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Ambient-Pressure Superconductivity at the Highest Temperature (5 K) Observed in an Organic System: β-(BEDT-TTF)$_2$AuI$_2$

Sir:

Superconducting transition temperatures (T_c) beyond the original 1–2 K, at ambient or under applied pressure, of (TMTSF)$_2$X and β-(BEDT-TTF)$_2$X (X = monovalent anion) organic superconductors have been realized very recently.[1,2] The ET system ("ET" is an abbreviation for BEDT-TTF) is the first to yield more than one ambient-pressure organic superconductor: β-(ET)$_2$I$_3$ ($T_c \simeq 1.6$ K),[3-7] γ-(ET)$_3$(I$_3$)$_{2.5}$ ($T_c \simeq 2.5$ K),[8] ε-(ET)$_2$I$_3$(I$_8$)$_{0.5}$ ($T_c \simeq 2.5$ K),[8] and β-(ET)$_2$IBr$_2$ ($T_c \simeq 2.8$ K).[9,10] β-(ET)$_2$IBr$_2$ represents the organic superconductor with the highest documented *ambient-pressure* bulk superconducting transition temperature. On the basis of data for β-(ET)$_2$I$_3$ only, much higher transition temperatures appear possible in crystals subjected to external pressure;[11,12] i.e., $T_c \simeq 7$–8 K at $p \cong 1.2$–1.3 kbar with β-(ET)$_2$I$_3$. However, while applied pressure (>1 kbar) increases T_c in β-(ET)$_2$I$_3$, it appears to suppress it in β-(ET)$_2$IBr$_2$.[13]

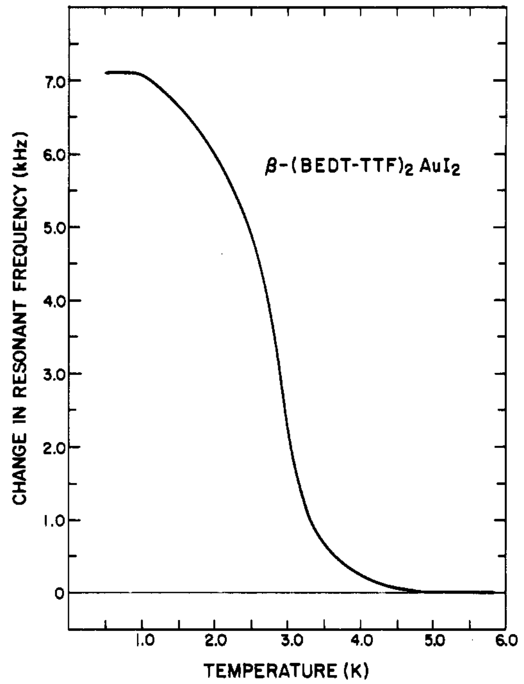

Figure 1. Rf field penetration depth measurement indicating an onset temperature for bulk superconductivity of 4.97 ± 0.06 K in β-(ET)$_2$AuI$_2$.

We have proposed that new ambient-pressure organic superconductors in the β-(ET)$_2$X class will likely contain *centrosymmetric* anions of rather *specific* "length", i.e., approximately equal to that of IBr$_2^-$ (~9.3 Å) or *between* the length of the IBr$_2^-$ anion and the I$_3^-$ anion (~10.2 Å).[4,6,9,14] This suggestion follows from our demonstration that by use of an asymmetric I$_2$Br$^-$ anion, having the intermediate length (~9.7 Å) specified above, the resulting β-(ET)$_2$I$_2$Br salt does *not* exhibit superconductivity at ambient pressure ($T \geq 0.45$ K) or up to 5 kbar applied pressure ($T = 1.05$–4.0 K).[14] We have attributed the absence of superconductivity to the presence of anion disorder. On the basis of the pressure effects described above, we surmise that the T_c for β-(ET)$_2$IBr$_2$ is normal but that for β-(ET)$_2$I$_3$ is severely depressed due to the partial disorder as reflected in the modulated structure.[15-17] The existence of a higher T_c state (8 K) in the pressurized β-(ET)$_2$I$_3$ system leads us to speculate that T_c's at ambient pressure which are well above 8–10 K are possible through the proper choice of experimental conditions and especially through the use of linear-symmetric anions.[14] In an attempt to produce

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higher T_c's, and as a further test of our hypotheses (vide supra), we have synthesized β-(ET)$_2$AuI$_2$. This is the first linear-symmetric (I–Au–I)$^-$ triatomic metal-containing anion in an (ET)$_2$X derivative, and one which has an anion length (~9.40 Å) intermediate between that of I_3^- and IBr_2^-. This new salt has an ambient-pressure superconducting transition temperature almost double (~5 K) that of β-(ET)$_2$IBr$_2$ and is the highest reported to date (vide infra).

Synthesis. Lustrous black crystals of β-(ET)$_2$AuI$_2$ were grown by electrocrystallization (anhydrous and light-free conditions) by use of 9.3 mg of ET (Strem Chemical Co., 1.6 mM) as organic donor and 157 mg of *n*-Bu$_4$NAuI$_2$ (15.1 mM) as supporting electrolyte at 23 °C in a standard H-cell. The anion and the supporting electrolyte were prepared by following a literature procedure.[18] Its purity was confirmed by its melting point (78–79 °C) and elemental analysis. Anal. Calcd (found)[19] for *n*-Bu$_4$NAuI$_2$: C, 27.72 (27.68); H, 5.23 (5.32); N, 2.02(1.96); I, 36.61 (36.83). Dry THF was used as solvent, and a 1.0 μA/cm^2 current density was applied. Crystal formation was observed within 24 h, and the fully grown distorted hexagons were harvested after about 1 week. The β-(ET)$_2$X crystals are characterized by their room-temperature ESR line width of ~20 G.[20]

Single-crystal X-ray analysis[21] revealed that β-(ET)$_2$AuI$_2$ is clearly isostructural (space group $P\bar{1}$, $V_c = 845.2$ (3) Å^3, $Z = 1$) with β-(ET)$_2$X, X = I_3^- and IBr_2^-. The unit cell volumes for β-(ET)$_2$X, X = I_3^- and IBr_2^-, are 855.9 (2) and 828.7 (3) Å^3, respectively, which indicates that, as expected, the (I–Au–I)$^-$ anion is of length intermediate between those of the two trihalide anions. The structure consists of discrete layers of AuI$_2^-$ anions between which is sandwiched a "corrugated sheet network"[9] of ET molecules with short ($d_{S\cdots S} \leq 3.60$ Å, the van der Waals radius sum for S) *inter*stack S···S interactions. The loosely packed stacking of the ET entities is characterized by *intra*stack S···S distances exceeding 3.60 Å.

Superconductivity. The occurrence of a superconducting state in β-(ET)$_2$AuI$_2$ was detected by rf penetration depth measurements at ambient pressure and at various applied magnetic fields, similar to measurements previously reported for the I_3^- and IBr_2^- derivatives.[5,6,10] Figure 1 shows the change in resonant frequency as a function of temperature at zero applied magnetic field for a sample consisting of three relatively large single crystals. This sample gave an apparent onset temperature for bulk superconductivity (T_c) of 4.97 ± 0.06 K, which is the highest T_c yet observed at ambient pressure for an organic superconductor. Like the inductive superconducting transition curves for the trihalide derivatives, this figure shows a broad transition below T_c. Measurements of the onset temperatures of the individual crystals gave T_c = 3.93 ± 0.04, 4.36 ± 0.04, and 4.98 ± 0.08 K, respectively. Thus, the crystals of β-(ET)$_2$AuI$_2$ have a range of T_c values like the trihalide derivatives but have a much larger spread in the extremes (~1 K in these experiments). Preliminary pressure studies using low-frequency ESR techniques described earlier[7] indicate superconductivity is strongly depressed with pressure at a rate of 1 K/kbar.

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Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1) and final atom positional and anisotropic temperature factors (Table X2) (2 pages). Ordering information is given on any current masthead page.

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(21) X-ray data were collected on a Syntex P2$_1$ diffractometer, and the triclinic unit cell data (space group $P\bar{1}$, $Z = 1$) are as follows (298 K): $a = 6.603$ (1) Å, $b = 9.015$ (2) Å, $c = 15.403$ (4) Å, $\alpha = 94.95$ (2)°, $\beta = 96.19$ (2)°, $\gamma = 110.66$ (1)°, $V = 845.2$ (3) Å^3 $\rho_{obsd} = 2.39$ (8) g/cm^3, and $\rho_{calcd} = 2.40$ g/cm^3. Diffraction data (ω scan, Mo K$\bar{\alpha}$ radiation, graphite monochromator, $\lambda = 0.7107$ Å) were collected at 298 K in the range $4° < 2\theta < 50°$, and 3406 data were averaged ($R_{av}(F)$ = 1.6%) to yield 2969 independent reflections, which were corrected for absorption ($\mu = 71.15$ cm^{-1}), with $T_{min} = 0.136$ and $T_{max} = 0.588$. Full-matrix least-squares refinement (all atoms except hydrogen were refined with anisotropic temperature factors, 178 parameters) yielded $R(F) = 4.3$% and R_w(F) = 3.4% (GOF = 1.85). The crystal structure is fully ordered, and the (I–Au–I)$^-$ anion Au–I bond distance is 2.5610 (6) Å.

(22) M.A.F., K.S.W., and L.N. are student research participants sponsored by the Argonne Division of Educational Programs from Indiana University of Pennsylvania, Indiana, PA, St. Michael's College, Winooski, VT, and DePaul University, Chicago, IL.

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Transformation of Monoclinic CfBr$_3$ to Orthorhombic CfBr$_3$ by the Application of Pressure

Sir:

It has been shown previously that the orthorhombic form of anhydrous CfBr$_3$ can be synthesized by preparing ^{249}BkBr$_3$ in its orthorhombic form and waiting for the ^{249}Bk ($t_{1/2}$ = 325 d) to transmute to ^{249}Cf ($t_{1/2}$ = 351 y) by β^- decay.[1] Both absorption spectrophotometric and X-ray powder diffraction analysis confirmed that, within the limits of sensitivity of these analytical techniques, the product of this transmutation is orthorhombic (PuBr$_3$-type structure) CfBr$_3$. Up to now this has been the only way known to prepare the orthorhombic modification of CfBr$_3$. Two other structural forms are known for CfBr$_3$: AlCl$_3$-type monoclinic and FeCl$_3$-type rhombohedral.[2] We report here a new synthetic route to the orthorhombic form of CfBr$_3$. The advantage of this route, which requires the application of pressure, is that it is an active rather than passive one, thus giving control over the process to the experimenter.

A few micrograms of monoclinic CfBr$_3$ was loaded into a triangular-shaped diamond anvil pressure cell similar to that reported by Merrill and Bassett.[3] A detailed description of the pressure cell and its use for spectral studies of actinide materials under pressure in conjunction with our microscope spectrophotometer[4] will be published separately. The CfBr$_3$ was handled in a helium-atmosphere glovebox and was placed, along with silicone oil and ruby chips, in the 0.2 mm diameter hole of an Inconel gasket mounted on one of the diamond anvils. The oil

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