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Inorganic Chemistry

Communications

Synthesis, ESR Studies, Band Electronic Structure, and Superconductivity in the (BEDT-TTF)$_2$M(NCS)$_2$ System (M = Cu, Ag, Au)

Sir:

Very recently the superconducting transition temperatures (T_c) at ambient pressure in organic systems derived from S-based BEDT-TTF (or "ET")[1] have doubled from 5 K in β-(ET)$_2$AuI$_2$[2] to ~10.4 K in κ-(ET)$_2$Cu(NCS)$_2$.[3] The ET system has now yielded the largest number of organic superconductors (over 10), and the T_c's have continued to double every few years.[4] Among these, the β-(ET)$_2$X superconductors, where X = a linear triatomic anion (X = I$_3^-$, T_c = 1.4 K; IBr$_2^-$, T_c = 2.8 K; AuI$_2^-$, T_c = 5 K), are important because they are isostructural,[4] and as a result structure–property correlations, based on anion length, have been developed.[5] These correlations suggest that centrosymmetric linear anions with lengths exceeding that of I$_3^-$, the largest known anion in this class, could give β-phase salts with T_c's exceeding ~8 K, which is the T_c obtained when 0.5 kbar pressure is applied to β-(ET)$_2$I$_3$ to produce structurally unique β^*-(ET)$_2$I$_3$.[6] However, when this strategy was used in an *attempt* to prepare new ET salts with linear anions, viz., (I–Ag–I)$^-$, (NC–Ag–CN)$^-$, and (NCS–Au–SCN)$^-$, it resulted in the synthesis of the first *polymeric* anion ET salts, (ET)Ag$_4$(CN)$_5$[7] and (ET)$_3$Ag$_x$I$_8$ (x ~ 6.4),[8] both of which are not superconductors. The Au(SCN)$_2^-$ derivative was also a nonsuperconducting derivative.[9] In the case of the "AgI$_2^-$" system and Au(SCN)$_2^-$ anion, new *cations*, other than the usual (Bu$_4$N)$^+$, were used successfully for the first time in the electrocrystallization reactions, i.e., [K(18-crown-6)]$^{+}$[8] and the bis(triphenylphosphine)nitrogen(1+) ion, (PPN)$^+$,[9] respectively. The crown ether route has now been employed successfully in the preparation[3] of κ-(ET)$_2$Cu(NCS)$_2$ by electrocrystallization of ET wherein Cu(SCN)$_2^-$ is generated in situ from CuSCN, KSCN, and 18-crown-6.

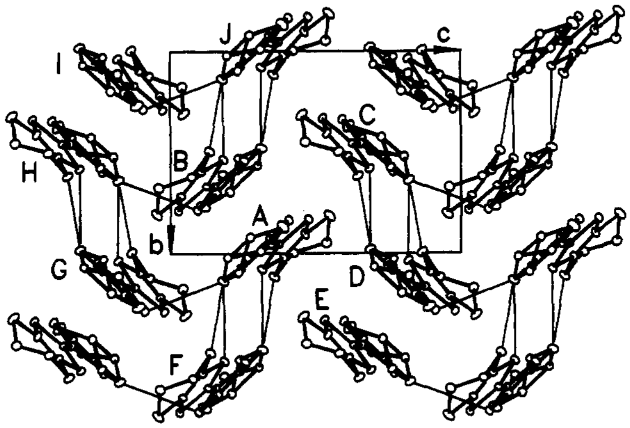

Figure 1. Packing of ET molecules within each donor layer of κ-(ET)$_2$Cu(NCS)$_2$. This packing is entirely different from that of the β-(ET)$_2$X organic superconductors.[5] The labels refer to the molecule designations of Table X3 (supplementary material). S⋯S contacts less than 3.6 Å are indicated by thin lines.

In this communication, we report the first comprehensive study of the electrocrystallization of κ-(ET)$_2$Cu(NCS)$_2$, the first ESR studies that allow one to distinguish between superconducting and nonsuperconducting phases, the first calculation of the electronic band structure, and verification of the superconducting state near 10 K. In addition, we report briefly on the electrocrystallization and properties of new Ag(SCN)$_2^-$ and Au(SCN)$_2^-$ salts of ET.

Synthesis and ESR Characterization. We have synthesized the (ET)$_2$M(NCS)$_2$ salts under various preparative conditions, by use of different solvents, different sources of M(SCN)$_2^-$ anions, and different current densities, to determine the optimum conditions for the preparation of the superconducting phase. The results are summarized in Table I. The superconducting κ-(ET)$_2$Cu(NCS)$_2$ salt was crystallized with all three different sources of the anion [K(18-crown-6)$^+$, (PPN)$^+$, (n-Bu$_4$N)$^+$] and with the solvents 1,1,2-trichloroethane (TCE) and chlorobenzene but not with dichloromethane and tetrahydrofuran (THF). The largest single crystals were obtained by the use of the CuSCN/(n-Bu$_4$N)SCN mixture as an in situ source of the Cu(SCN)$_2^-$ anion. Other nonsuperconducting phases of the ET–Cu(SCN)$_2^-$ system were found to occur under several conditions as indicated. In the Ag(SCN)$_2^-$ and Au(SCN)$_2^-$ systems, we have only attempted the 18-crown-6 route for the former and the PPN$^+$ route for the latter. Both of the ET salts of these anions are nonsuperconducting.

The room-temperature ESR line widths of superconducting crystals of κ-(ET)$_2$Cu(NCS)$_2$ were found to be 60–70 G. All nonsuperconducting phases had line widths in the ranges 15–20

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(1) BEDT-TTF or ET is bis(ethylenedithio)tetrathiafulvalene (C$_{10}$S$_8$H$_8$).
(2) Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Nuñez, L.; Crabtree, G. W.; Carlson, K. D.; Williams, J. M.; Azevedo, L. J.; Kwak, J. F.; Schirber, J. E. *Inorg. Chem.* **1985**, *24*, 2465. Carlson, K. D.; Crabtree, G. W.; Nuñez, L.; Wang, H. H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Williams, J. M. *Solid State Commun.* **1986**, *57*, 89.
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Table I. Electrocrystallization of $(ET)_2M(NCS)_2$

anion source[a]	solvent[b]	current density, $\mu A/cm^2$	cryst morphology	ESR peak-to-peak line width,[c] G	T_c,[d] K
		M = Cu			
CuSCN, KSCN, 18-C-6	TCE	1.0	thin flakes	70	9.4 ± 0.3
CuSCN, KSCN, 18-C-6	TCE	0.1	plates	60–70	9.4 ± 0.3
CuSCN, KSCN, 18-C-6	C_6H_5Cl	0.1	very thin plates	60–70	*e*
CuSCN, KSCN, 18-C-6	CH_2Cl_2	0.1	treelike clusters	33–35	*e*
CuSCN, KSCN, 18-C-6	THF	0.4	blocks	15–20	*f*
$PPN^+Cu(SCN)_2^-$	TCE	0.5	plates	61–62	9.4 ± 0.3
			blocks	16	*e*
			needles	39	*e*
CuSCN, (n-Bu_4N)SCN	TCE	0.25	thick plates	69	9.4 ± 0.3
		M = Ag			
AgSCN, KSCN, 18-C-6	TCE	0.19	plates	32–38	*f*
		M = Au			
$PPN^+Au(SCN)_2^-$	TCE	0.8	clusters	30–33	*f*
$PPN^+Au(SCN)_2^-$	THF	1.0	clusters	31	*f*

[a] 18-C-6 = 18-crown-6 and PPN^+ = bis(triphenylphosphine)nitrogen(1+). Where more than one compound is listed, they were mixed in situ in the electrochemical cell. [b] TCE = 1,1,2-trichloroethane and THF = tetrahydrofuran. [c] A range of values for peak-to-peak line widths is given when several crystals from a given batch were analyzed. [d] Measured by rf penetration depth measurements. [e] Not measured. [f] Nonsuperconducting.

and 30–40 G. Thus, ESR characterization is a useful tool for the identification of the superconducting κ-phase salt.

Crystal Structure. Single-crystal X-ray diffraction studies of our synthesized salts of κ-$(ET)_2Cu(NCS)_2$ at room temperature[10] gave lattice parameters, bond geometries, and overall crystal packing in good agreement with previous results.[3] However, in our choice of unit cell setting, the b axis has reversed polarity. The ET donor molecule packing is shown in Figure 1, and it is very similar to that found in κ-$(ET)_2I_3$[11] and $(MT)_2Au(CN)_2$[12] [MT is bis(methylenedithio)tetrathiafulvalene]. The crystal structure of the $Ag(SCN)_2^-$ salt with ET[13] is considerably different from that of the $Cu(SCN)_2^-$ salt and somewhat similar to that of $(ET)_3Ag_xI_8$.[8] X-ray studies of the $Au(SCN)_2^-$ salt were not successful because the product was poorly crystallized.

Superconductivity. The existence of bulk superconductivity in the $M(SCN)_2^-$ (M = Cu, Ag, Au) derivatives was examined by rf penetration depth measurements using methods previously described.[2] The κ-$(ET)_2Cu(NCS)_2$ samples from all synthetic routes showed the presence of superconductivity with comparable T_c's. The rf penetration depth measurements gave a superconducting onset temperature of 9.4 ± 0.3 K, a large increase in the resonant frequency beginning near 8.85 K, and a constant maximum signal beginning at 6.0 K. The resistive transition was found to be much broader, with an onset temperature near 11.5 K, zero current within instrument resolution near 6.5 K, and a transition midpoint of 10.5 ± 0.1 K. Our measurements of the resistivity curve from 300 K to low temperatures exhibited the same features as those previously reported.[3]

The rf penetration depth measurements of the Ag- and Au-containing salts gave no indication of superconductivity down to temperatures of 0.6 K. Preliminary measurements of the resistance of the $Ag(SCN)_2^-$ salt indicated that it is semiconducting, although problems with high lead resistances were encountered. Crystals of the $Au(SCN)_2^-$ salt were too small generally for the mounting of resistance probes.

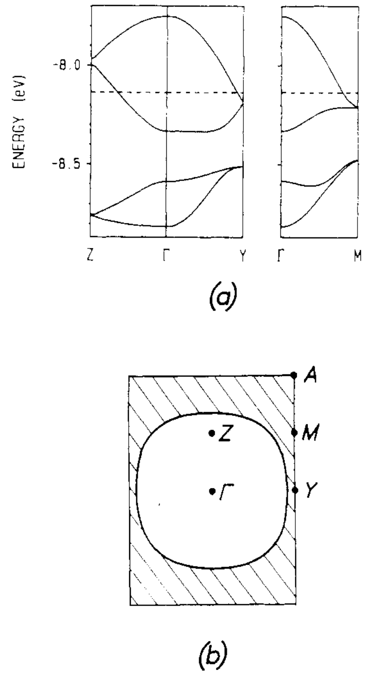

Figure 2. (a) Dispersion relations of the top two occupied bands of κ-$(ET)_2Cu(NCS)_2$. The dashed line is the Fermi level, and $\Gamma = (0,0,0)$, $Y = (0,b^*/2,0)$, $Z = (0,0,c^*/2)$, $M = (0,b^*/2,c^*/2)$. (b) Fermi surface associated with the half-filled band of Figure 2a, where $A = (0,b^*/2,c^*)$. The closed and nearly circular Fermi surface separates wave vector regions of filled (shaded) and empty (blank) band levels.

Band Electronic Structure. To determine how effectively donor molecules interact in each donor layer of κ-$(ET)_2Cu(NCS)_2$, we have calculated as described elsewhere[14] the HOMO interaction energies, $\beta_{ij} = \langle\psi_i|H^{eff}|\psi_j\rangle$, where ψ_i and ψ_j are the HOMO's of donor molecules i and j. We note that all $(ET)_2^+$ dimers of Figure 1 are equivalent by symmetry, but the two ET molecules of each dimer are slightly different in structure. From the interaction energies, we find that the donor molecules interact most strongly within each dimer, but it is noteworthy that dimers interact quite strongly in all directions of the donor-layer plane. Thus, κ-$(ET)_2Cu(NCS)_2$ is expected to possess a two-dimensional (2D) metallic character.

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(10) X-ray data were collected on a Nicolet P3/F diffractometer, where the lattice parameters (298 K) were as follows: a = 16.256 (3) Å, b = 8.4564 (13) Å, c = 13.143 (3) Å, β = 110.276 (14)°, V = 1694.8 (5) Å^3; space group $P2_1$, $Z = 2$, ρ_{calcd} = 1.853 g/cm^3. ω-Scan data (Mo Kα radiation, graphite monochromator, λ = 0.7107 Å) were collected at 298 K in the range $4° < 2\theta < 55°$, and 5315 reflections were averaged ($R_{av}(F)$ = 0.031) to 4145 unique, allowed reflections, which were corrected for absorption (μ = 17.3 cm^{-1}), with T_{min} = 0.778 and T_{max} = 0.891. Full-matrix least-squares refinement using 3217 reflections with $F_o > 3\sigma$ yielded $R(F)$ = 0.053 and $R_w(F)$ = 0.043 (GOF = 1.49). 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, 1986.

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(13) $(ET)_4Ag_x(SCN)_8$, $x \simeq 6.4$: orthorhombic, space group $Pbca$, $Z = 1$, a = 4.257 (2) Å, b = 11.588 (3) Å, c = 40.19 (2) Å (298 K).

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Figure 2 shows the dispersion relations of the two highest lying occupied bands of κ-$(ET)_2Cu(NCS)_2$, which we calculated for its room-temperature crystal structure by employing the tight-binding band scheme[15] based upon the extended Hückel method.[16] To better represent the interstack S···S interactions between adjacent donor molecules, double-ζ Slater-type orbitals were used for the s and p orbitals of carbon and sulfur as reported earlier.[15] The two bands of Figure 2 are derived mainly from the HOMO's of four ET molecules in each unit cell. The HOMO's of two ET molecules in each dimer interact to give the bonding and antibonding levels ψ_+ and ψ_-, respectively. The upper and lower bands of Figure 2 are represented largely by the ψ_- and ψ_+ orbitals, respectively. Since there are two $(ET)_2^+$ dimers per unit cell, the upper band becomes half-filled. This band is cut by the Fermi level, represented by the dashed line, in all three directions of the reciprocal space shown in Figure 2.

Also shown in Figure 2 is the Fermi surface associated with the half-filled band of κ-$(ET)_2Cu(NCS)_2$. The Fermi surface is shown in an extended Brillouin zone scheme, due to the folded nature of the two bands in Figure 2. The Fermi surface is closed and approximately circular, so that this salt is expected to be a 2D metal. This is consistent with our analysis of the HOMO interaction energies described above. In this 2D electronic structure, the new ambient-pressure superconductor κ-$(ET)_2Cu(NCS)_2$ is similar to the series of ambient-pressure superconductors β-$(ET)_2X$,[14,15,17] although the two classes of salts have widely *different* packing patterns of donor molecules.

$(MT)_2Au(CN)_2$ would be similar to κ-$(ET)_2Cu(NCS)_2$ in band electronic structure since the two salts have a nearly identical packing pattern of donor molecules and since the HOMO's of ET and MT are almost the same. When the temperature is lowered, however, $(MT)_2Au(CN)_2$ does not become a superconductor but undergoes a metal-to-semiconductor transition.[12] Therefore, κ-$(ET)_2Cu(NCS)_2$ must possess certain translational or librational modes of vibration critical for superconductivity. Recently, it has been suggested[18] that an important factor controlling the superconductivity of the β-$(ET)_2X$ salts is the lattice softness associated with the intermolecular hydrogen···anion and hydrogen···hydrogen contacts. The same factor might also operate in κ-$(ET)_2Cu(NCS)_2$.

Conclusion. We have shown that the new ET-based superconducting salt κ-$(ET)_2Cu(NCS)_2$ can be prepared by at least three different synthetic routes. We have verified superconductivity at ambient pressure of this product in the region 9–10 K, with all three synthetic routes yielding crystals of comparable T_c. The route involving the use of $(n\text{-}Bu_4N)SCN$, however, yields crystals of the largest dimensions and highest diffraction quality. We have also shown that other, as yet unidentified, phases of the ET-$Cu(SCN)_2^-$ system are produced and that the ESR line widths at room temperature can be employed to select the superconducting κ-phase materials. We have found that the ET derivatives of the $Ag(SCN)_2^-$ and $Au(SCN)_2^-$ anions yield nonsuperconducting phases, different from the κ-phase at least in the case of the $Ag(SCN)_2^-$ salt. The electronic band structure of κ-$(ET)_2Cu(NCS)_2$ indicates that this is a 2D metal, similar to the superconducting β-$(ET)_2X$ materials. Thus, an entirely new organic material (the κ-phase) has been found to be superconducting at a T_c exceeding, for the first time, the highest T_c of the elements (9 K in Nb). Because the structure of the κ-phase is different from that of the β-$(ET)_2X$ superconductors, there is now considerable promise for deriving new and extended structure–property relationships and obtaining even higher T_c's.

Acknowledgment. Work at Argonne National Laboratory and at North Carolina State University was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Contract W-31-109-ENG-38 and Grant DE-FG05-86-ER45259, respectively. We express our appreciation for computing time on the ER-Cray X-MP computer, made available by DOE. L.K.M. is a Scientist in Residence, sponsored by the Argonne Division of Educational Programs, on leave from the Department of Chemistry, Indiana University (Bloomington, IN); C.S.C. is a student research participant sponsored by the Argonne Division of Educational Programs from Humboldt State University (Arcata, CA). We especially thank Joseph S. Gregar for the design and construction of special glassware used in the electrocrystallization syntheses.

Note Added in Proof. Gärtner[19] et al. confirm a T_c of 10.2 K at ambient pressure in $(BEDT\text{-}TTF)_2Cu(NCS)_2$. They also report a room-temperature ESR line width of ~26 G for the superconducting phase which is substantially different from that we observe of 60–70 G.

Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1), final atom positional parameters and anisotropic temperature factors (Table X2), and HOMO interaction energies (Table X3) and a figure showing the superconducting transitions as measured by rf penetration and four-probe resistance (Figure X1) for κ-$(ET)_2Cu(NCS)_2$ (5 pages). Ordering information is given on any current masthead page.

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Isolation of a Bis-Oxo-Bridged $Mn^{III}Mn^{IV}$ Intermediate by Regulated Air Oxidation. Synthesis, Structure, and Properties of $[Mn_2O_2(tren)_2](CF_3SO_3)_3$

Sir:

Manganese is known to participate in a variety of biological reactions related to the metabolism and evolution of molecular oxygen. Evidence for this conclusion derives from the fact that manganese is required for activity in enzymes such as pseudocatalase,[1] superoxide dismutase,[2] and the oxygen-evolving complex in photosystem II (PSII).[3] For the S_2 state in PSII, the multiline signal in the EPR spectrum[4] and the short Mn···Mn distance (2.70 Å, as indicated by X-ray absorption spectroscopy[5]) are both

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