higher than 8 K are possible if β-salts with linear anions longer than I_3^- can be synthesized. During the search for new linear anions, a variety of compounds was discovered with polymeric anions. For example, with the $Ag(CN)_2^-$ anion, in addition to the expected $(ET)_2Ag(CN)_2$ salt,[10] afforded the first ET salt with a polymeric anion, $(ET)Ag_4(CN)_5$.[11] The linear AgI_2^-[12] or cubic $Ag_4I_6^{2-}$ [13] anions, yielded $(ET)_3Ag_{6.4}I_8$.[13] In a similar fashion the CuI_2^- anion leads to $(ET)_2Cu_5I_6$.[14,15] The latter two compounds are good metals to low temperatures and consist of layers of donor molecules and polymeric anions. The report of superconductivity in κ-$(ET)_4Hg_3X_8$ (X = Cl, T_c 5.3 K 29 kbar[16] and X= Br, T_c 4.3 K ambient pressure[17] and 6.7 K 3.5 kbar[18]) and κ-$(ET)_2Cu(NCS)_2$ (Tc 10.4 K)[19] further stimulated the search for novel polymeric anions. A general synthetic strategy for preparing new salts containing polymeric anions is to couple a coordinatively unsaturated neutral transition metal halide/pseudohalide with a simple halide or pseudohalide during an electrocrystallization synthesis. A number of new compounds have been made in this way, for example, $(ET)BiI_4$,[20] $(ET)Ag_{1.6}(SCN)_2$,[21] and $(ET)Ag_{2.4}Br_3$.[22] In an attempt to replace the halide in κ-$(ET)_4Hg_3X_8$ with a pseudo halide, a β-like $(ET)_4Hg_3(SCN)_8$[23,24] compound was obtained. Using slightly different experimental conditions during electrocrystallization, two entirely different salts, α-$(ET)_2(M)Hg(SCN)_4$ ($M^+ = K^+$ and NH_4^+), have been reported by Oshima *et al.*[25,26] In this article, we discuss three new ambient pressure organic superconductors with novel polymeric anions, α-$(ET)_2(NH_4)Hg(SCN)_4$,[27] βm-$(BO)_3Cu_2(NCS)_3$,[28] and κ-$(ET)_2Cu[N(CN)_2]Br$.[29]

α-$(ET)_2(M)Hg(SCN)_4$, $M^+ = K^+$, NH_4^+, and Rb^+

The α-phase salts are prepared by electrocrystallization of ET (one eq), $Hg(SCN)_2$ (10 eq), MSCN (20 eq $M^+ = K^+$, NH_4^+, and Rb^+), and 18-crown-6 (10 eq) in 1,1,2-trichloroethane with 10% (vol) ethanol. The applied current density is maintained in the range of 0.2 to 0.5 $\mu A/cm^2$. Crystal growth is carried out at room temperature for approximately two to six weeks. The resulting crystals are shiny black thick platelets. The room temperature ESR peak-to-peak linewidth falls in the range of 55 to 85 G for all three compounds (*vide infra*). Screening of crystals employing ESR spectroscopy reveals a second minor unidentified phase with a linewidth of less than 10 G. The typical morphology for the minor phase is thin needle-like platelets. It is worth noting in this regard that a 3:1 salt, $(ET)_3[Hg(SCN)_3]$, has been reported.[25]

The α-phase potassium and ammonium salts were identified by their unit cell parameters,[25-27] and a single-crystal structural determination was carried out on the rubidium salt. Detailed structural results of the rubidium salt will be published elsewhere. The unit cell parameters of all three compounds are listed in Table 1.

Table 1. Unit Cell Parameters for α-$(ET)_2(M)Hg(SCN)_4$

	K^+ [25]	NH_4^+ [26,27]	Rb^+
a (Å)	10.082	10.089	10.087 (b)
b (Å)	20.565	20.613	20.642 (c)
c (Å)	9.933	9.968	9.998 (a)
α (°)	103.70	103.67	103.54 (β)
β (°)	90.91	90.47	90.53 (γ)
γ (°)	93.06	93.36	93.23 (α)
V (Å^3)	1997.0	2010	2020.1

The unit cell volume increases by approximately 0.5% in going from potassium to ammonium and another 0.5% in continuing from ammonium to rubidium. The two-dimensional polymeric anion layer is shown in Figure 1. The mercury atoms are located in tetrahedral sites with four sulfur bonded SCN^- ligands. The rubidium atoms on the other hand are located in eight coordination sites with four sulfur bonded SCN^- ligands on one side and four nitrogen bonded NCS^- ligands on the other side in an overall square antiprism configuration. The donor layer belongs to a typical α-type packing motif.

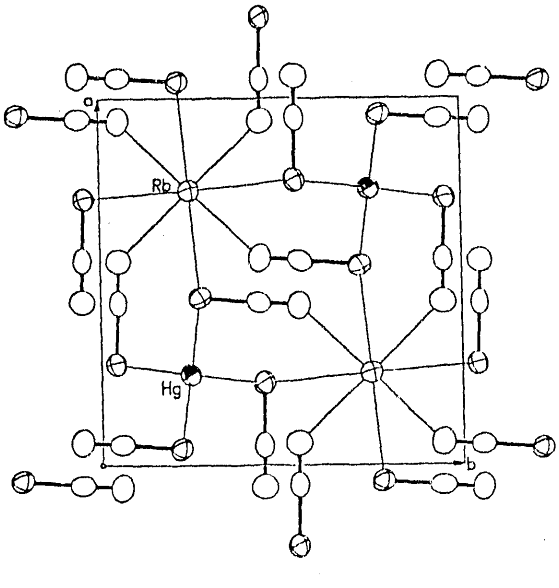

Figure 1. The anion layer of α-$(ET)_2RbHg(SCN)_4$ viewing along c^* axis

An oriented single-crystal ESR study has been carried out on the rubidium salt. A square platelet crystal of α-$(ET)_2RbHg(SCN)_4$ was mounted on a quartz rod with the crystal plane oriented vertically in the microwave cavity. The *b* axis (see Table 1, Rb salt) pointed upward. The zero and ninety degree orientations correspond to the static magnetic field parallel and perpendicular to the crystal plane, respectively. The measured g-values (circles) and peak-to-peak linewidths (triangles) are plotted in Figure 2. The corresponding solid curves are the least squares fit to the measured data with the following equations:

$$g_{obs}^2 = \sum_{i,j=1}^{3} g_{ij}^2\, l_i\, l_j \qquad \text{and } \Delta H = \sum_{i,j=1}^{3} \Delta H_{ij}\, l_i\, l_j$$

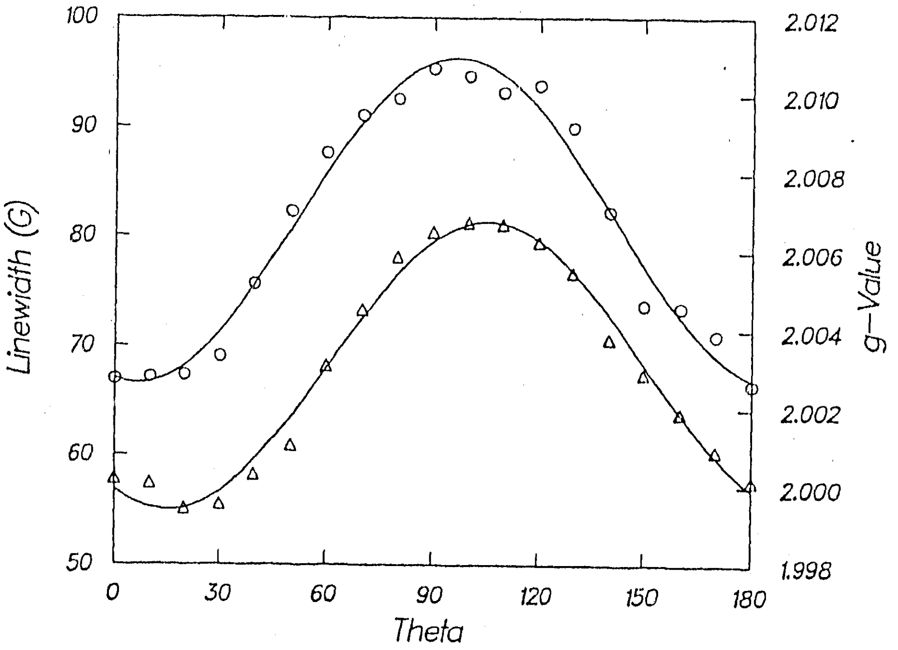

Figure 2. Orientation dependence of g-values (circles) and linewidths (triangles) of α-$(ET)_2RbHg(SCN)_4$ at room temperature.

The l_i and l_j are the direction cosines of the principal axes. The g-values and linewidths for the rubidium salt range from 2.002 to 2.011 and 55 G to 81 G, respectively. The results are very similar to that of the ammonium salt.[27] As shown in Figure 2, the minimum and maximum g-values correspond to the static magnetic field parallel to the crystallographic *a* and *c** axes. The g-value maximum near 90^o, where the static field is approximately parallel to the central C=C double bond of each ET molecule, is commonly observed in other ET salts, such as α-$(ET)_2(NH_4)Hg(SCN)_4$[27] and α-$(ET)_2I_3$.[30]

The temperature dependences of the ESR linewidth (ΔH) and the relative spin susceptibility (χ) of α-$(ET)_2RbHg(SCN)_4$ from 300 to 100 K are plotted in Figure 3. The peak-to-peak linewidth decreases monotonically with decreasing temperature from 81 G at 300 K to 24 G at 100 K. The spin susceptibility remains constant in the temperature range measured, which is consistent with the Pauli paramagnetism of a metallic sample. This behavior is a common feature of the α,[27] β,[31,32] and θ-phase[33] salts of ET. The decrease in linewidth with decreasing temperature can be qualitatively understood by use of the Elliott formula:[34,35]

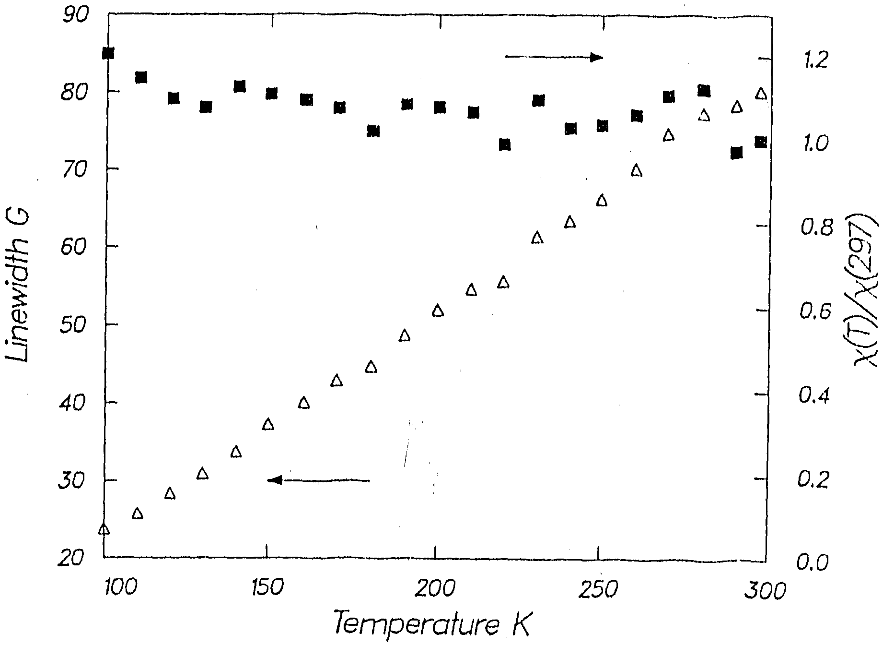

Figure 3. The temperature dependence of linewidth and relative spin susceptibility of α-$(ET)_2RbHg(SCN)_4$.

$$\Delta H \sim (\Delta g)^2/\tau \qquad \text{and} \qquad \sigma = ne^2\tau/m_{eff}$$

where $\Delta g = g_{obs} - 2.0023$ (a constant within experimental error) and τ is the conduction electron relaxation time. Since the conductivity (σ) increases with decreasing temperature, the linewidth is expected to become sharper as the temperature is lowered. Low temperature ESR measurements have been carried out on α-$(ET)_2(NH_4)Hg(SCN)_4$ from 150 to 4.2 K. The behavior between 150 K and 20 K is identical to that of the 300 K to 100 K, namely, the linewidth decreases with decreasing temperature and the spin susceptibility remains constant. Below 20 K, the relative spin susceptibility starts to drop, which is very likely due to a microwave penetration depth effect.[36] The penetration depth becomes smaller when the conductivity increases significantly, and only outer portion of the sample is measured. The linewidth decreases at a much slower rate below 20 K and is 0.33G at 4.2 K. This linewidth is even sharper than some of the β-phase crystals at a similar temperature.[37] One possible reason for the extremely sharp linewidth of α-$(ET)_2(NH_4)Hg(SCN)_4$ is that the contribution from the conduction electrons becomes negligible at 4 K (*vide supra*) and only the residue linewidth (similar to the residue resistivity) remains. The residue linewidth could be caused by chemical impurities or crystal defects. Further experiments are needed to clarify this point.

The possible presence of superconductivity in the three α-phase salts was explored with RF penetration depth measurements at 0.5 K. In this method, superconductivity is exhibited by an increase in resonant frequency over that of the empty coil caused by the exclusion of the RF field from the sample by the persistent shielding currents. Only the ammonium salt displayed a strong superconducting signal (onset 1.15 K).

All known α-phase ET salts are listed in Table 2 along with their conductive properties. The *a* x *b* cross section area of the unit cell is also included so that the packing of the donor layers of different salts can be compared directly. A cross section area near 100 $Å^2$ seems to favor conductivity. One remaining question is that why does not the structure-property correlation for the β-phase salts, i.e., larger unit cell volume give rise to higher T_c's apply to the α-$(ET)_2(M)Hg(SCN)_4$ salts. No apparent structural disorder is observed in these materials. One difference among the K^+, NH_4^+ and Rb^+ salts is that the NH_4^+ cation is a molecular species and might provide a unique phonon mode that leads to superconductivity.

Table 2. Summary of α-Phase ET Compounds

Compounds	Conductance	Unit Cell Volume ($Å^3$)	Cross Section a x b ($Å^2$)	Reference
α-$(ET)_2[RbHg(SCN)_4]$	metal	2020.1	100.85	this work
α-$(ET)_2(NH_4)Hg(SCN)_4$	$T_c = 1.15$	2010	100.54	27
α-$(ET)_2[KHg(SCN)_4]$	metal at 1.5K	1997	100.14	25
θ-$(ET)_2I_3$	metal	3386	100.03	38
α-$(ET)_2I_3$	T_{MI}= 135K	1698	99.21	39
α-$(ET)_2I_2Br$	T_{MI}= 245K	1688	98.9	40
α-$(ET)_2Cu(NCS)_2$	T_{MI}= 200K	1672	98.25	41
α-$(ET)_2IBr_2$	semiconductor	1652	107.14	42
α-$(ET)_2BrICl$	semiconductor	1647	106.86	43

β_m-(BEDO-TTF)$_3$Cu$_2$(NCS)$_3$

The new donor molecule BEDO-TTF, bis(ethylenedioxy)tetrathiafulvalene (abbreviated herein as BO) contains four outer oxygen atoms and four inner sulfur atoms[44]. The BO donor molecule is more susceptible to oxidation than ET. Electrocrystallization syntheses of BO salts are preferably carried out under inert atmosphere. Three BO salts have been characterized structurally , i.e., (BO)$_2$AuBr$_2$,[45] (BO)$_{2.4}$(I$_3$),[46] and (BO)$_3$Cu$_2$(NCS)$_3$.[28] Several other BO salts suffer from inferior crystal quality, e.g., (BO)$_2$AuI$_2$, (BO)$_2$PF$_6$. In the case of (BO)$_2$ClO$_4$[45] only the structure of the donor layer can be solved. The β_m-(BO)$_3$Cu$_2$(NCS)$_3$ crystals are prepared by electrocrystallization of BO (one eq), CuSCN (10 eq), KSCN (10 eq), and 18-crown-6 (10 eq) in 1,1,2-trichloroethane and 10% (vol) ethanol. The current density employed is ~0.1μA/cm^2, and the crystal growth is carried out in a nitrogen-purged drybox. Typical crystals are rectangular boxes. Moreover the crystal size is generally very small due to facile nucleation. During sample preparation, the electrode polarity was inadvertently reversed for one of the cells for a period of two days. The polarity was subsequently switched back. The polarity switch substantially reduced the rate of nucleation and larger crystals were obtained. It is interesting to note that this observation is reproducible. The larger crystals were used for structural determinations.

The detailed crystal structure of βm-(BO)$_3$Cu$_2$(NCS)$_3$ has been reported elsewhere.[28] The novel polymeric anion layer is shown in Figure 4. Both Cu1 and Cu2 are three coordinate with a trigonal planar configuration. The Cu1 atom coordinates to two sulfur and one nitrogen atoms, while the Cu2 atom coordinates to two nitrogen and one sulfur atoms. All SCN$^-$ ligands are bridged. The resulting anion network is an infinite two-dimensional layer. This is in constrast to the anion layer in κ-(ET)$_2$Cu(NCS)$_2$, where Cu(NCS)$_2^-$ forms a zigzag chain with one bridging and one terminal SCN$^-$ group. Two different anion layers (Cu$_2$(NCS)$_3^-$ and Cu(NCS)$_2^-$) are both "self-assembled" considering the almost identical synthetic conditions for both salts. Apparently the anion cavity created by the donor packing predetermines the appropriate polymeric anion to be accommodated.

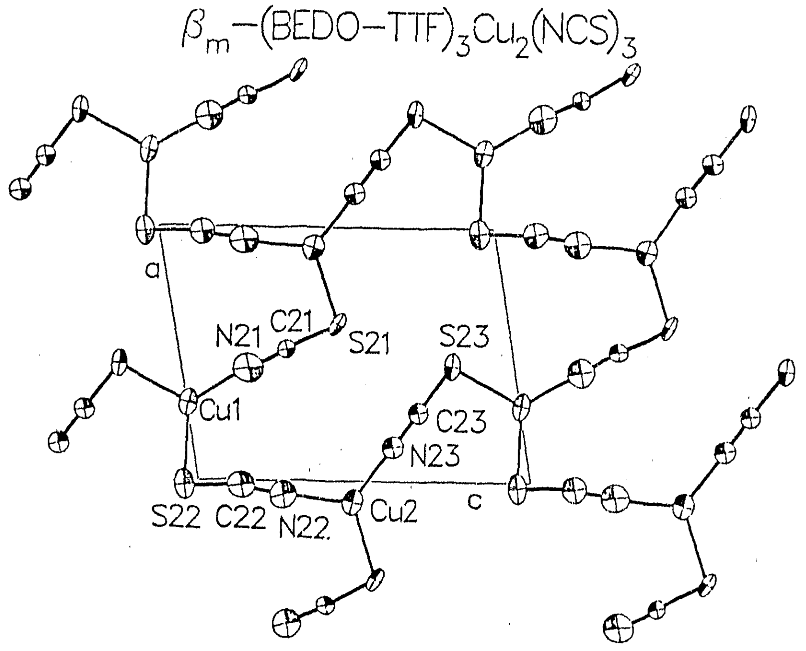

Figure 4. The polymeric anion layer of $(BO)_3Cu_2(NCS)_3$.

An oriented single-crystal ESR study was carried out on β_m-$(BO)_3Cu_2(NCS)_3$. The measured g-values (circles) and peak-to-peak linewidths (triangles) are plotted in Figure 5. The platelet crystal of β_m-$(BO)_3Cu_2(NCS)_3$ was mounted horizontally in the microwave cavity. The 0° and 90° positions correspond to orientations where the static magnetic field is approximately parallel and perpendicular to the *b* axis, respectively.[28] The correlation between crystallographic axes and the crystal morphology in this BO salt is different from the majority of the $(ET)_2X$ derivatives. The two solid lines in Figure 5 are the least square fits employing the same equations as discussed above The linewidths range from 17.5 to 26.6 G and the g-values from 2.002 to 2.012. It is worth noting that the ESR linewidth for β_m-$(BO)_3Cu_2(NCS)_3$ is different from all other BO salts.[45] This is reasonable, since the linewidth is sensitive to the crystal symmetry and crystal structure. Accordingly, a linewidth near 20 G might well serve as an indication of new BO-based superconductors.

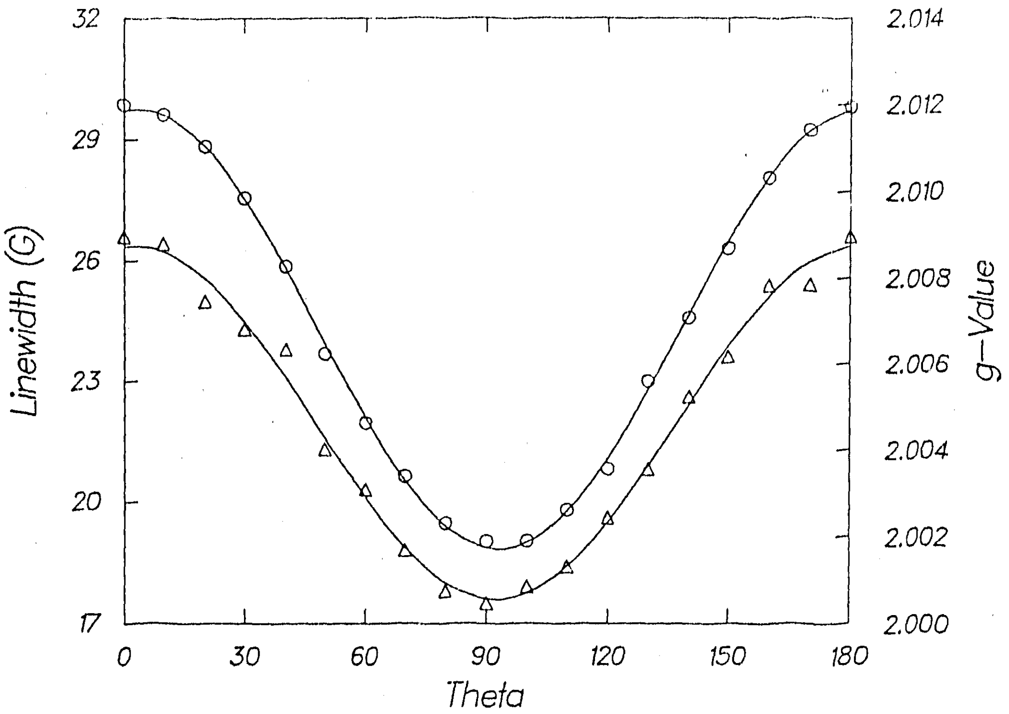

Figure 5. The orientation dependence of g-values (circles) and linewidths (triangles) of $(BO)_3Cu_2(NCS)_3$ at room temperature.

κ-$(ET)_2Cu[N(CN)_2]Br$

κ-phase compounds similar to the 10.4 K superconductor κ-$(ET)_2Cu(NCS)_2$ have long been actively sought since 1988. The $Cu(NCS)_2^-$ polymeric network consists of tri-coordinated Cu(I) with two bridging SCN^- ligands that form a zigzag chain and a terminal SCN^- that completes the third coordination site. Many attempts to replace the terminal SCN^- group with other halides or pseudohalides such as I^- or CN^- and maintain the zigzag chain, have been in vain. The resulting products are usually a mixture of the κ-$(ET)_2Cu(NCS)_2$ and intractable materials. During attempts to prepare $(ET)_2Cu[N(CN)_2]_2$, κ-$(ET)_2Cu[N(CN)_2]Br$ was isolated.[29] The synthesis will be published elsewhere.

The crystal structure has been determined[29] and yielded the following unit cell parameters: orthorhombic space group *Pnma*, $a = 12.942$ Å, $b = 30.016$ Å, $c = 8.539$ Å, $V = 3317$ Å^3. The donor packing motif is typical of κ-phase salts. The polymeric anion layer is shown in Figure 6. The $Cu[N(CN)_2]Br^-$ layer consists of tri-coordinated Cu(I) with two bridging $(NC)N(CN)^-$ ligands forming a zigzag chain and a terminal bromide to complete the coordination around Cu atom. The terminal bromine atom has a close contact with a nitrogen atom from an adjacent chain so that each zigzag chain is not totally isolated.

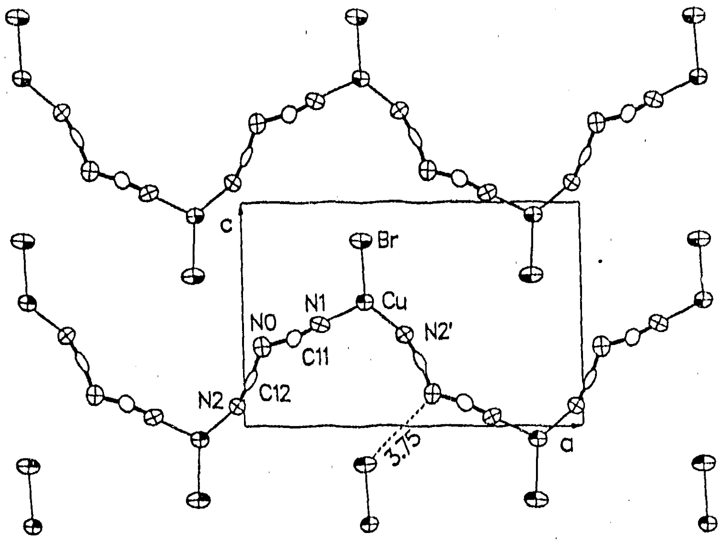

Figure 6. The polymeric anion layer of κ-(ET)$_2$Cu[N(CN)$_2$]Br viewing along *b* axis.

An oriented single-crystal ESR study was carried out on κ-(ET)$_2$Cu[N(CN)$_2$]Br. The typical crystal morphology is a thick diamond-shaped platelet. The *b* axis is normal to the crystal plane and the *a* axis is coincident with one of the diagonals of the platelet. A platelet crystal was mounted vertically in the microwave cavity (*a* axis pointed upward). The measured g-values (circles) and peak-to-peak linewidths (triangles) are plotted in Figure 7. The 0° and 90° angles correspond to the static magnetic field parallel and perpendicular to the crystal plane, respectively. The two solid lines are the least squares fit to the experimental values. The maximum g-value occurs at 90°, where the static magnetic field is parallel to the *b* axis and the central C=C double bond of the ET molecules. This observation parallels what is observed in other ET salts. The maximum g-value at 90° corresponds to the minimum linewidth. This behavior appears to be unique to the κ-phase and has also been observed in κ-(ET)$_2$Cu(NCS)$_2$.[42] The linewidth varies from 60 G to 80 G, which is characteristic of κ-phase salts.

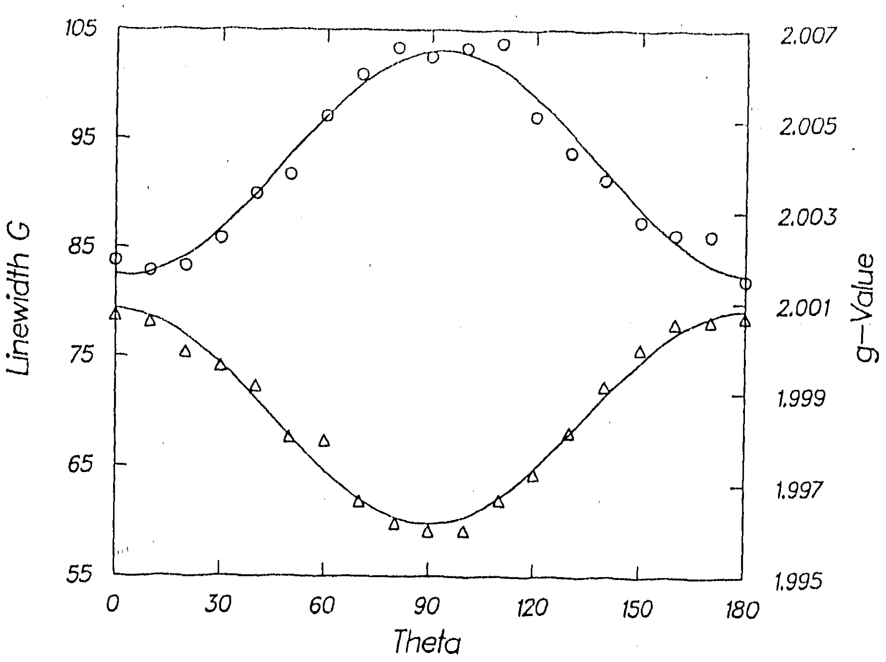

Figure 7. The orientation dependence of g-values (circles) and linewidths (triangles) of κ-$(ET)_2Cu[N(CN)_2]Br$ at room temperature.

Four probe conductivity measurements on a single crystal of κ-$(ET)_2Cu[N(CN)_2]Br$ reveal metallic character between 300 and ~220 K, a large resistive hump near 100 K, and strongly metallic behavior below 60 K.[9] The superconductive onset temperature is 12.5 K, with midpoint at 11.2 K and zero resistance at 10.5 K. Superconductivity was also detected with RF penetration depth measurements and low field dc magnetization experiments employing single crystals weighing ~200μg.[29] The onset temperatures for these two measurements were both 11.6 K. The RF signal reaches saturation near 9.8 K. All the measurements for superconductivity indicate a very sharp transition.

The single crystal that was used for the RF penetration depth measurements was also used for low temperature ESR studies. It was oriented with the *b* axis (90° in the aforementioned orientation study) parallel to the static magnetic field. The linewidth increases slowly with decreasing temperature from 60 G at 300 K to 79 G at 60 K with a rate of increase of about 0.08 G/K. The linewidth and relative spin susceptibility are plotted against temperature in Figure 8. The ESR behavior of κ-$(ET)_2Cu[N(CN)_2]Br$ between 300 and 60 K is similar to that of κ-$(ET)_2Cu(NCS)_2$[47,48] and κ-$(ET)_4Hg_{2.89}Br_8$.[33] Below 60 K, the linewidth starts to decrease with decreasing temperature. At 40 K, in addition to the main absorption peak, a second peak with a sharper linewidth and ~3% intensity starts appearing. The second peak behaves in a paramagnetic fashion between 40 and 15 K. The origin of the new peak could be either a small amount of chemical impurities or crystal defects. It should be pointed out that a sharp uncharacterized peak has also been observed in κ-$(ET)_2Cu(NCS)_2$ below 20 K.[47,48] Further experiments are in progress. The linewidth of the main absorption peak decreases with decreasing temperature from 79 G at 60 K to 40 G at 10 K with a rate of decrease at 0.8 G/K, which is one order of magnitude faster than the aforementioned linewidth increase rate between 300 and 60 K. The observed linewidth decrease in κ-$(ET)_2Cu[N(CN)_2]Br$ below 60 K contrasts with the behavior of κ-$(ET)_2Cu(NCS)_2$ and κ-$(ET)_4Hg_{2.89}Br_8$. Nevertheless, the linewidth behavior of the title compound is totally consistent with the conductivity measurements, i.e. the apparent semiconductive to metallic behavior.[9] The spin susceptibility (squares) shows a slight increase between 300 and 100 K. Below 100 K, it starts to drop. At 15 K, it reaches 80% of the room temperature value. Below 10 K the main ESR absorption disappears,which is in agreement with the onset of superconductivity.

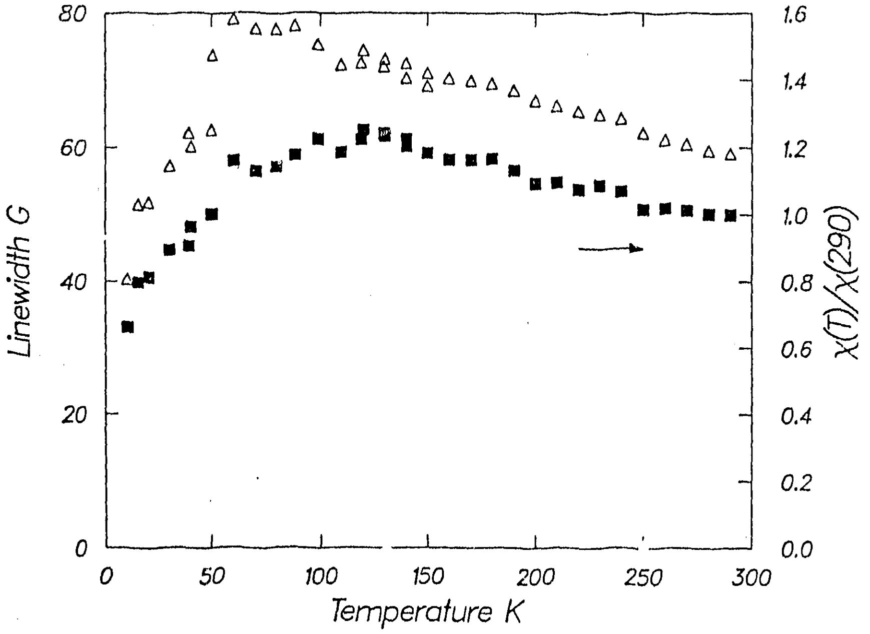

Figure 8. The temperature dependence of linewidths (triangles) and spin susceptibility (square) of κ-$(ET)_2Cu[N(CN)_2]Br$.

CONCLUSIONS

The use of polymeric anions continues to generate interesting new conducting materials, including the two highest T_c organic superconductors, κ-$(ET)_2Cu(NCS)_2$ and κ-$(ET)_2Cu[N(CN)_2]Br$. In contrast to the limited number of known linear monovalent anions, the possibilities for synthesizing new and previously unknown polymeric anions are considerable. Further research along these lines should prove to be rewarding.

Over the past decade, the T_c's of organic superconductors have increased by an order of magnitude from the 1.2 K value of $(TMTSF)_2ClO_4$ to 12.5 K for κ-$(ET)_2Cu[N(CN)_2]Br$. The oxide superconductors have made a greater jump from 11 K for $BaBi_{0.75}Pb_{0.25}O_3$ to 125 K of the Tl based high T_c materials. Considering the similarities among these two systems, it is not unreasonable to expect the organic superconductors to make major improvements in the future.

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