the carbon and oxygen content of the films, however, and on this basis, the carbon content is estimated to be less than 0.5 at.% and the oxygen 1.5-3 at.%. The source of the oxygen contamination is probably oxygen diffusion from the quartz reactor, whereas the carbon must come from the amide ligands in the silicon-containing precursors. The binding energies of the Si 2p and N 1s peaks were 101.8 and 397.5 eV, respectively, which are in accord with literature values for stoichiometric Si$_3$N$_4$.[14] The absolute binding energies were referenced to the C 1s peak at 284.6 eV.

The refractive indexes (n_f) of the films were also determined (Table I). They varied from 1.84 to 1.89. Refractive indexes for silicon nitride films are normally 1.8-2.0, with values below 1.9 indicating the presence of small amounts of oxygen contamination.[14,15]

In control experiments, film depositions using the Si-(NMe$_2$)$_n$H$_{4-n}$ compounds without ammonia were carried out at 750 °C.[16] For all three precursors, films were obtained but at slower growth rates and with large amounts of carbon (22-30%) and oxygen (15-17%) contamination (Table I). The high oxygen content in these films is probably due to the extended time the precursors and films were exposed to oxygen-containing impurities in the carrier gas at 750 °C, which is a reflection of the slow growth rates.

In conclusion, we have shown Si(NMe$_2$)$_n$H$_{4-n}$ (n = 2-4) compounds and ammonia are promising precursors to silicon nitride coatings at 750 °C. Our preparation provides higher growth rates than the existing APCVD and LPCVD routes at comparable temperatures. Also, the Si-(NMe$_2$)$_n$H$_{4-n}$ precursors appear to be safer to handle than SiH$_4$ and SiH$_2$Cl$_2$, which is another advantage over existing systems.[17]

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Synthesis of the New Highest T_c Ambient-Pressure Organic Superconductor, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, by Five Different Routes

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The synthesis of new superconducting compounds is a topic of intense interest today. Very recently the superconducting transition temperature (T_c) of a new BEDT-TTF-based superconductor [BEDT-TTF or "ET" is bis-(ethylenedithio)tetrathiafulvalene, C$_{10}$H$_8$S$_8$], κ-(ET)$_2$Cu-[N(CN)$_2$]Br, was raised to a new high for these systems (resistive onset T_c = 12.5 K, midpoint 11.2 K).[1,2] The previous highest T_c was observed in κ-(ET)$_2$Cu(NCS)$_2$ (resistive midpoint 10.4 K).[3] Since the introduction of polymeric anions into the synthesis of ET-based materials[4,5] and the development of useful structure-property correlations for β-phase ET superconductors,[6] numerous new superconducting materials have been prepared, including recently, e.g., α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ (T_c = 1.15 K)[7] and β$_m$-(BEDO-TTF)$_3$Cu$_2$(NCS)$_3$ (T_c = 1.06 K),[8] but κ-(ET)$_2$Cu(NCS)$_2$ and κ-(ET)$_2$Cu[N(CN)$_2$]Br represent the only organic superconductors to break the 10 K barrier. In contrast to the synthesis of κ-(ET)$_2$Cu(NCS)$_2$, which is usually carried out by use of electrocrystallization of ET in the presence of CuSCN and SCN$^-$ anion, the synthesis of κ-(ET)$_2$Cu[N(CN)$_2$]Br can be achieved by use of different starting materials, and thus provides an opportunity to probe the complex solution chemistry involved during electrocrystallization. In this communication we report five synthetic routes, and the related solution chemistry, for the electrocrystallization of κ-(ET)$_2$Cu[N(CN)$_2$]Br. One of these syntheses, which is the easiest to use (entry 3, Table I), utilizes all commercially available materials.

The new organic superconductor κ-(ET)$_2$Cu[N(CN)$_2$]Br belongs to the orthorhombic space group *Pnma*, Z = 4, a = 12.942 (3) Å, b = 30.016 (4) Å, c = 8.539 (3) Å, V = 3317 (1) Å^3 (298 K).[1] The donor molecular packing motif is typical of κ-phase salts. The polymeric anion Cu[N(C-N)$_2$]Br$^-$, consists of tricoordinated Cu(I) with two bridging (NC)N(CN)$^-$ ligands forming a zigzag chain and a terminal bromide to complete the coordination around the Cu atom.[1] On the basis of the anion stoichiometry, the polymeric chain can be synthesized, in principle, from CuBr with N(CN)$_2^-$ or from CuN(CN)$_2$ with Br$^-$. We have explored these possibilities, and the results are summarized in Scheme I.

The CuBr/N(CN)$_2^-$ system leads to at least three different anionic species depending on the reaction conditions. We have found that the reaction of CuBr with 2 equiv of dicyanamide anions (as the PPh$_4^+$ salt)[9] in re-

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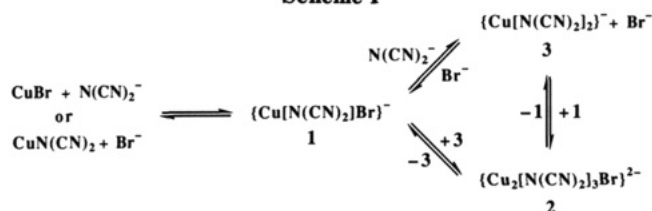
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Table I. Electrocrystallization of κ-(ET)$_2$Cu[N(CN)$_2$]Br by Multiple Routes

electrolyte	solvent	current density, μA/cm^2	crystal morphology	room temp ESR line width, G	T_c, K
(PPh$_4$)$_2$Cu$_2$[N(CN)$_2$]$_3$Br^a	TCE^f + 10% EtOH	0.2 (35 days) 0.1 (41 days)	thin plates thick plates, blocks	63, 70	onset 11.6 saturation ~9^g
CuBr, PPh$_4$[N(CN)$_2$]^b	TCE + 10% EtOH	0.1 (10 days)	thick plates	60–80	onset 11.6 saturation ~9
CuBr, Na[N(CN)$_2$], 18-crown-6^c	TCE + 10% EtOH	0.2 (15 days)	thin plates	68	onset 11.4 saturation ~8
Cu[N(CN)$_2$]^d, N(n-Bu)$_4$Br	TCE + 10% EtOH	0.15 (8 days)	thick plates	72	onset 11.6 saturation ~9
(PPh$_4$)Cu[N(CN)$_2$]$_2$,^{e} N(n-Bu)$_4$Br	TCE + 10% EtOH	0.1 (26 days)	thick plates	66, 71	onset 11.6 saturation ~9

^{a}Reference 1. ^{b}Reference 9. ^{c}Reference 12. ^{d}Reference 13. ^{e}Reference 10. ^{f}1,1,2-Trichloroethane. ^{g}Measured on crystals grown at 0.1 μA/cm^2.

Scheme I

$$CuBr + N(CN)_2^- \text{ or } CuN(CN)_2 + Br^- \rightleftharpoons \{Cu[N(CN)_2]Br\}^- \quad 1$$

$$\{Cu[N(CN)_2]_2\}^- + Br^- \quad 3$$

$$\{Cu_2[N(CN)_2]_3Br\}^{2-} \quad 2$$

fluxing acetonitrile leads to two different isolated crystalline products depending on the reaction time. After 30 min of reflux and subsequent cooling, anion **2** is isolated as the tetraphenylphosphonium salt, (PPh$_4$)$_2$Cu$_2$[N-(CN)$_2$]$_3$Br.[1] However, by use of the same reaction conditions and after 16 h of reflux and cooling, compound **3**, (PPh$_4$)Cu[N(CN)$_2$]$_2$, is isolated.[10] It should be pointed out that the anions **2** and **3** are likely to be polymeric as suggested by their limited solubilities in organic solvents. After the discovery[1,2] of the title superconductor by use of compound **2** as the supporting electrolyte during electrocrystallization, we attempted the synthesis of the polymeric anion, **1**, from several different starting materials. A list of five different electrolyte systems used for the electrocrystallization of κ-(ET)$_2$Cu[N(CN)$_2$]Br is tabulated in Table I.

A typical procedure for the electrocrystallization synthesis[11] of κ-(ET)$_2$Cu[N(CN)$_2$]Br with 1 equiv of ET (Strem Chemical Co.) and 10 equiv of supporting electrolyte components (e.g., CuBr, NaN(CN)$_2$, 18-crown-6, 10 equiv each)[12] in 1,1,2-trichloroethane (TCE) or TCE and 10% (vol) absolute ethanol as the solvent at a current density of 0.1–0.2 μA/cm^2. The H cells are usually assembled inside a drybox to avoid CuBr oxidation, and the crystal growth is carried out at room temperature for 2–5 weeks. As shown in Table I, the supporting electrolyte for the first entry is a "preformed" Cu$_2$[N(CN)$_2$]$_3$Br^{2-} anion, **2**.[1] The molecular structure of this anion is not presently known, but significant dissociative rearrangement is expected in solution in order to form the Cu[N(CN)$_2$]Br$^-$ polymeric anion, **1**. Entries 2–4 are in situ preparations starting from either CuBr and the N(CN)$_2^-$ anion or CuN(CN)$_2$[13] and the Br$^-$ anion. The third entry is based on all commercially available starting materials. The crystal growth for entries 2–4 in Table I is quite facile, and tiny crystals begin to grow within 3–4 h. The fifth entry
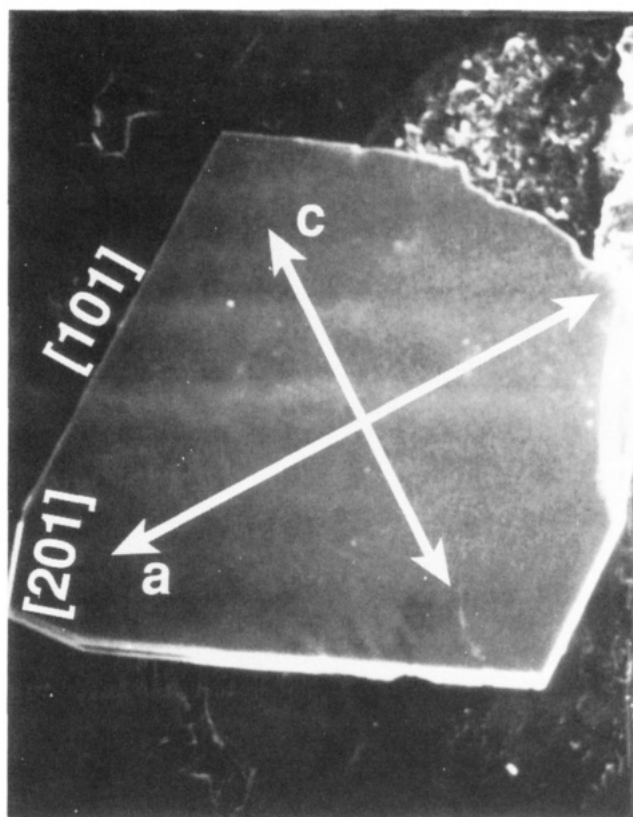
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(13) CuN(CN)$_2$ was synthesized following the general procedure for the preparation of copper(I) halides (Keller, R. N.; Wycoff, H. D. Inorg. Synth. 1946, 2, 1). Anal. Found (Calcd) for: CuC$_2$N$_3$: C, 18.60 (18.54); N, 32.22 (32.43).

Figure 1. Scanning electron micrograph of a typical κ-(ET)$_2$Cu[N(CN)$_2$]Br crystal, viewed along the b axis. The a and c crystal axes as well as the Miller indices of the boundary faces are indicated.

is based on Cu[N(CN)$_2$]$_2^-$, **3**, and Br$^-$. The formation of the polymeric anion, Cu[N(CN)$_2$]Br$^-$, in the crystals is consistent with the displacement of one dicyanamide ligand by Br$^-$ under equilibrium conditions. The most typical morphology for κ-(ET)$_2$Cu[N(CN)$_2$]Br is that of a rhombus-shaped plate, and the crystal dimensions are approximately 1 × 1 × 0.3 mm^3 for thick plates and 1 × 1 × 0.1 mm^3 for thin plates. A scanning electron micrograph for a thin platelet crystal prepared from entry 3 is shown in Figure 1 at 100× magnification.

The long diagonal of the rhombus-shaped platelet is the crystallographic a axis, which bisects the 105.7° angle formed by the [201] faces. The pointed angle (66.8°) formed by the two [101] faces, rounded out by the two [201] faces, is a characteristic feature of κ-(ET)$_2$Cu[N-(CN)$_2$]Br crystals. The c axis is perpendicular to the a axis and follows the short diagonal of the platelet. The b axis is the normal to the crystal plane. As shown in Table I, a lower current density (e.g., 0.1 μA/cm^2) favors slow crystal growth, and the resulting crystal morphology usually is a thick plate. On the other hand, a slightly higher current density (e.g., 0.2 μA/cm^2) favors rapid crystal

growth, and thin platelet crystals are formed. Under slow growth conditions, in a few cases the sample thickness is comparable to its width, and the crystal morphology appears to favor blocks (entry 1).

All the crystals listed in Table I have been surveyed by use of ESR spectroscopy at arbitrary orientations, and the peak-to-peak line widths all fall within the range 60–80 G, which is consistent with the reported values for κ-$(ET)_2Cu[N(CN)_2]Br$.[1,14]

Listed in the last column of Table I are the T_c's of different samples as determined from rf (radio frequency) penetration depth measurements.[15] 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. Both the onset temperatures and the signal saturation temperatures are listed. All samples show similar onset temperatures (11.4–11.6 K), indicating that the crystals are of comparable high quality. Entries 1, 2, 4 and 5 all give narrow superconducting transition widths (2.6 K) while entry 3 shows a broader transition width (3.4 K). The slightly broader transition width indicates increased inhomogeneity in the samples.

In summary, all five synthetic routes give high-quality crystals of κ-$(ET)_2Cu[N(CN)_2]Br$. The in situ preparations are the most straightforward syntheses. On the basis of Scheme I, anionic species **1–3** are in equilibrium in solution. The anions **2** and **3** are isolated as $PPh_4{}^+$ salts, while anion **1** is stabilized as an ET salt. The title superconductor can be reached by use of in situ preparations (entries 2–4) or from compounds **2** and **3**. This study indicates that the crystal morphology can be modified from thin platelets to chunky blocks by varying the applied current density. A low current density favors slow crystal growth and thicker crystals elongated along the *b* axis. The anionic rearrangements, as seen in this study, have been postulated in the synthesis of nonsuperconducting $(ET)_3Ag_{6.4}I_8$ from either $[K(18\text{-crown-6})]_2Ag_4I_6$ or $[K(18\text{-}crown\text{-}6)]AgI_2$.[5,14] It is encouraging that five synthetic routes, from different starting materials, all lead to the same organic superconducting compound with the highest T_c reported to date.

Note Added in Proof.

We have discovered[16] that κ-$(ET)_2Cu[N(CN)_2]Cl$, isostructural to the Br salt reported herein, can be prepared by the same routes. The Cl salt is superconducting (T_c = 12.8 K, 0.3 kbar)[16] and superconductivity can be stabilized at "ambient pressure" by simply coating the crystals with G. E. varnish or Apiezon N grease prior to cooling.

Electrochromic Molybdenum Trioxide Thin Film Preparation and Characterization

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Molybdenum trioxide is a very interesting material because it has applications in catalysis,[1] in lithium batteries as cathode material,[2] and in electrochromic devices.[3,4] Techniques that have been used to prepare molybdenum trioxide include chemical vapor deposition,[5] vacuum evaporation,[6] and sol–gel.[7] Moreover, molybdenum trioxide has recently been prepared by electrodeposition from hexavalent molybdate solution ($Li_6Mo_7O_{24}$)[8] and molybdenum–hydrogen peroxide solution.[9]

Our laboratory has recently been interested in molybdenum trisulfide thin films obtained by electrodeposition from an aqueous solution of ammonium tetrathiomolybdate.[10,11] It is well-known that thermal oxidation of molybdenum trisulfide yields molybdenum trioxide.[12] With this in mind, we have decided to prepare molybdenum trioxide thin film coated tin oxide electrode from molybdenum sulfide thin film by thermal oxidation in air. This paper deals with the preparation of molybdenum trioxide thin films and their characterization by X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, cyclic voltammetry, and UV–visible spectroscopy.

The preparation of molybdenum trioxide thin films comprises two steps. In the first step, a molybdenum trisulfide thin film is electrodeposited at a potential of 0.6 V vs SCE on a conducting substrate such as tin oxide coated glass electrode from a 10 mM aqueous ammonium tetrathiomolybdate solution.[10,11] The thickness of the molybdenum sulfide film can be varied by changing the deposition time. In the second step, the electrodeposited

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