presently understood, but efforts are in progress to produce additional EPR-active low-valent Mn complexes to test its generality.

The Mn(III)–Mn(IV) dimers served as useful prototypes for studies[21] of the EPR spectrum exhibited by the Mn in photosystem II of photosynthesis (PS II), where it is now postulated that either a Mn(III)–Mn(III) or Mn(II)–Mn(III) dinuclear species is present.[21] Although **2** is not a realistic model for the Mn site in PS II, a study of its spectral properties increases the limited body of knowledge available on mixed-valent Mn complexes and in this sense may aid in the general understanding of the biological system.

Acknowledgment. The author thanks Dr. L. D. Rosenhein for assistance with acquiring the low-temperature electronic spectra and Drs. G. D. Watt and W. E. Newton for useful discussions. This work was kindly supported by an internal research grant from Battelle Memorial Institute.

Registry No. **1**, 96212-29-2; **2**, 96212-30-5; **3**, 96212-31-6; $Mn_2(CO)_{10}$, 10170-69-1.

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A Test of Superconductivity vs. Molecular Disorder in (BEDT-TTF)$_2$X Synthetic Metals: Synthesis, Structure (298, 120 K), and Microwave/ESR Conductivity of (BEDT-TTF)$_2$I$_2$Br

Sir:

For the first time two *ambient*-pressure synthetic metal superconductors have been reported in a single organic radical-cation donor system, with two different *symmetric* trihalide anions, and based on BEDT-TTF,[1] abbreviated "ET". They are β-(ET)$_2$I$_3$, with a reported superconducting transition temperature[2-6] (T_c) of 1.2–1.6 K, and β-(ET)$_2$IBr$_2$, with a T_c (2.3–2.8 K) twice[7,8] that of the I_3^- derivative. These two systems are isostructural with a characteristic structural motif of an extended "corrugated sheet" network of short *inter*stack S···S ($d_{S\cdots S} < 3.60$ Å) interaction distances.[9-11] The S···S orbital overlap within the two-dimensional *inter*stack network comprises the main electron conduction pathway in these synthetic metals, thereby constituting the conduction band.[12] Only β-(ET)$_2$I$_3$ possesses a "modulated"[13-15] structure, and a disordered $-CH_2$ group, with the former property being observed for the first time in any organic superconductor. However, these structural novelties do *not* appreciably affect the overall pattern of S···S orbital overlaps or the occurrence of superconductivity. In β-(ET)$_2$IBr$_2$, which is completely ordered at 125 K and contains no structural modulations, the IBr_2^- anion is ~8% shorter than the I_3^- anion and as a result the network S···S distances are *systematically* shortened due to cation–anion [$-CH_2\cdots(X_3)^-$] interactions.[7] These findings suggest that one might prepare a new anion derivative, with a length *intermediate* between that of I_3^- and IBr_2^-, such as the *asymmetric* $(I-I-Br)^-$ anion,[16] which might also have S···S distances and T_c (expectedly at ambient pressure) intermediate between those of the two parent superconducting salts. More importantly, the $(I_2Br)^-$ anion provides a unique test of the effect of the dipolar anion and molecular order/disorder on the superconducting ground state in these unusual systems. While the $(I-I-I)^-$ and $(Br-I-Br)^-$ derivatives of ET are centrosymmetric and crystallographically ordered, the isostructural (ET)$_2$(I–I–Br) derivative *requires* a disordered anion configuration in the crystal due to its site symmetry ($\bar{1}$). Thus an "average" $(I_2Br)^-$ anion configuration results from a superposition of two allowed site-packing configurations, viz. $(I-I-Br)^-$ and $(Br-I-I)^-$. Structural disorder of this type generates a *random* electrostatic potential throughout the lattice, which is "sensed" by the electrons in the conducting radical-cation S···S network, or the corresponding Se···Se network in (TMTSF)$_2$X

Table I. Selected Intermolecular Interstack S···S Distances (all $D \leq$ 3.6 Å) for β-(BEDT-TTF)$_2$X (X = I_3^-, I_2Br^-, IBr_2^-) at 298 and 120 K

		dist		
interstack contact		β-(ET)$_2$I$_3$[a]	β-(ET)$_2$I$_2$Br	β-(ET)$_2$IBr$_2$
S(5)···S(2)	298 K	3.574 (2)[b]	3.558 (3)	3.559 (2)
	120 K	3.555 ± 0.033	3.522 (1)	3.514 (2)
	diff[c]	0.019	0.036	0.045
S(7)···S(8)	298 K	3.598 (2)	3.582 (3)	3.560 (2)
	120 K	3.534 ± 0.022	3.548 (1)	3.510 (2)
	diff	0.064	0.035	0.050
S(5)···S(6)	298 K	3.600 (2)	3.582 (3)	3.593 (2)
	120 K	3.551 ± 0.048	3.578 (1)	3.551 (2)
	diff	0.049	0.034	0.042
S(5)···S(7)	298 K	3.628 (2)	3.611 (3)	3.572 (2)
	120 K	3.548 ± 0.033	3.530 (1)	3.498 (2)
	diff	0.080	0.052	0.074
S(6)···S(8)	298 K	3.593 (2)	3.578 (3)	3.564 (2)
	120 K	3.552 ± 0.094	3.515 (2)	3.504 (2)
	diff	0.041	0.062	0.060

[a] Each distance in the modulated structure[13] of β-(ET)$_2$I$_3$ at 120 K is an *average* value accompanied by the range allowed by the modulation and cannot be *directly* compared[27] to analogous distances in β-(ET)$_2$I$_2$Br or β-(ET)$_2$IBr$_2$, which are not modulated. [b] Estimated standard deviations are enclosed in parentheses and are ±0.003–0.005 for the average distances at 120 K for β-(ET)$_2$I$_3$. [c] The differences cited are those between 298 and 120 K values.

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[9] In the (ET)$_2$X, X = $(I_3)^-$,[3,10,11] $(I_2Br)^-$, and IBr_2^-,[7,8] systems, the intermolecular *intra*stack S···S interaction distances are longer than the van der Waals radius sum of 3.6 Å while several *inter*stack distances are shorter. The degree to which these distances can be correlated with the degree of orbital overlap interaction is presently under investigation.[12]

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systems.[17] Only one analogous case in the $(TMTSF)_2X$ series can be compared to the β-$(ET)_2X$, X = I_3^- and IBr_2^-, systems, viz. the sole Se-based *ambient-pressure* organic superconductor[18] $(TMTSF)_2ClO_4$, which also contains anion disorder.[19] In quickly cooled crystals the ClO_4^- anion disorder is "frozen in", which *suppresses* the superconducting state.[20,21] However, "slow-cooled" specimens undergo a crystallographic transition (a, $2b$, c) at 24 K, resulting in *ordered* ClO_4^- anions[22] and the onset of superconductivity at 1.2 K. No cooling-rate affects are observed for the onset of superconductivity in β-$(ET)_2X$, X = I_3^- and IBr_2^-. Although $(ET)_2I_2Br$ is strictly isostructural with β-$(ET)_2X$, X = I_3^- and IBr_2^-, and is metallic over the temperature range 1.07 K $< T <$ 298 K, it does not exhibit superconductivity at ambient pressure nor under hydrostatic pressure up to 5 kbar.

Shiny black distorted-hexagon-shaped crystals of $(ET)_2I_2Br$ were grown by electrocrystallization ($T = 23.4 \pm 0.1$ °C) in dry tetrahydrofuran as solvent at a current density of 0.8 $\mu A/cm^2$ (Pt electrodes) with 1.73 mM ET and 0.10 M $(n\text{-}Bu_4N)I_2Br$. Extensive literature searching revealed no reported synthesis of $(n\text{-}Bu_4N)I_2Br$, but after some experimentation a synthesis was developed that yielded the $(I_2Br)^-$ derivative.[23] Identical results were obtained by use of ET synthesized in our laboratory[24] or purchased from Strem Chemical Co. Whereas numerous crystalline phases of $(ET)_2X$, X = I_3^- and IBr_2^-, are obtained by use of electrochemical growth procedures, only one phase was obtained in this case, which we have designated as β-$(ET)_2I_2Br$.

Crystals of β-$(ET)_2I_2Br$ are isostructural[25] with β-$(ET)_2I_3$ and β-$(ET)_2IBr_2$, with the I_2Br^- anion being crystallographically disordered.[26] As in the cases of β-$(ET)_2X$, X = I_3^- and IBr_2^-, the loose stacking of the nonplanar ET molecules leads to *intra*stack S···S distances that are all greater than the van der Waals radii sum (3.60 Å) while some of the *inter*stack S···S distances are less than 3.6 Å (see Table I). In all of these salts, a layered structure[3,7] results from alternating two-dimensional sheets of (1) the linear anions and (2) the "corrugated sheet" network of ET molecules linked by short *inter*stack S···S interactions. The I_2Br^- anion is ~4% longer than the IBr_2^- anion (including van der Waals radii of I and Br at 2.15 and 1.95 Å, respectively); however, the *inter*stack S···S contacts in β-$(ET)_2I_2Br$ are only 0.2–1.1% longer (i.e., 0.008–0.037 Å longer) than in superconducting β-$(ET)_2IBr_2$ see Table I).[27] This result is especially significant in regard to the lack of superconductivity even under pressure in the isostructural β-$(ET)_2I_2Br$.

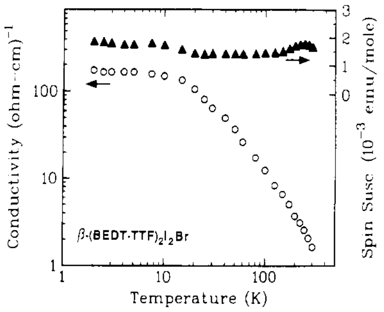

Figure 1. Microwave conductivity (calculated) and spin susceptibility of β-$(ET)_2I_2Br$ (T = 1.07–298 K).

The ambient-pressure ESR experiments were performed by use of a rectangular microwave cavity operated at 9.8 GHz. the line shape was Dysonian[28] from 2 to 300 K and could be accurately characterized at all temperatures by a linear combination of Lorentzian absorption and dispersion. The peak-to-peak linewidth of the absorption portion of the ESR signal decreases with decreasing temperature from 19.3 (5) Oe at 300 K to 2.7 (1) Oe at 5 K and then increases very slightly between 5 and 2 K to ~3 Oe.

With use of a thin-plate calculation[29] for resonance in metallic samples, the spin susceptibility, corrected for microwave skin depth plus the skin depth/plate thickness ratio, was obtained from the ESR signal. As shown in Figure 1, the spin susceptibility is independent of temperature from 2 to 300 K at 1.5×10^{-3} emu/mol, indicative of the Pauli spin paramagnetism of a metal. Also shown in Figure 1 is the calculated microwave conductivity, which rises with decreasing temperature from 300 to 15 K and then appears to saturate near 200 Ω^{-1} cm^{-1} at lower temperatures. This "saturation" may reflect the use of a thin-plate calculation[29] for ESR in a sample whose thickness is nearly half the cross-sectional dimensions, far from a true thin-plate geometry. Hence the microwave conductivity shown in Figure 1 will be confirmed by four-probe dc measurements below 25 K when large enough crystals become available.

Low-field ESR measurements were also performed on the same sample at a resonant field of 10 Oe (T = 1.07–4 K). The peak-to-peak line width at low field is somewhat larger than at microwave frequencies, on the order of 10 Oe. The temperature dependence of the spin susceptibility at low field is consistent with that at microwave frequencies; i.e., the susceptibility is independent of temperature. We did not observe any evidence for superconductivity (complete disappearance of ESR signal) down to a

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(23) A 10.0-g amount of $(n\text{-}Bu_4N)Br$ (31 mmol) was dissolved in 200 mL of boiling absolute ethanol, followed by the *slow* addition of 7.8 g of I_2 (31 mmol). The dark brown solution was filtered hot and boiled until the volume was 150 mL. After slow cooling to room temperature, the solution was stored in a freezer overnight. The reddish brown needles of $(n\text{-}Bu_4N)I_2Br$ were collected, vacuum-dried, twice recrystallized from hot absolute ethanol, and stored in a closed container in a refrigerator. Approximately 14.6 g of product (91% yield) was obtained; mp 56.5–57.5 °C. Anal. Calcd (found) for $(n\text{-}Bu_4N)I_2Br$: C, 33.35 (33.34); H, 6.30 (6.44); N, 2.43 (2.61); I, 44.05 (43.94). Analyses were performed by Midwest Microlab, Indianapolis, IN.

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(26) In all trihalide anions studied to date, the atom of highest atomic number always occupies the central position,[16] and the $(I\text{–}Br\text{–}I)^-$ configuration has been ruled out by electron density plots from our X-ray studies.

(27) The range of *inter*stack S···S, or any other intermolecular distances in β-$(ET)_2I_3$ at 120 K cannot be directly compared to those in the I_2Br^- and IBr_2^- salts at 120 K because the structure of the I_3^- derivative is *modulated*. For a discussion see ref 13.

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temperature of 1.07 K at both ambient pressure and a pressure of 5 kbar. Further experiments using rf penetration depth measurements[4] showed no evidence of superconductivity at ambient pressure down to a temperature of ~0.45 K. We cannot rule out a possible superconducting transition at $T > 4$ K and under applied pressure.

Thus, contrary to the $(TMTSF)_2X$ systems in which anion disorder/order transitions appear to cause metal/insulator transitions, the β-$(ET)_2X$ synthetic metals may remain metallic to the lowest temperatures regardless of anion disorder.

Acknowledgment. Work at Argonne National Laboratory and Sandia National Laboratories is sponsored by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences, under Contracts W-31-109-Eng-38 and KC020202, respectively. We express our appreciation for computing time made available by the DOE on the ER-CRAY. We wish to thank D. L. Overmyer for his expert technical assistance.

Note Added in Proof. As a further test of the effect of molecular and anionic order on superconducting transitions in β-$(ET)_2X$ salts, we have synthesized β-$(ET)_2$(I–Au–I). The unit cell volume is 845.2 Å^3, compared to 842.3 Å^3 for β-$(ET)_2I_2Br$ reported herein; however, the AuI_2^- derivative is completely ordered. It also has the highest ambient-pressure superconducting transition temperature (onset $T_c \approx 5$ K, rf penetration depth measurements) reported for any organic conductor.

Registry No. ET, 66946-48-3; $(ET)_2I_2Br$, 96164-65-7; $(n\text{-}Bu_4N)I_2Br$, 3419-99-6; $(n\text{-}Bu_4N)Br$, 1643-19-2; I_2, 7553-56-2.

Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1) and final atom positional and anisotropic temperature factors (Table X2) and a figure showing the S-atom labeling scheme for the ET molecule (Figure X1) (3 pages). Ordering information is given on any current masthead page.

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(30) M.A.F., H.C.J., and J.D.C. are student undergraduate research participants sponsored by the Argonne Division of Educational Programs from Indiana University of Pennsylvania, Indiana, PA, The University of North Carolina, Chapel Hill, NC, and Carnegie-Mellon University, Pittsburgh, PA, respectively.

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Articles

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Theoretical Studies on N-Bonded Pyrazole Derivatives of Boron

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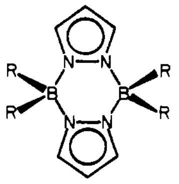
CNDO calculations on the sequential processes (1) $R_2BH + Hpz \rightarrow R_2Bpz + H_2$ and (2) $2R_2Bpz \rightarrow R_2B(\mu\text{-}Pz)_2BR_2$ (where pz = pyrazolyl = $N_2C_3H_3$) indicate that for R = H both steps are energetically favorable, particularly the dimerization (2). In addition, the latter also leads to electronic saturation of the boron atom, and the energy of the resultant pyrazabole is independent of the conformation of the molecule. For $R = {}^1/_2\ CH_3N(CH_2)_2NCH_3$, only step 1 yielding the monomer is exothermic, whereas step 2 is greatly dependent on the geometry of the central B_2N_4 ring (in addition to provoking a considerable charge increase on the boron atom). Another process, i.e., (3) $R_2Bpz + Hpz \rightarrow R_2B(\mu\text{-}pz)_2H$, is exothermic in both cases, but for R = H the pyrazabole formation (2) is much more strongly favored. The theoretical data are in good agreement with experimental results.

Introduction

When a trigonal borane, BR_3, is reacted with pyrazole, Hpz, or a C-substituted derivative thereof in a 1:1 molar ratio, ready condensation occurs to yield a transient pyrazol-1-ylborane, R_2Bpz. As a rule, the latter species immediately dimerizes to form a pyrazabole of the general structure **1**.[1]



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The pyrazaboles, $R_2B(\mu\text{-}pz)_2BR_2$, have been found to be chemically extremely stable. For example, they are generally unaffected by air or water, and various organic transformations have been accomplished at the carbon sites of the bridging pyrazole groups without destruction of the central B_2N_4 ring.[2] This stability has been rationalized in terms of steric as well as electronic factors.[1] However, some monomeric pyrazol-1-ylboranes, i.e., symmetrical cleavage products of pyrazaboles, have recently become available.[3-7] Experimental data appear to indicate that monomeric pyrazol-1-ylboranes exist only when the boron atom is simultaneously bonded not only to a pyrazolyl group but also to strongly electron-donating substituents. In order to better understand these observations and the general electronic and steric features of pyrazole derivatives of boron, several semiempirical studies have been performed on these species.

Experimental Section

The method chosen was the CNDO (complete neglect of differential overlap) molecular orbital approach of Pople and co-workers.[8] This

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