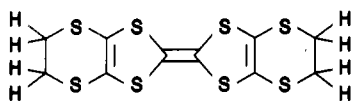# Communications

Ambient-Pressure Superconductivity at 2.7 K and Higher Temperatures in Derivatives of (BEDT-TTF)₂IBr₂: Synthesis, Structure, and Detection of Superconductivity
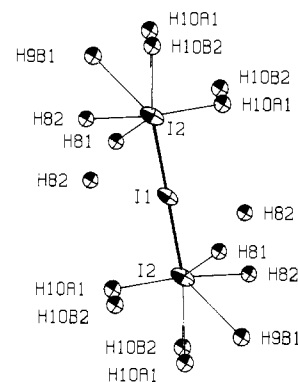
Sir:

Very recently, superconductivity at *ambient pressure* has been observed in anionic (X⁻) derivatives of Se-based TMTSF and S-based BEDT-TTF (1) or "ET".[1]   Only one such

1, BEDT-TTF or "ET"

TMTSF derivative is known, i.e., (TMTSF)₂ClO₄ ($T_c = 1.2$ K),[2] while for the ET system exactly the same 2:1 stoichiometry yields two structurally and electrically different phases: α-(ET)₂I₃, with a metal insulator transition[3] at 140 K; β-(ET)₂I₃, the first ambient-pressure S-based organic superconductor with $T_c = 1.4-1.6$ K.[4-7]   Until now, β-(ET)₂I₃ possessed the highest reported superconducting transition temperature of any ambient-pressure organic superconductor. In this paper we report the synthesis and structure of the first *mixed* polyhalide derivatives of ET derived from the ET–IBr₂ system and having the highest transition temperatures[8] ($T_c \simeq 2.7$ K and a metastable state at approximately 4.2 K) yet observed in an organic superconductor. We also present a strategy for the design of new organic synthetic metals with possibly high superconducting transition temperatures for the onset of superconductivity.

Figure 1. Hydrogen atom surroundings of the linear-centrosymmetric I₃⁻ anion in β-(BEDT-TTF)₂I₃. The anion resides in a cavity created by the –CH₂ groups of BEDT-TTF and can be replaced by a polyhalide anion such as IBr₂⁻, producing isostructural β-(BEDT-TTF)₂IBr₂. Disordered H atoms of one –CH₂ group are designated HA and HB.

Previously,[5,9,10] we noted three novel structural features that influence the electrical properties of the (ET)₂X (X = BrO₄⁻, ReO₄⁻, I₃⁻) conducting systems and also provide insight into a possible strategy for new materials synthesis: (i) In β-(ET)₂I₃ the linear-centrosymmetric I₃⁻ triiodide anion resides in a cavity created by –CH₂ group hydrogen atoms (Figure 1)[10] so that a possible technique for the synthesis of new conductors is to replace the I₃⁻ anion by a polyhalide series of different length (e.g., I₂Br⁻, IBr₂⁻, ICl₂⁻, etc.). (ii) These systems contain a novel two-dimensional "corrugated-sheet" network[5,9] of short *inter*stack S⋯S contacts ($d_{S⋯S} < 3.60$ Å, the van der Waals radius sum), which constitutes the main pathway for the anisotropic electrical conduction and within which the chalcogenide contact distances may possibly, by analogy with the Se⋯Se network distances in the (TMTSF)₂X conductors,[11] be systematically varied through anion replacement.   (iii) β-(ET)₂I₃ is the only organic superconductor known to undergo an incommensurate structural modulation below ∼200 K caused by relatively large sinusoidal displacements of both the ET molecules and I₃⁻ anions [0.124 (3) and 0.281 (1) Å], respectively.[10,12]

(1) TMTSF is tetramethyltetraselenafulvalene (C₁₀H₁₂Se₄) and BEDT-TTF or "ET" is bis(ethylenedithio)tetrathiafulvalene (C₁₀S₈H₈).

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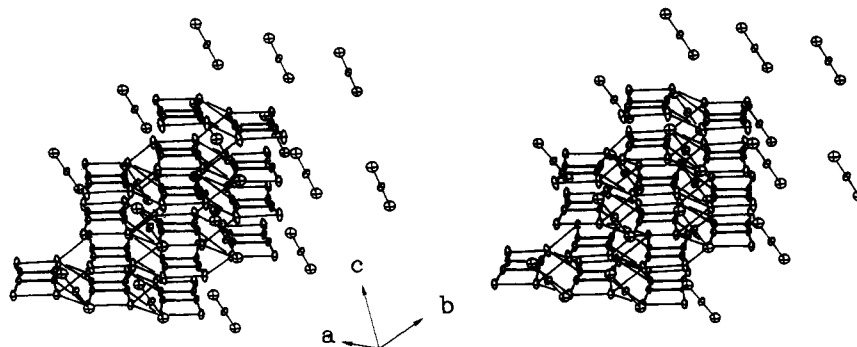
Figure 2. Stereoview of the novel sandwich or *layered* structure of β-$(BEDT-TTF)_2IBr_2$ composed of alternating two-dimensional sheets of linear $(Br-I-Br)^-$ anions between which a "corregated-sheet" network of short *inter*stack S···S interactions is inserted. Only the S atoms of the BEDT-TTF molecules are shown in the network, and light lines indicate the *inter*stack ($d_{S···S}$ < 3.60 Å) interactions. The $-CH_2$ groups of BEDT-TTF protrude from both ends of the molecule (directly out of the plane of the page) and grasp the X_3^- anions in a pincer hold. Therefore, when the length of the X_3^- anion is varied, the *inter*stack S···S distances can be directly altered.

Observation iii may be due, in part, to short intermolecular I···I contacts [$d_{I···I}$ = 4.211 Å, 298 K], resulting in a contribution to the unusual electronic properties of β-$(ET)_2I_3$. We have replaced the polyhalide anion in $(ET)_2I_3$ with the IBr_2^- anion in an effort to shorten the interstack S···S distances and hopefully increase S atom orbital overlap, thereby modifying the electrical properties. On the basis of calculations made by using ionic radii, IBr_2^- is ~7% shorter than I_3^-, while ICl_2^- is ~10% shorter than I_3^- (for the case of linear anions). Assuming the formation of isostructural salts, we *expect* the S···S network *inter*stack contact distances to decrease concomitantly with decreased anion size by virtue of the diminished H atom cavity volume and its effect on the corregated-sheet network of interstack S···S distances (see Figure 2).

Constant-current (~2 μA) electrocrystallization of ET (1.7 × 10^{-3} M) in the presence of $(n-Bu_4N)IBr_2$ (4.7 × 10^{-2} M)[13] with THF as solvent resulted in the simultaneous growth of metallic-like black crystals with two or more different crystallographic phases of $(ET)_2IBr_2$ on the Pt electrodes. At this time, we have identified two phases (α and β).[14] Both are triclinic (space group $P\bar{1}$), with the unit cell volume of the α phase being nearly double that of the β phase as is the case for α- and β-$(ET)_2I_3$.[5,15] We also find that β-$(ET)_2IBr_2$ and β-$(ET)_2I_3$ are strictly isostructural [V_c = 828.7 (3) Å³ vs. 855.9 (2) Å³, respectively]. The Br–I distance of 2.702 (1) Å in $(Br-I-Br)^-$ is ~7% shorter than the I–I distance in I_3^- (I–I = 2.912 (1) Å), which results in the decreased unit cell volume of β-$(ET)_2IBr_2$ vs. β-$(ET)_2I_3$. In both systems the lose packing of the ET molecules leads to the *intra*stack S···S packing distances all being greater than 3.60 Å in length, while nearly the reverse is observed for the *inter*stack separations. The short S···S interstack contact distances in β-$(ET)_2I_3$ and β-$(ET)_2IBr_2$ are compared in Table I, and the result of shortening the

Table I. Interstack S···S^a Distances (Å) in β-$(BEDT-TTF)_2I_3$ vs. β-$(BEDT-TTF)_2IBr_2$

	I_3^-	IBr_2^-
S(3)···S(8)	3.651 (2)	3.652 (2)
S(5)···S(2)	3.574 (2)	3.559 (2)
S(5)···S(6)	3.600 (2)	3.572 (2)
S(7)···S(8)	3.598 (2)	3.560 (2)
S(5)···S(7)	3.628 (2)	3.593 (2)
S(4)···S(6)	3.691 (2)	3.754 (2)
S(8)···S(6)	3.593 (2)	3.564 (2)
av S···S^b	3.591 (5)	3.570 (5)
I(2)···I'(2)^c	4.211 (1)	
Br(1)···Br'(1)^c		4.157 (1)

^{a} The ET molecule S atom labeling scheme is given in Figure 3 (supplementary material); temperature was 298 K. ^{b} Average of distances is less than the S···S van der Waals radius sum of ~3.60 Å. ^{c} Shortest nonbonded X···X contact distance (van der Waals radius sums for I···I and Br···Br are 4.24 and 4.0 Å, respectively).

polyhalide anion length is the striking decrease, by an average of ~0.02 Å, of the interstack S···S distances. These structural changes are accompanied by a large rise in T_c, by a factor of 2–3, of β-$(ET)_2IBr_2$ over β-$(ET)_2I_3$ while still maintaining ambient pressure superconductivity (vide infra).

By use of rf penetration depth measurements,[6,8,16,17] we have observed that fast- or slow-cooled α-$(ET)_2IBr_2$ does not become superconducting at the lowest temperature achieved (0.45 K) while β-$(ET)_2IBr_2$ has the highest critical transition temperatures yet observed in any organic system. We have also measured the superconducting transition temperatures and critical fields of β-$(ET)_2IBr_2$. Our measurements gave T_c's in the range of 2.3–2.7 K in different samples (possibly due to particle size effects) and values of H_{c2} in excess of 1000 Oe at ~0.45 K, with indications of strong critical field anisotropy for different crystallographic orientations of the specimens. In addition, we obtained evidence in one sample for superconductivity at T_c = 4.22 ± 0.04 K in a metastable phase. The T_c was unaltered by very slow cooling or rapid quenching below 40 K. However, the rf signal indicative of superconductivity disappeared near 4 K after application of a weak magnetic field, and remeasurements of the superconducting transition gave T_c = 2.4 K. After aging, the sample gave T_c = 2.7 K, suggesting some annealing of crystal strains and/or defects. The nature of the 4.2 K state is unclear, but the measurements suggest it is a metastable state of β-$(ET)_2IBr_2$. Details of these rf measurements are reported elsewhere.[8]

(13) The $(n-Bu_4N)IBr_2$ electrolyte was prepared in the same fashion as described in ref 8 of ref 5 here. Bromine was used in place of iodine, and the solvent was methanol. Anal. Calcd (Found) for $(n-Bu_4N)IBr_2$: C, 36.31 (36.53); H, 6.86 (6.90); N, 2.65 (2.68); I, 23.98 (24.14); Br, 30.20 (30.16). Analyses were performed by Midwest Microlabs, Indianapolis, IN.

(14) X-ray data at 298 K were collected on a Syntex P2$_1$ diffractometer. The triclinic crystals of β-$(ET)_2IBr_2$ (space group $P\bar{1}$, Z = 1) have unit cell parameters (298 K) a = 6.593 (1) Å, b = 8.975 (2) Å, c = 15.093 (4) Å, α = 93.79 (2)°, β = 94.97 (2)°, γ = 110.54 (2)°, and V = 828.7 (3) Å³. For β-$(ET)_2IBr_2$ (298 K) in the range 4° < 2θ < 60°, 4838 multiple Bragg data were corrected for absorption (μ = 43.3 cm^{-1}, T_{min} = 0.41, T_{max} = 0.72) and 4416 unique data with F_o > 0 (202 parameters) were used in the final full-matrix least-squares analysis, yielding $R(F)$ = 0.060, $R_w(F)$ = 0.039, and goodness-of-fit = 1.84. For α-$(ET)_2IBr_2$ (298 K) a = 8.905 (5) Å, b = 12.031 (5) Å, c = 16.402 (7) Å, α = 85.16 (3)°, β = 88.66 (3)°, γ = 70.86 (3)°, and V = 1654 (1) Å³.

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Temperature Dependence of the Quantum Yields for the Photoanation of Ru(bpy)$_2$L$_2$$^{2+}$ Complexes
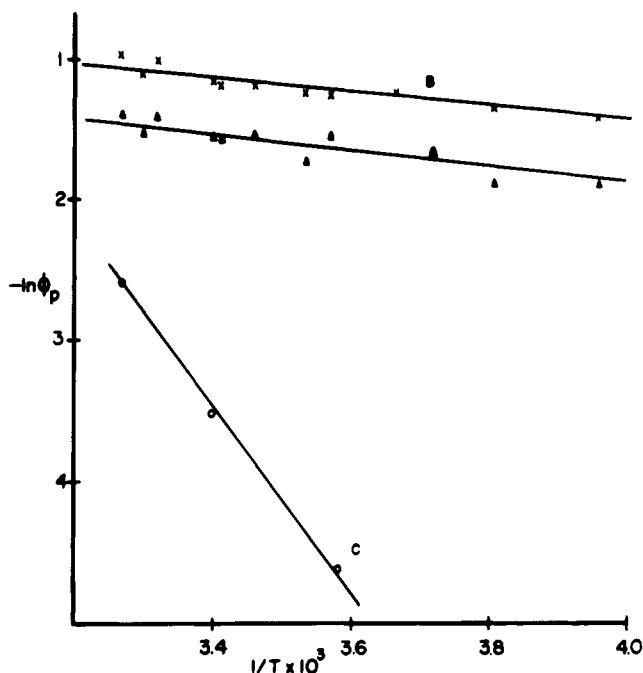
Sir:

Recently, we reported[1] a correlation between the quantum yield for the photoanation of Ru(bpy)$_2$L$_2$$^{2+}$ complexes and the energy of the low-temperature emission. The observed linear correlation appeared to be consistent with the excited-state model proposed by Watts and co-workers[2] for Ru(bpy)$_3$$^{2+}$. We interpreted the variations in quantum yields in terms of changes in the energy difference between the emitting charge-transfer state and a thermally populated d–d state. It was clear at that time that an alternative explanation for the quantum yield dependence might lie in an activation process following population of the d–d state. In order to test this hypothesis, we embarked on a series of experiments designed to measure the temperature dependence of the photoanation process. The results of these experiments indicate that the excited-state description previously proposed[1,3] for Ru(bpy)$_2$L$_2$$^{2+}$ complexes is inadequate in its treatment of photosubstitution.

The quantum yields for the photoanation reactions

$$\text{Ru(bpy)}_2\text{L}_2{}^{2+} + \text{Cl}^- \rightarrow \text{Ru(bpy)}_2\text{LCl}^+ + \text{L}$$
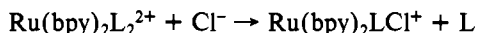
where L is pyridine or acetonitrile, over the temperature range of –20 to +33 °C, are illustrated in Figure 1. The temperature dependence of the quantum yield for the photoanation of Ru(bpy)$_3$$^{2+}$ has been included for comparison. The variations in the quantum yield for photoanation of Ru(bpy)$_2$(py)$_2$$^{2+}$ and Ru(bpy)$_2$(CH$_3$CN)$_2$$^{2+}$ are small but at the present time appear to be slightly larger than the expected experimental error. For discussion purposes we have calculated an Arrhenius activation energy of 700 cm^{-1} for the photoanation of Ru-

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Figure 1. Temperature dependence of the quantum yields for photoanation of (A) Ru(bpy)$_2$(py)$_2$$^{2+}$, (B) Ru(bpy)$_2$(CH$_3$CN)$_2$$^{2+}$, and (C) Ru(bpy)$_3$$^{2+}$ in dichloromethane in the presence of excess tetrabutylammonium chloride.

(bpy)$_2$(py)$_2$$^{2+}$ and Ru(bpy)$_2$(CH$_3$CN)$_2$$^{2+}$. In view of the difficulty of the determination, this value should be viewed only as an order of magnitude measurement. The experimental procedures as well as the data analysis have been described in a previous publication.[1] Similar determinations have been carried out with Ru(bpy)$_2$(3-iodopyridine)$_2$$^{2+}$ and Ru(bpy)$_2$-(4-acetylpyridine)$_2$$^{2+}$, and comparable activation energies have been observed.

The very low activation energies observed with Ru(bpy)$_2$-(py)$_2$$^{2+}$ and the other closely related complexes indicate that the excited-state description suggested by Watts and co-workers for Ru(bpy)$_3$$^{2+}$ does not apply to the photoanation of complexes of the type *cis*-Ru(bpy)$_2$L$_2$$^{2+}$. A consideration of some results recently reported by Caspar and Meyer[3] makes this observation especially surprising. These investigations examined the luminescence lifetimes of a series of *cis*-Ru-(bpy)$_2$L$_2$$^{2+}$ complexes as a function of temperature. The results indicated that the excited-state description of Ru(bpy)$_3$$^{2+}$ provided a very good model for the luminescence lifetime data obtained with a variety of Ru(bpy)$_2$L$_2$$^{2+}$ complexes. We have carried out similar measurements on the complexes used in this study and have observed variations in luminescence lifetimes as a function of temperature that are consistent with those observed by Meyer and co-workers. The characteristic temperature dependencies of these compounds are illustrated in Figure 2 and sharply contrast that displayed by the quantum yields for photoanation.

The different temperature dependencies exhibited by the luminescence lifetimes and the photoanation quantum efficiencies clearly indicate that photosubstitution in ruthenium complexes containing only two bipyridine ligands is not a result of thermal population of the d–d state indicated in the previous excited-state description. A d–d state is probably involved,[4] but either it must be different from the one involved in the luminescence decay or, if it is indeed the same state, it must be populated by a different pathway.

The validity of extending these results to Ru(bpy)$_3$$^{2+}$ is difficult to assess. In the case of Ru(bpy)$_3$$^{2+}$, the quantum

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