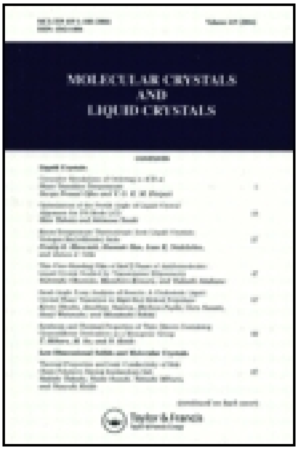

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Synthesis, Characterization, and Physical Properties of Two New Magnetic Organic Metals, $[BEDT\text{-}TTF]_4[C(CN)_2CONH_2]CuX_2$ (X = Cl and $Br_{0.77}Cl_{0.22}$)

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SYNTHESIS, CHARACTERIZATION, AND PHYSICAL PROPERTIES OF TWO NEW MAGNETIC ORGANIC METALS, $[BEDT\text{-}TTF]_4[C(CN)_2CONH_2]CuX_2$ ($X = Cl$ AND $Br_{0.77}Cl_{0.22}$)

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Abstract Two new BEDT-TTF based charge transfer salts, $[BEDT\text{-}TTF]_4[C(CN)_2CONH_2]CuX_2$ ($X = Cl$ and $Br_{0.77}Cl_{0.22}$) have been synthesized and characterized with use of x-ray diffraction, Energy Dispersive Spectroscopy (EDS), and Raman spectroscopy. ESR spectroscopy reveals that the anion layer contains 3% of paramagnetic Cu(II) species which exhibit Curie-Weiss behavior with a Weiss constant of $\theta = -2.8$ K. Both compounds are metallic below 150 K. AC susceptibility, RF penetration depth, and RF impedance measurements under pressure do not reveal signals of superconductivity.

INTRODUCTION

Nearly 200 BEDT-TTF based charge transfer salts have been reported to date with a wide range of electrical properties, including insulators, semiconductors, metals, and superconductors.[1] The electron donor molecule, BEDT-TTF, is bis(ethylenedithio)-tetrathiafulvalene or abbreviated ET. The two-dimensional layer network in the crystal structure, and the close S···S contacts between ET molecules, are believed to be the key elements for high conductivity in these materials. To prepare new highly conductive ET salts, two synthetic strategies have been quite successful. By the use of large segregated anions, a new family of superconductors, $\kappa\text{-}(ET)_2[M(CF_3)_4](Solv)$ (M = Cu, Ag, Au and Solv = 1,1,2-trihaloethane), were recently reported.[2] "Self-assembled" polymeric anions have led to the discovery of a series of metals and superconductors such as $\kappa\text{-}(ET)_4Hg_{2.89}Br_8$,[3] $\alpha\text{-}(ET)_2MHg(SCN)_4$,[4] $\kappa\text{-}(ET)_2Cu(NCS)_2$,[5] $\kappa\text{-}(ET)_2Cu[N(CN)_2]X$ (X= Cl, Br, CN),[6-8] in the past years. Following these guidelines, we have taken the approach of complexing segregated organic anions with metal halides in order to build either a larger anion or a new polymeric anion. Our previous attempts with the complexation reaction between $PPN[C(CN)_3]$ [PPN is bis(triphenylphosponium)-imminium cation] and metal halides during electrocrystallization were not successful, and the only product isolated was $(ET)_2C(CN)_3$.[9] In this article, we report a successful complexation reaction during electrocrystallization with the use of cuprous halides and carbamyldicyanomethanide, $[C(CN)_2CONH_2]^-$,[10] an amide derivative of $[C(CN)_3]^-$. The synthesis, chemical characterization, and physical properties of $(ET)_4[C(CN)_2CONH_2]CuX_2$ are presented herein.

SYNTHESIS

Synthesis of $PPN[C(CN)_2CONH_2]$: 1.08 g of $KC(CN)_2CONH_2$[10] (7.3 m mol) was added to an aqueous solution containing 4.24 g of PPNCl (7.4 m mol) at ~75°C. The resulting white precipitate was dried under vacuum and recrystallized from methylene chloride/diethyl ether to give 2.5 g of $PPN[C(CN)_2CONH_2]$ (3.9 m mol). Yield = 53%. mp. = 189 – 192 °C. Elem. anal. for $C_{40}H_{32}N_4OP_2$, Found (Calcd)%, C: 74.17 (74.29); H: 5.00 (4.99); N: 8.60 (8.66)%.

Electrocrystallization of the $(ET)_4[C(CN)_2CONH_2]CuCl_2$ salt was carried out with the use of 146 mg (0.23 m mole) of $PPN[C(CN)_2CONH_2]$, 23 mg (0.23 m mole) of CuCl (Aldrich), and 10 mg of ET in the presence of TCE with 10% (vol) ethanol. Crystal growth was noticed after a few days under 0.3 μA/cm² current density and the resulting platelet crystals were harvested after 6 to 8 weeks. The related bromide salt was prepared similarly with use of CuBr instead of CuCl (source of Cl discussed below).

CHARACTERIZATION

A. Structure

Crystals of the salts formed by ET, $PPN[C(CN)_2CONH_2]$, and cuprous halide (Cl and Br) were examined on a four-circle X-ray diffractometer. Both exhibited an isomorphous diffraction pattern dominated by an *I*-centered orthorhombic subcell and weak diffraction spots corresponding to a supercell with doubled *a*- and *b*-axes (see Table I for cell parameters). The supercell is *C*-centered. Intensity data were collected at room temperature for the Cl-derivative (subcell reflections only) and at 117 K for the Br-derivative (all reflections). A solution for the ET radical cations was found in the subcell space group *I*222, and a projection of the ET molecules along the *c*-axis is shown in Figure 1. The ET molecules are located on two-fold rotation axes parallel to the central C=C double bond. The molecules form slipped, uniform stacks along the *a*-axis. However, the interplanar distance between neighboring molecules along the stack is 3.9Å (Cl-salt), whereas the intermolecular S···S network is dominated by shorter *inter*stack distances (shown with thin lines on Figure 1). The normal to the plane through the conjugated portion of the ET molecule forms an angle of 41(1)° (Cl-salt) with the *a*-axis. This inclination angle is in the opposite direction on adjacent stacks, thus forming a herring-bone arrangement in the plane typical of the α-phase packing found in many ET salts.

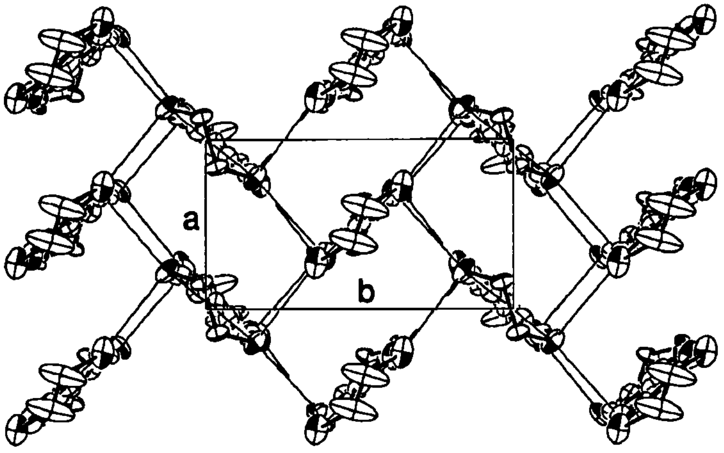

FIGURE 1 Projection of the crystal structure of the chloride derivative along the *c*-axis. The subcell is indicated as a rectangle, and intermolecular S···S distances less than 3.60 Å are drawn as thin lines.

Many attempts have been made with a number of techniques (direct methods, Patterson maps, difference electron density maps) to obtain a structure solution for the anion layer which must be located between ET molecule layers for crystal packing reasons. No refineable solutions have been obtained to date with either of the data sets available. At this stage, the only inference from the crystallographic data about the identity of the anions is the fact that the chlorine and bromine derivative possess different lattice parameters, thus the halide ion must be incorporated in the crystal structure.

TABLE I Orthorhombic lattice parameters of the salts studied.

Sample	*T* (K)	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
Cl subcell	298	5.099(1)	9.320(2)	34.114(4)	1621.2(4)
Cl supercell	298	10.199(1)	18.639(4)	34.115(4)	6485(2)
Br subcell	298	5.124(1)	9.338(3)	34.175(9)	1635(1)
Br supercell	298	10.247(2)	18.676(5)	34.175(9)	6540(3)
Br supercell	117	10.148(1)	18.535(5)	34.134(6)	6421(2)

B. Energy Dispersive Spectroscopy (EDS)

In order to characterize the anion composition and the overall stoichiometry, quantitative chemical analysis of the title compounds for sulfur, copper, and halogen contents was carried out with the use of an Oxford Link ISIS EDS unit attached to a scanning electron microscope. Each crystal was checked for both chlorine and bromine contents and the results were compared with the κ-$(ET)_2Cu[N(CN)_2]Br$[7] standard. For each sample, at least three analyses were carried out on different surface locations, and the averaged atomic percentages were standardized to 16 or 32 sulfur atoms for $(ET)_2$ or $(ET)_4$ formula units. The results are summarized in Table II.

TABLE II Atomic percentages from EDS analysis of the title compounds.

Compound	S	Cu	Br	Cl
κ-$(ET)_2Cu[N(CN)_2]Br$	16	1.02±0.02	1.17±0.03	None
$(ET)_4[C(CN)_2CONH_2]CuCl_2$	32	1.19±0.07	None	2.28±0.21
$(ET)_4[C(CN)_2CONH_2]CuBr_2$[a]	32	1.12±0.07	1.72±0.04	0.49±0.04

[a] see text for its composition

As shown in Table II, the total halogen to copper ratios in the title compounds are very close to 2:1. The atomic ratio of Cl/Cu for $(ET)_4[C(CN)_2CONH_2]CuCl_2$ is 1.92, and no bromine is detected. For the corresponding $(ET)_4[C(CN)_2CONH_2]CuBr_2$ compound, the total halogen to copper ratio is 1.97, but approximately 22% of the total halogen consists of chlorine. The stoichiometry of the Br-salt is therefore, $(ET)_4[C(CN)_2CONH_2]CuBr_{1.54}Cl_{0.44}$. The only possible chlorine source from our $[C(CN)_2CONH_2]^-$/CuBr electrochemical synthesis is the solvent, 1,1,2-trichloroethane.

Significant solvent fragmentation likely triggered by the nucleophilicity of carbamyldicyanomethanide anion, must have occurred during electrocrystallization.

C. Raman Spectroscopy

Raman studies of the title compounds were carried out at room temperature on a Renishaw Raman microscope spectrometer equipped with a He–Ne laser (6328 Å). The Raman spectrometer was calibrated against a standard Si scattering peak at 520 cm^{-1}. Low incident laser intensity (0.06 mW) was applied to avoid sample decomposition, and each sample was run at a 1 cm^{-1} resolution. Each final spectrum was an average over 40 scans. In this study, we focused mainly on the C=C and C≡N stretching vibrations. The results are summarized in Table III.

TABLE III Raman shift (cm^{-1}) in the C=C and C≡N regions of the $(ET)_4[C(CN)_2CONH_2]CuX_2$ compounds. The polarization angle of the incident beam with respect to an edge of the crystal is also indicated.

Compound	ν_{CN} (1)	ν_{CN} (2)	$\nu_2 A_g$	$\nu_3 A_g$
$PPN[C(CN)_2CONH_2]$	2186.0	2146.9		
$(ET)_4[C(CN)_2CONH_2]CuCl_2$ (0°)	2199.5	2155.3	1494.6	1466.3
$(ET)_4[C(CN)_2CONH_2]CuCl_2$ (90°)	2199.5	2155.4	1493.5	1467.4
$(ET)_4[C(CN)_2CONH_2]CuBr_2$[a] (0°)	2200.0	2156.5	1493.5	1466.3
$(ET)_4[C(CN)_2CONH_2]CuBr_2$[a] (90°)	2200.7	2156.7	1494.6	1468.5

[a] see previous section for its composition

As listed in Table III, the results from the 0° and 90° scans were practically the same indicating largely isotropic optical properties within the conductive plane. The $(ET)_4[C(CN)_2CONH_2]CuX_2$ salts gave a similar CN stretching pattern as compared with the $PPN[C(CN)_2CONH_2]$ salt with an approximately 10 cm^{-1} shift to higher frequency. These observations were consistent with the following inferences: (1) the $[C(CN)_2CONH_2]^-$ anion was intact in the ET based charge transfer salts, and (2) the anion was coordinated to a metal center such as a CuX_2 salt to form a larger $\{[C(CN)_2CONH_2]CuX_2{}^{2-}\}$ dianion.

The observed ν_2 and ν_3 A_g frequencies allow one to estimate the oxidation state of the ET molecules in the $(ET)_4[C(CN)_2CONH_2]CuX_2$ salts. With the use of equation 3 of reference 11, the oxidation state of ET in $(ET)_4[C(CN)_2CONH_2]CuX_2$ salts was determined to be 0.49, implying an oxidation state for the Cu atoms of ~1.03. The oxidation state of Cu is largely +1, but the presence of small amount of Cu(II) is suggested from our analysis.

PHYSICAL PROPERTIES

A. ESR Studies

A room temperature orientation study of the ESR peak-to-peak line widths and of the *g*-values in $(ET)_4[C(CN)_2CONH_2]CuCl_2$ was carried out on an IBM ER 200D X-band spectrometer equipped with a TE_{102} microwave cavity. The 0° and 90° orientations indicated that the crystal plane was parallel and perpendicular to the static magnetic field, respectively. The resulting angular dependent line widths (triangles) and g-values (circles) were plotted in Figure 2. The two thin lines were the least-squares fit to the measured data by a procedure described previously.[12]

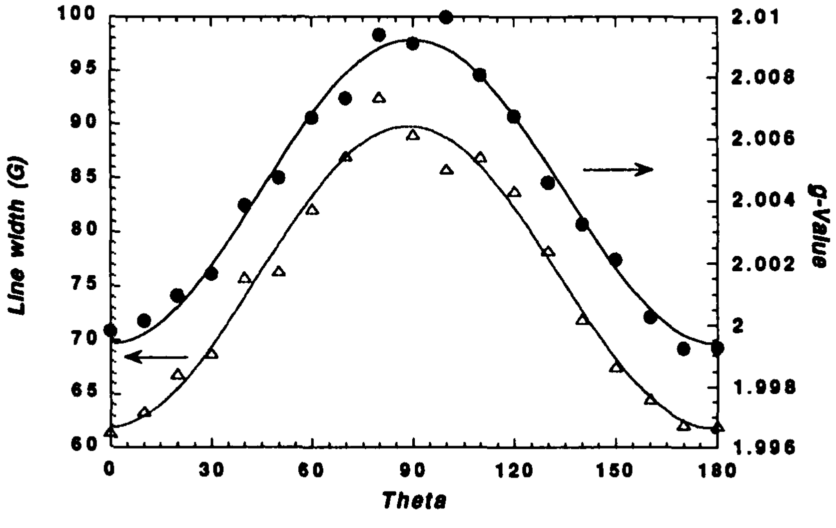

FIGURE 2 Angular-dependent peak-to-peak line widths (triangles) and *g*-values (circles) of $(ET)_4[C(CN)_2CONH_2]CuCl_2$.

As shown in Figure 2, the line width ranged from 60 to 90 G and the associated *g*-value ranged from 1.999 to 2.010. The 75 ± 15 G line width range was typical of an α-type crystal packing of the ET donor layer, as indicated by the X-ray diffraction study (see above). Additional support for the α-type packing came from the in-phase angular dependency of the line widths and the *g*-values. The maximum *g*-value at 90° was caused by the largest *g*-value contribution along the central C=C bond of the ET radical cations.

Low temperature ESR measurements were performed with the use of an Oxford ESR 900 cryostat attachment. A platelet crystal of $(ET)_4[C(CN)_2CONH_2]CuCl_2$ was oriented at the 90° angle orientation. Spectra were recorded between 5 and 300 K with LabView® and locally developed interface/data acquisition software. Selected spectra at 300, 150, 75, and 5 K are shown in Figure 3.

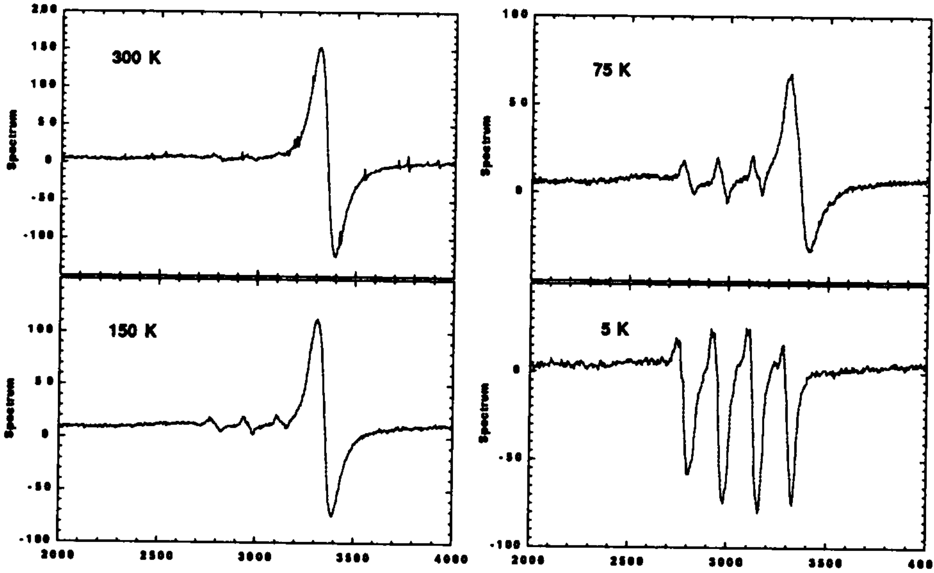

FIGURE 3 Variable temperature ESR spectra of $(ET)_4[C(CN)_2CONH_2]CuCl_2$ at 300, 150, 75, and 5 K as indicated. The X-axis is the field (G) and the Y-axis is drawn with an arbitrary scale for clarity.

Two sets of ESR signals were clearly distinguished at low temperature. At 300 K, the main ESR signal was shown to be associated with the ET radical cations from the previous orientation studies. A set of four absorption peaks, which increased in intensity with decreasing temperature, was assigned to the Cu(II) signal from the anion layer due to the Cu ($I = 3/2$) quartet splitting. From the 300 K spectrum, the intensity ratio of the Cu(II) to ET radical cations was 3.6%. A plot of the temperature dependent ESR line width and the spin susceptibility of the main (ET) signal between 300 and 50 K is shown in Figure 4. The spin susceptibility dropped slowly by 40% between 300 and 150 K and indicated semiconductive behavior. However, the spin susceptibility became constant between 150 and 50 K, suggesting metallic behavior in this temperature range. Below 50 K, the main signal broadened and overlapped significantly with the Cu(II) signal, and it became impossible to extract the spin susceptibility.

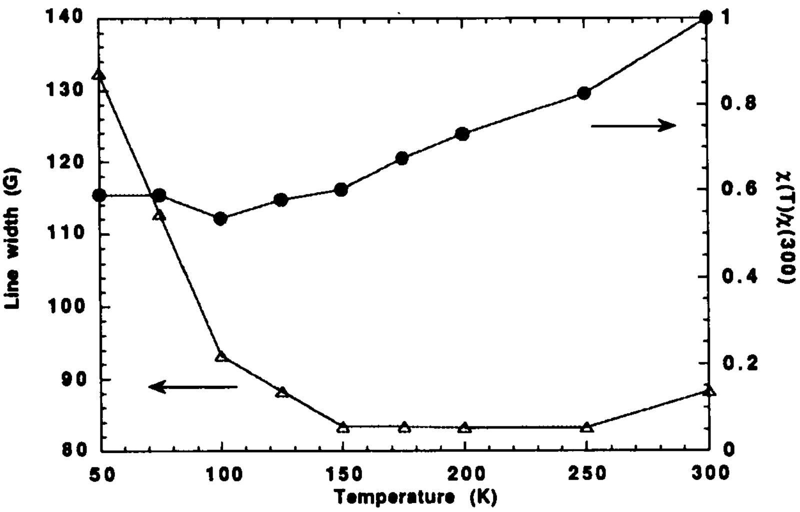

FIGURE 4 Temperature dependent line width (triangles) and relative spin susceptibility (circles) from the ET radical cation contribution of the $(ET)_4[C(CN)_2CONH_2]CuCl_2$ salt.

From the 5 K spectrum, the Cu(II) signal gave a *g*-value of 2.216, typical of a Cu^{2+} ion with the field parallel to the elongation direction of the ligand field, and a coupling constant of 172 G is nearly identical to that of a well characterized square planar Cu(II) (~170 G) in $(ET)_4Cu(C_2O_4)_2$.[13] The line width of the Cu(II) signal showed no significant temperature dependence, but its integrated intensity increased with decreasing temperature as shown in Figure 5. A Curie-Weiss plot ($1/\chi$ vs. T) between 5 and 100 K revealed a Weiss constant of −2.8 K which was consistent with a dilute Cu(II) system in the anion layer.

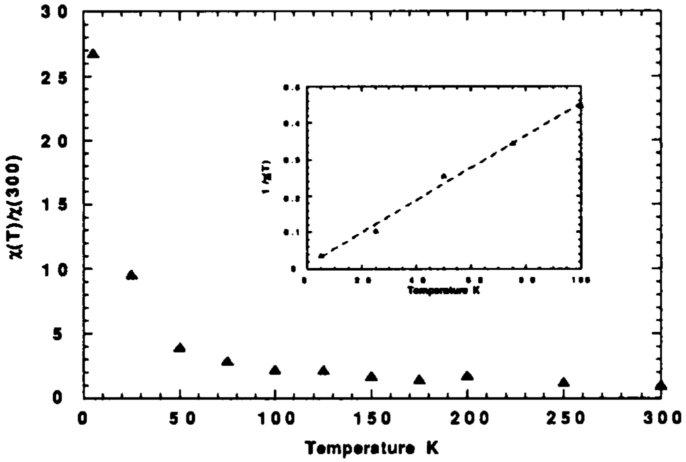

FIGURE 5 The relative spin susceptibility from the Cu(II) contribution of the $(ET)_4[C(CN)_2CONH_2]CuCl_2$ salt. A Curie-Weiss plot of the low temperature region is also shown as an inset.

B. Conductivity And Tests For Superconductivity

Standard four-probe resistivity measurements were carried out between 300 and 14 K on the $(ET)_4[C(CN)_2CONH_2]CuX_2$ salts (X = Cl and $Br_{0.77}Cl_{0.22}$) as shown in Figure 6. The chloride salt (circles and scale to the left) exhibited a much higher conductivity throughout the temperature range compared to the $Br_{0.77}Cl_{0.22}$ salt (crosses and scale to the right). Except for the difference in slope in the semiconducting 200 – 300 K region, the temperature dependence of the resistivity for both compounds was quite similar, i.e., both compounds exhibited a resistivity maximum around 150 K, and both compounds became metallic below 150 K. This pattern is reminiscent of many of the superconducting κ-phase salts, which exhibit similar resistivity maxima.

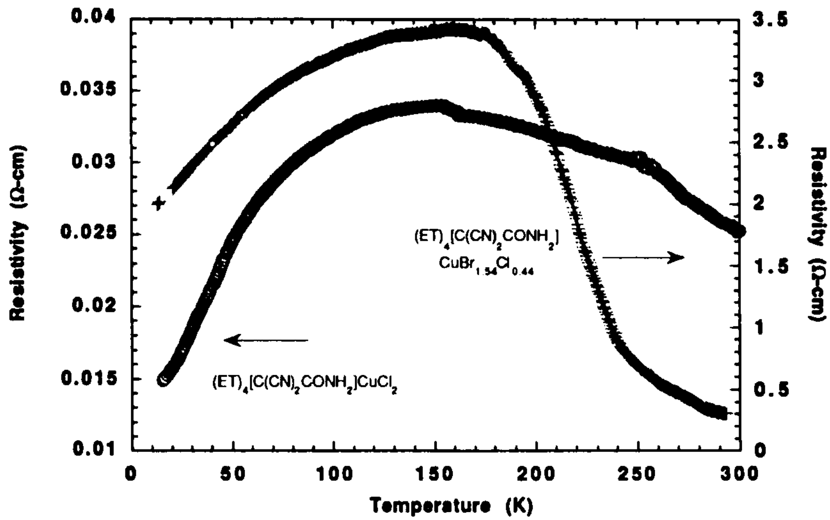

FIGURE 6 Resistivities of the $(ET)_4[C(CN)_2CONH_2]CuX_2$ salts

In order to check for signals of superconductivity, AC susceptibility and RF penetration depth measurements were carried out. The AC susceptibility measurements (LakeShore 7000 Susceptometer) were made on 2.567 mg of the chloride salt and 3.667 mg of the $Br_{0.77}Cl_{0.22}$ salt between 4.5 and 15 K. The RF penetration depth measurements were performed on 0.577 mg of the chloride salt and 1.024 mg of the $Br_{0.77}Cl_{0.22}$ salt. The lowest temperature reached was 0.75 K. Both measurements did not indicate signals of superconductivity.

By use of solid He pressure technique,[14] we have searched for superconductivity in the $(ET)_4[C(CN)_2CONH_2]CuCl_2$ salt down to 1.2 K at pressures of 0.5, 1.2, and 4 kbar. An RF impedance technique was used with an internal Nb temperature marker which assures that the system is sufficiently sensitive and is operating properly. No superconductivity due to the sample was detected.

CONCLUSIONS

Two new ET based charge transfer salts, $(ET)_4[C(CN)_2CONH_2]CuX_2$ (X = Cl and $Br_{0.77}Cl_{0.22}$), were synthesized and characterized. The donor molecule layer exhibits the α-type packing motif. The anion layer contains $[C(CN)_2CONH_2]^-$ anions which are coordinated to CuX_2 units as confirmed by Raman and EDS studies. The Cu sites are mixed-valent with ~ 3% of Cu(II) as evidenced from the ESR studies. Both compounds exhibit metallic behavior below 150 K but no superconductivity was detected. In summary, complexation reactions between organic anions and inorganic metal halides offer a viable route for the preparation of new highly conductive charge transfer salts. Different metal salts with carbamyldicyanomethanide anions and similar ligands will be explored in the future.

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