Chem. Mater. 1991, 3, 508-513

BEDT-TTF-Based Synmetal: Synthesis, Structure, ESR, and Electrical Properties of (BEDT-TTF)Hg$_{0.776}$(SCN)$_2$

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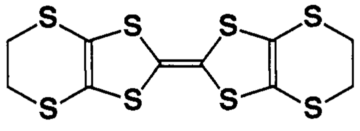
Received December 12, 1990. Revised Manuscript Received February 5, 1991

A new charge-transfer salt, (BEDT-TTF)Hg$_{0.776}$(SCN)$_2$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene), has been synthesized and found to exhibit metallic conductivity to 13 K. This new synmetal has a composite columnar stack structure in which the BEDT-TTF donor molecule and SCN$^-$ ligands form one subsystem with a triclinic cell ($P\bar{1}$, with unit-cell dimensions a = 6.746 (2) Å, b = 4.114 (1) Å, c = 20.580 (3) Å, α = 83.06 (1)°, β = 105.93 (2)°, γ = 119.01 (2)°, V_c = 480.23 Å^3, Z = 1), and the Hg atoms form a subsystem with a second triclinic cell ($P\bar{1}$, with unit-cell dimensions a = 6.758 (2) Å, b = 5.302 (2) Å, c = 21.352 (6) Å, α = 73.10 (2)°, β = 110.44 (3)°, γ = 119.17 (3)°, V_c = 618.85 Å^3, Z = 1). The two sublattices share the b-axis direction, which is the direction of molecular stacking, but the periodicity in this direction differs for the two sublattices. Since the SCN$^-$ ligands and the Hg atoms occur in different subsystems, the Hg coordination varies from unit cell to unit cell. The interaction between the two sublattices gives rise to each being modulated. The modulation has been analyzed by use of the intensities of the satellite reflections. Four-probe resistivity and single-crystal ESR measurements show that (BEDT-TTF)Hg$_{0.776}$(SCN)$_2$ is metallic down to at least 13 K. Radio-frequency penetration depth studies at ambient pressure indicate that superconductivity is not observed down to 0.6 K. Tight-binding band electronic structure calculations on the "average structure" of the BEDT-TTF stacks show this material to be strictly one-dimensional. The conflict between this theoretical result and conductivity measurements appears to be resolved by use of a commensurate approximation to the modulation of the BEDT-TTF lattice in the band structure calculations. The Fermi surfaces based on the commensurate approximation are all closed; therefore, (BEDT-TTF)Hg$_{0.776}$(SCN)$_2$ is expected to be a two-dimensional metal.

Introduction



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Synthetic metals (synmetals) based on the organic electron-donor molecule BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene, or ET, 1] have been synthesized with transport properties that range from semiconducting to metallic to superconducting.[1] In the isostructural β-(ET)$_2$X salts, where X$^-$ is a monovalent linear triatomic anion (e.g., I$_3^-$, IBr$_2^-$, or AuI$_2^-$), the superconducting transition temperatures (T_c) have been shown to increase with increasing anion size, viz., T_c = 2.8 K in β-(ET)$_2$IBr$_2$,[2] T_c = 4.98 K in β-(ET)$_2$AuI$_2$,[3] and T_c = 1.5 K in β-(ET)$_2$I$_3$[4,5] (T_c = 8 K in β^*-(ET)$_2$I$_3$ under mild applied pressure[6,7] and a resultant structure change[8]). For these salts, changes in the donor-to-anion hydrogen-bonding interactions that accompany anion size changes have been correlated to the lattice "softness" and phonon frequencies and therefore, to the T_c values.[9] In the β-(ET)$_2$X system, a trihalide or

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(1) (a) Williams, J. M.; Wang, H. H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J.; Whangbo, M. H. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed; Wiley: New York, 1987; Vol. 35, pp 51-218. (b) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors, Synthesis, Structure, Properties and Theory*; Prentice Hall: Old Tappen, NJ.

(2) Williams, J. M.; Wang, H. H.; Beno, M. A.; Emge, T. J.; Sowa, L. M.; Copps, P. T.; Behroozi, F.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 3839.

(3) 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. *Inorg. Chem.* **1985**, *24*, 2465.

(4) Yagubskii, E. B.; Shchegolev, I. F.; Laukhin, V. N.; Kononovich, P. A.; Karatsovnik, M. W.; Zvarykina, A. V.; Buravov, L. I. *Pis'ma Zh. Eksp. Teor. Fiz.* **1984**, *39*, 12; *JETP Lett.* (*Engl. Transl.*) **1984**, *39*, 12.

(5) Williams, J. M.; Emge, T. J.; Wang, H. H.; Beno, M. A.; Copps, P. T.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 2558.

(6) Laukhin, V. N.; Kostyuchenko, E. E.; Sushko, Yu. B.; Shchegolev, I. F.; Yagubskii, E. B. *Pis'ma Zh. Eksp. Teor. Fiz.* **1985**, *41*, 68.

(7) Murata, K.; Tokumoto, M.; Anzai, H.; Bando, H.; Saito, G.; Kajimura, K.; Ishiguro, T. *Phys. Soc. Jpn.* **1985**, *54*, 1236.

(8) (a) Schultz, A. J.; Wang, H. H.; Williams, J. M.; Filhol, A. *J. Am. Chem. Soc.* **1986**, *108*, 7853. (b) Schultz, A. J.; Beno, M. A.; Wang, H. H.; Williams, J. M. *Phys. Rev. B: Condens. Matter* **1986**, *33*, 7823.

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similar anion longer than I_3^- is predicted to give salts possessing enhanced electrical properties[1,9] (i.e., T_c's > 8 K); however, I_3^- is the longest anion of this type known.

Attempts to utilize anions longer that I_3^-, e.g., the Cu(NCS)_2^- anion, result in the production of a new superconducting phase, κ-(ET)$_2$Cu(NCS)$_2$ (T_c = 10.4 K),[10-12] which contains a polymeric anion and a completely different donor molecule packing arrangement than occurs in the superconducting β-(ET)$_2$X salts. The κ-phase type donor molecule packing is also observed in a number of superconducting salts {κ-(ET)$_2$X (X$^-$ = Cu[N(CN)$_2$]Br$^-$, T_c = 11.6 K;[13] Cu[N(CN)$_2$]Cl$^-$, T_c = 12.8 K at 0.3 kbar;[14] I_3^-, T_c = 3.6 K;[15,16] Ag(CN)$_2^-$·H$_2$O, T_c = 5.0 K[17,18]), in two mercury halide salts (κ-(ET)$_4$Hg$_{2.89}$Br$_8$ (T_c = 4.3 K, and 6.7 K at 3.5 kbar)[19,20] and κ-(ET)$_4$Hg$_3$Cl$_8$ (T_c = 1.8 K at 12 kbar, and 5.3 K at 29 kbar)),[21-23] in (MDT-TTF)$_2$AuI$_2$ (T_c = 4.5 K),[24,25] and in (DMET)$_2$AuBr$_2$ (T_c = 1.9 K)[26]} and also in nonsuperconducting salts {κ-(ET)$_2$Cu[N(CN)$_2$]I[27] and (BMDT-TTF)$_2$Au(CN)$_2$}.[28] All organic superconductors with T_c's higher than 10 K are κ-phase salts. The recently discovered κ-phase salts κ-(ET)$_2$Cu[N(CN)$_2$]X (X$^-$ = Cl$^-$, Br$^-$, I$^-$)[13,14,27,53] are isostructural but differ in their superconducting properties. The Br salt is an ambient pressure superconductor, the Cl salt becomes superconducting under a slight pressure up to 5 kbar. An analysis of the 127 K crystal structures of these salts leads to a conclusion similar to that reached from the study of the isostructural β-(ET)$_2$X salts,[9] i.e., for an organic conductor to become a superconductor, its lattice should be soft and also be free from random potentials such as those caused by crystallographic disorder.

Table I. Data Collection and Refinement

	all	main	satellite
no. of refns	6184	4311	1873
no. of unique reflns	3353	2922	431
no. of reflns with $T > 2.0\sigma(I)$	2869	2506	363
no. of params	154		
R	0.073	0.066	0.162
R_w	0.116	0.092	0.288
$(\sin\theta/\lambda)_{\max}$, Å^{-1}	0.594		
cryst size, mm^3	0.5 × 0.25 × 0.05		
abs coeff, cm^{-1}	74.0		

In an attempt to synthesize new κ-phase salts, such as κ-(ET)$_4$Hg$_3$X$_8$ (X$^-$ = Cl$^-$, Br$^-$), we have prepared the supporting electrolyte (n-Bu)$_4$NHg(SCN)$_3$. With TTF (tetrathiofulvalene) as the donor molecule, the new anion, Hg(SCN)$_3^-$, leads to (TTF)$_5$Hg$_6$(SCN)$_{16}$.[29] Electrocrystallization of ET with a mixture of electrolytes KNCS, Hg(SCN)$_2$, and 18-crown-6 leads to α-(ET)$_2$KHg(SCN)$_4$.[30] In contrast to the synthesis of κ-(ET)$_2$Cu(NCS)$_2$, an alkali-metal cation is encapsulated in the KHg(SCN)$_4^-$ anion network. Two isostructural salts have also been reported, i.e., α-(ET)$_2$MHg(SCN)$_4$ (M$^+$ = NH$_4^+$ and Rb$^+$).[30-33] The ammonium salt was subsequently identified as an ambient pressure superconductor with T_c = 1.15 K.[31] Electrocrystallization of ET with (n-Bu)$_4$NHg(SCN)$_3$ leads to a new highly conductive compound, (ET)Hg$_{0.776}$(SCN)$_2$, with a stoichiometry very close to that of the κ-(ET)$_4$Hg$_3$X$_8$ but a completely different crystal packing. We report here the synthesis, structure, physical properties and band electronic structure of this new (ET)Hg$_{0.776}$(SCN)$_2$ salt.

Experimental Section

All chemicals used were reagent grade from Aldrich Chemical Co. except ET, which was purchased from Strem Chemical Co., Inc. Elemental analyses were performed at Midwest Microlab, Indianapolis, IN.

(n-Bu)$_4$NHg(SCN)$_3$. (n-Bu)$_4$NSCN (2.86 g, 9.5 mmol) in 10 mL of absolute ethanol was added to a 300-mL ethanol solution containing 3.0 g of Hg(SCN)$_2$ (9.5 mmol) at room temperature. The resulting mixture was concentrated to 50 mL and stored in a freezer; 5.22 g of product (8.5 mmol) was obtained (89% yield). The product was recrystallized from ethanol/diethyl ether, mp 56–59 °C. Anal. for C$_{19}$H$_{36}$N$_4$S$_3$Hg, found (calcd): C, 36.87 (36.97); H, 5.98 (5.88); N, 8.79 (9.08); S, 15.32 (15.58).

(ET)Hg$_{0.776}$(SCN)$_2$. The title compound was prepared by use of standard electrocrystallization techniques. ET (26 mg, 0.068 mmol) and (n-Bu)$_4$NHg(SCN)$_3$ (0.59 g, 0.96 mmol) were dissolved in 45 mL of 1,1,2-trichlorethane (TCE) that was distilled from

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(9) Whangbo, M. H.; Williams, J. M.; Schultz, A. J.; Emge, T. J.; Beno, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 90.

(10) Urayama, H.; Yamochi, H.; Saito, G.; Nozawa, K.; Sugano, T.; Kinoshita, M.; Sato, S.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, 55.

(11) Gärtner, S.; Gogu, E.; Heinen, T.; Keller, H. J.; Klutz, T.; Schweitzer, D. *Solid State Commun.* **1988**, *65*, 1531.

(12) Carlson, K. D.; Geiser, U.; Kini, A. M.; Wang, H. H.; Montgomery, L. K.; Kwok, W. K.; Beno, M. A.; Williams, J. M.; Cariss, C. S.; Crabtree, G. W.; Whangbo, M.-H.; Evain, M. *Inorg. Chem.* **1988**, *27*, 965.

(13) Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W. K.; Vandervoort, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 2555.

(14) Williams, J. M.; Kini, A. M.; Wang, H. H.; Carlson, K. D.; Geiser, U.; Montgomery, L. K.; Pyrka, G. J.; Watkins, D. M.; Kommers, J. M.; Boryschuk, S. J.; Strieby-Crouch, A. V.; Kwok, W. K.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 3272.

(15) Kobayashi, A.; Kato, R.; Kobayashi, H.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1987**, 459.

(16) Kato, R.; Kobayashi, H.; Kobayashi, A.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1987**, 507.

(17) Mori, H.; Hirabayashi, I.; Tanak, S.; Mori, T.; Inokuchi, H. *Solid State Commun.*, in press.

(18) Kurmoo, M.; Talham, D. R.; Pritchard, K. L.; Day, P.; Stringer, A. M.; Howard, J. A. K. *Synth. Met.* **1988**, *27*, A177.

(19) Lyubovskaya, R. N.; Zhilyaeva, E. I.; Pesotskii, S. I.; Lyubovskii, R. B.; Atovmyan, L. O.; D'yachenko, O. A.; Takhirov, T. G. *JETP Lett.* (*Engl. Transl.*) **1987**, *46*, 188.

(20) Schirber, J. E.; Overmyer, D. L.; Venturini, E. L.; Wang, H. H.; Carlson, K. D.; Kwok, W. K.; Kleinjan, S.; Williams, J. M. *Physica C* **1990**, *161*, 412.

(21) Lyubovskaya, R. N.; Lyubovskii, R. B., Shibaeva, R. P.; Aldoshina, M. Z.; Gol'denberg, L. M.; Rozenberg, L. P.; Khidetel', M. L.; Shul'pyakov, Yu. F. *JETP Lett.* **1985**, *42*, 468.

(22) Lyubovskii, R. B.; Lyubovskaya, R. N.; Kapustin, N. V. *Sov. Phys. JETP* **1987**, *66*, 1063.

(23) Shibaeva, R. P.; Rozenberg, L. P. *Sov. Phys. Crystallog.* **1988**, *33*, 834.

(24) MDT-TTF is methylenedithiotetrathiafulvalene. Papavassiliou, G. C.; Mousdis, G. A.; Zambounis, J. S.; Terzis, A.; Hountas, A.; Hilti, B.; Mayer, C. W.; Pfeiffer, J. *Synth. Met.* **1988**, *27*, B379.

(25) Kini, A. M.; Beno, M. A.; Son, D.; Wang, H. H.; Carlson, K. D.; Porter, L. C.; Welp, U.; Vogt, B. A.; Williams, J. M.; Jung, D.; Evain, M.; Whangbo, M.-H.; Overmyer, D. L.; Schirber, J. E. *Solid State Commun.* **1989**, *69*, 503.

(26) DMET is dimethyl(ethylenedithio)diselenadithiafulvalene. Kikuchi, K.; Honda, Y.; Ishikawa, Y.; Saito, K.; Ikemoto, I.; Murata, K.; Anzai, Y.; Ishiguro, L.; Kobayashi, K. *Solid State Commun.* **1988**, *66*, 405.

(27) Wang, H. H.; Carlson, K. D.; Geiser, U.; Kini, A. M.; Schultz, A. J.; Williams, J. M.; Montgomery, L. K.; Kwok, W. K.; Welp, U.; Vandervoort, K. G.; Boryschuk, S. J.; Strieby Crouch, A. V.; Kommers, J. M.; Watkins, D. M.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Novoa, J. J.; Whangbo, M.-H. *Synth. Met.*, in press.

(28) BMDT-TTF is bis(methylenedithio)tetrathiafulvalene. Nigrey, P. J.; Morosin, B.; Kwak, J. F.; Venturini, E. L.; Baughman, R. J. *Synth. Met.* **1986**, *16*, 1.

(29) Thorup, N.; Beno, M. A.; Cariss, C. S.; Carlson, K. D.; Geiser, U.; Kleinjan, S.; Porter, L. C.; Wang, H. H.; Williams, J. M. *Synth. Met.* **1988**, *27*, B15.

(30) Oshima, M.; Mori, H.; Saito, G.; Oshima, K. *Chem. Lett.* **1988**, 1159.

(31) Wang, H. H.; Carlson, K. D.; Geiser, U.; Kwok, W. K.; Vashon, M. D.; Thompson, J. E.; Larsen, N. F.; McCabe, G. D.; Hulscher, R. S.; Williams, J. M. *Physica C* **1990**, *166*, 57.

(32) Wang, H. H.; Beno, M. A.; Carlson, K. D.; Geiser, U.; Kini, A. M.; Montgomery, L. K.; Thompson, J. E.; Williams, J. M. In *Proc. Int. Conf. Organic Superconductors*; South Lake Tahoe, CA, May 1990. Kresin, V., Little, W., Eds. *Organic Superconductivity*; Plenum Press: New York, 1990; pp 45–61.

(33) Mori, H.; Tanaka, S.; Oshima, K.; Saito, G.; Mori, T.; Maruyama, Y.; Inokuchi, H. *Synth. Met.*, in press.

Table II. Final Coordinates and *R* Factors

atom	x	y	z
ET Cell: a = 6.746 (2)Å, b = 4.114 (1)Å, c = 20.580 (3)Å, α = 83.06 (1)°, β = 105.93 (2)°, γ = 119.01 (2)°			
S1	0.7435 (4)	0.0750 (6)	0.4413 (1)
S2	0.2726 (4)	0.0062 (6)	0.4022 (1)
S3	0.2357 (3)	0.0546 (5)	0.2558 (1)
S4	0.8051 (3)	0.1564 (6)	0.3042 (1)
C1	0.504 (1)	0.019 (2)	0.4672 (4)
C2	0.404 (1)	0.056 (2)	0.3370 (4)
C3	0.400 (2)	0.011 (2)	0.2039 (5)
C4	0.660 (1)	0.277 (2)	0.2254 (4)
C5	0.621 (1)	0.087 (2)	0.3556 (4)
H31	0.32 (2)	0.11 (2)	0.153 (5)
H32	0.40 (2)	0.10 (3)	0.197 (6)
H41	0.68 (1)	0.51 (2)	0.227 (4)
H42	0.74 (1)	0.28 (2)	0.185 (5)
S5	0.9160 (4)	0.1501 (6)	0.0839 (1)
C6	0.635 (2)	−0.152 (2)	0.0729 (5)
N	0.444 (2)	−0.360 (3)	0.0701 (5)
Hg Cell: a = 6.758 (2)Å, b = 5.302 (2)Å, c = 21.352 (6)Å, α = 73.10 (2)°, β = 110.44 (3)°, γ = 119.17 (3)°			
Hg	0	0	0

P_2O_5 and passed through an alumina column. A constant-current density of 0.2 $\mu A/cm^2$ was applied at 23 °C, and thin black platelet crystals were harvested after approximately 3 weeks. The room-temperature ESR peak-to-peak line width is around 30 G. No evidence for other phases was found in ESR studies of more than 10 crystals. Anal. for $C_{12}H_8N_2S_{10}Hg_{0.776}$, found (calcd): C, 22.07 (21.95); H, 1.36 (1.23); N, 4.91 (4.27); S, 45.59 (48.84). The imperfect analyses (N and S) may be due to the very limited sample size. The sample is subsequently characterized by single-crystal X-ray diffraction.

Resistivity. Measurements of the temperature dependence of the electrical resistivity of $(ET)Hg_{0.776}(SCN)_2$ were carried out by use of the conventional four-probe technique. The current and voltage probes consisted of gold wires attached to the crystal with silver conducting paste along the needle axis.

ESR Study. ESR measurements were carried out on an IBM ER-200 X-band spectrometer equipped with a TE_{102} microwave cavity and an Oxford EPR-900 flow cryostat with an ITC4 temperature controller. The angular dependence experiment was performed on five needlelike platelet crystals oriented side by side with the needle axis vertical in the cavity. At 0° and 90°, the static magnetic field is parallel and perpendicular, respectively, to the promient (001) face of the crystal. A variable temperature measurement was carried out on a single crystal at 90°.

X-ray Analysis. X-ray oscillation photographs indicate that the crystals have a composite structure, with two mutually incommensurate sublattices coexisting in the same crystal.[34] Intensity data, including reflections from both sublattices[35] and satellite reflections, were collected on a CAD4 diffractometer using Mo Kα radiation (λ = 0.71069 Å). Details are summarized in Table I. A Fourier projection based on the $h0l$ reflections, which are common to both reciprocal lattices, showed, in addition to the Hg atoms at the origin, all the atoms of the ET and SCN^- ions. The two sublattices were initially refined separately excluding the common reflections and neglecting the satellite intensities. Initial y coordinates of the ET molecule were taken to be zero. It was clear from this refinement that the atoms of the SCN^- group are located in the ET sublattice; their starting coordinates were derived by Fourier methods. Good agreement was obtained by use of the space group $P\bar{1}$ for each of the sublattices. The program COMPREF[36] was used in the composite structure refinement of the full data set. The modulational translations and rotations of the ET and SCN^- ions were described by a rigid-body model. Since the SCN^- ion is linear, only two rotations around axes perpendicular to the molecule were included in the model. Details on the refinement are also given in Table I. Positional parameters are listed in Table II.

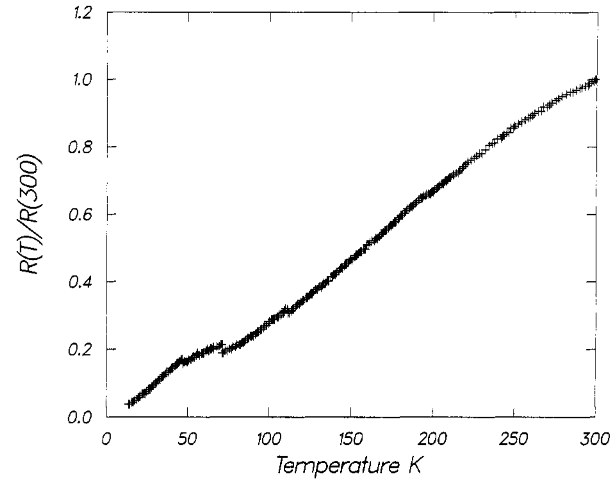

Figure 1. Normalized resistivity of $(ET)Hg_{0.776}(SCN)_2$ between 300 and 13 K showing metallic behavior.

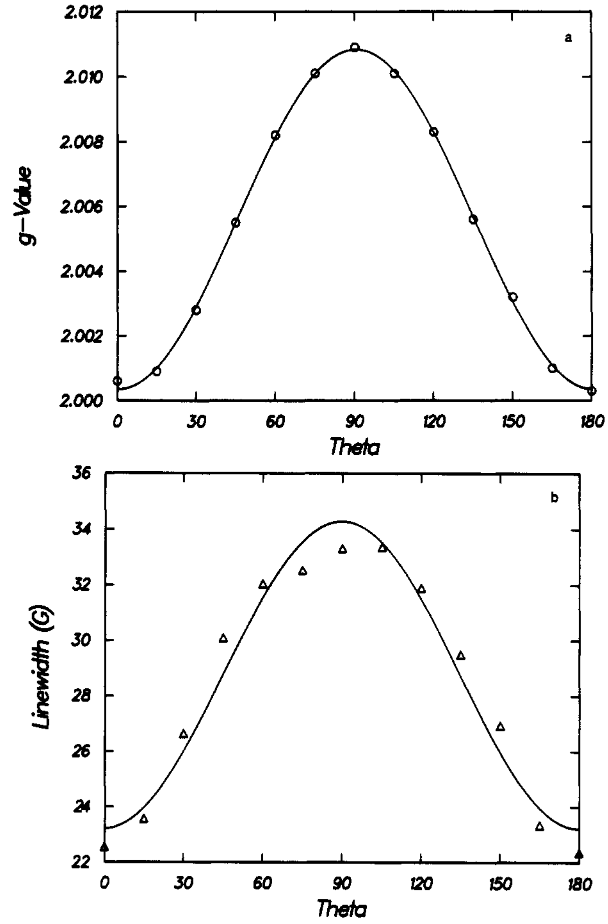

Figure 2. Angular dependence of the g values (a) and line widths (b) of $(ET)Hg_{0.776}(SCN)_2$ at room temperature.

Results

Resistivity. The dc resistivity measurements of $(ET)Hg_{0.776}(SCN)_2$ were carried out between 300 and 13 K. The conductivity at 300 K is 4.4 S/cm. As shown in Figure 1, the solid is metallic in the entire temperature range of the measurements. At 13 K, the conductivity is approximately 120 S/cm. Because of the highly conductive

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(34) Coppens, P.; Maly, K.; Petricek, V. *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 81.

(35) Unit cell dimensions are as follows: Hg lattice a = 6.758 (2) Å, b = 5.302 (2) Å, c = 21.352 (6) Å, α = 73.10 (2)°, β = 110.44 (3)°, γ = 119.17 (3)°, V = 618.85 Å^3, Z = 1; ET-SCN lattice a = 6.746 (2) Å, b = 4.114 (1) Å, c = 20.580 (3) Å, α = 83.06 (1)°, β = 105.93 (2)°, γ = 119.01 (2)°, V = 480.23 Å^3, Z = 1.

(36) Maly, K.; Petricek, V.; Coppens, P.; Bu, X.; Cisarova, I.; Frost-Jensen, A. *Acta Crystallogr.*, in press.

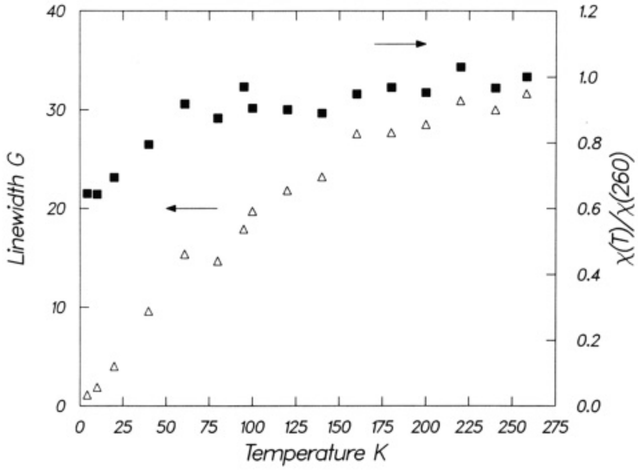

Figure 3. Temperature dependence of line width and relative spin susceptibility between 260 and 4.2 K of (ET)$Hg_{0.776}(SCN)_2$.

behavior, we carried out radio-frequency penetration depth measurements[37] to test for superconductivity. At 0.6 K, with approximately 620 μg of sample, we did not detect any signs of superconductivity with a detection limit of ~20 μg. We also carried out superconductivity measurements under hydrostatic pressure conditions with solid He techniques.[38] With pressure up to 5 kbar and temperature at 1.2 K, again, we did not detect superconductivity.

ESR Measurements. The room-temperature angular dependences of the g values (open circles) and peak-to-peak line widths (open triangles) of (ET)$Hg_{0.776}(SCN)_2$ are plotted in parts a and b of Figure 2 respectively. The anisotropic g values and line widths (ΔH) can be described by the following equations:[39,40]

$$g_{\text{obs}}{}^2 = \sum_{i,j=1}^{3} g_{ij}{}^2 l_i l_j \qquad \Delta H = \sum_{i,j=1}^{3} \Delta H_{ij} l_i l_j$$

where l_i and l_j are the direction cosines of the principal axes. The solid lines in Figure 2 are the calculated g values and line widths. The g values range from 2.000 to 2.011, and the line widths range from 22 to 34 G. The maximum g and ΔH occur at 90°, at which angle the static magnetic field is approximately parallel to the central C=C bond of the ET molecule. Similar observations have been made for other layered ET salts.[40]

Variable-temperature ESR measurements were carried out at 90° on a long thin platelet crystal of (ET)$Hg_{0.776}(SCN)_2$ over the temperature range 300–4.2 K. The ESR peak-to-peak line width (ΔH) and spin susceptibility (χ) are plotted as a function of temperature in Figure 3. The line width (triangle) decreases with decreasing temperature from 33 G at 300 K to 1.1 G at 4.2 K. The line width is related to the conductivity (σ) by the Elliott formula:[41]

$$\Delta H \sim (\Delta g)^2/\tau \qquad \tau = \sigma m/ne^2$$

where $\Delta g = g_{\text{obs}} - 2.0023$ and is a constant within our experimental accuracy, τ is the relaxation time for the conduction electrons, m is effective mass, and n is the number of carriers. Since σ increases as the temperature decreases in (ET)$Hg_{0.776}(SCN)_2$ (vide supra), the line width is expected to decrease with decreasing temperature. This behavior is similar to other β-$(ET)_2X$ salts (X = I_3^-, IBr_2^-, and AuI_2^-),[42,43] α-$(ET)_2MHg(SCN)_4$ salts (M^+ = K^+, NH_4^+, and Rb^+),[31,32,44] and θ-$(ET)_2I_3$ salt.[45]

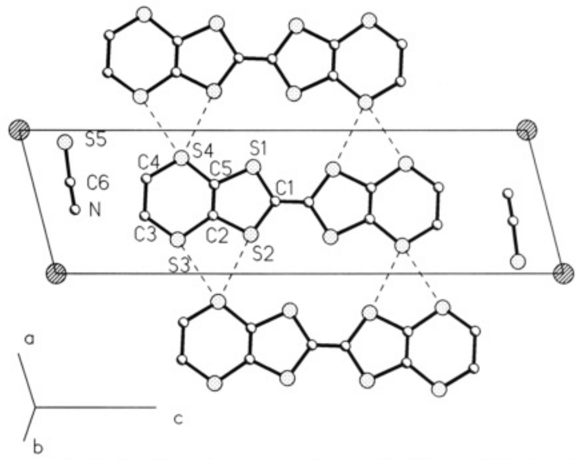

Figure 4. Projection of the structure of $ETHg_{0.776}(SCN)_2$ down the common b-axis direction, showing the numbering of the atoms.

The ESR spin susceptibility of the title compound is nearly temperature independent from 300 to 60 K. The constant spin susceptibility is consistent with the Pauli paramagnetism of a metal. At temperatures below 60 K, χ decreases with decreasing temperature. This is likely due to the much reduced microwave skin depth at low temperature rather than a phase transition since the salt is measured to be metallic down to 13 K. Similar behavior, i.e., χ dropping below the constant value of the spin susceptibility measured at higher temperature, has been reported previously in β-$(ET)_2I_3$.[46] In summary, no anomaly in the ESR properties, which might indicate the occurrence of a phase transition, has been measured between 300 and 4.2 K.

Crystal Structure. The occurrence of a composite structure is related to the mixed valency of the ET molecules in (ET)$Hg_{0.776}(SCN)_2$. As reported above, the ratio of the two unit-cell volumes V(ET–SCN)/V(Hg), (480.23/618.85) is 0.776 and leads to the reported stoichiometry.

The projection of the average structure down the common b axis is shown in Figure 4. The Hg atoms are coordinated by sulfur and nitrogen atoms, the latter at a somewhat larger distance. Because of the incommensurability of the b-axis repeats, the vertical separation (i.e., along the b axis) between Hg and S atoms is continuously variable and equal to zero in some of the unit cells. At those points the Hg–S distance would be only 1.90 Å, far shorter than the typical coordination distance of 2.30 Å between mercury and sulfur.[47] This strong interaction

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(37) Crabtree, G. W.; Carlson, K. D.; Hall, L. N.; Copps, P. T.; Wang, H. H.; Emge, T. J.; Beno, M. A.; Williams, J. M. *Phys. Rev. B* **1984**, *30*, 2958.

(38) Schirber, J. E. *Cryogenics* **1970**, *10*, 418.

(39) Drago, R. S. In *Physical Methods in Chemistry*; W. B. Saunders Co.: Philadelphia, PA, 1977; Chapter 9.

(40) (a) Sugano, T.; Saito, G.; Kinoshita, M. *Phys. Rev. B: Condens. Matter* **1986**, *34*, 117. (b) Sugano, T.; Saito, G.; Kinoshita, M. *Phys. Rev. B: Condens. Matter* **1987**, *35*, 6554.

(41) Enoki, T.; Imaeda, K.; Kobayashi, M.; Inokuchi, H.; Saito, G. *Phys. Rev.* B: *Condens. Matter* **1986**, *33*, 1553.

(42) Venturini, E. L.; Azevedo, L. J.; Schirber, J. E.; Williams, J. M.; Wang, H. H. *Phys. Rev. B: Condens. Matter* **1985**, *32*, 2819.

(43) Talham, D. R.; Kurmoo, M.; Day, P.; Obertelli, D. S.; Parker, I. D.; Friend, R. H. *J. Phys. C: Solid State Phys.* **1986**, *19*, L383.

(44) Oshima, M.; Mori, H.; Saito, G.; Oshima, K. *The Physics and Chemistry of Organic Superconductors*; Saito, G., Kagoshima, S., Eds.; Springer-Verlag: Heidelberg, 1990; p 257.

(45) Wang, H. H.; Vogt, B. A.; Geiser, U.; Beno, M. A.; Carlson, K. D.; Kleinjan, S.; Thorup, N.; Williams, J. M. *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 135.

(46) Hurdequint, H.; Creuzet, F.; Jerome, D. *Synth. Met.* **1988**, *27*, A183.

Table III. Major Amplitudes of Modulation Displacements

	translation, Å			rotation, deg		
wave	sin	cos	approx direction	sin	cos	approx direction
ET molecule						
1st harmonic	0.103 (3)		long molecular axis		0.5 (1)	around long axis of molecule
SCN molecule						
1st harmonic	0.14 (1)	0.21 (1)	*b* axis	8.3 (2)	9.5 (2)	perp axis
Hg atom						
1st harmonic	0.435 (2)					
2nd harmonic	0.305 (3)					
3rd harmonic	0.375 (5)					

Table IV

Distances in the Average Structure (Å)

Intramolecular			
S1–C1	1.739 (9)	S1–C5	1.736 (8)
S2–C1	1.741 (8)	S2–C2	1.745 (8)
S3–C2	1.743 (8)	S3–C3	1.813 (10)
S4–C4	1.798 (9)	S4–C5	1.746 (8)
C1–C1[a]	1.35 (1)	C2–C5	1.35 (1)
C3–C4	1.52 (1)	N–C6	1.14 (1)
S5–C6	1.656 (9)		
Intermolecular			
S2–S4[b]	3.535 (3)	S3–S4[a]	3.531 (3)
S3–S4[c]	3.656 (3)		

Variation of Hg–S Distances (Å) Due to the Modulation

	min	max to closest atom	av
without modulation			
Hg–S5	1.900 (3)	2.194 (3)	1.991
including modulation			
Hg–S5	2.25 (4)	2.46 (4)	2.34

[a] $1 - x, -y, 1 - z$. [b] $-1 + x, y, z$. [c] $-1 + x, -1 + y, z$.

leads to a periodic modulation wave in each of the sublattices, which gives rise to the satellite reflections in the diffraction pattern and relieves the Hg–S repulsions. The analysis of the complete diffraction pattern, using methods described elsewhere,[36] shows modulational displacements that are especially large for Hg, as well as displacements and rotations for the BEDT-TTF and SCN ions (Table III).

The analysis includes three harmonics for the Hg atom displacements and the SCN translational and rotational rigid-body amplitudes. No further improvements in *R* factor were obtained upon introduction of higher harmonics for the ET molecule. The modulation has a very large effect on the Hg coordination (Figure 5, Table IV). It leads to a lengthening of the shortest Hg–S distance from 1.90 Å to the more acceptable value of 2.25 (4) Å and shortens some very large Hg–S separations, as illustrated in Figure 5. The main displacement of the ET molecule is along its long molecular axis, with an amplitude of 0.103 (3) Å. Though smaller than those of Hg and SCN, the ET molecule modulational amplitude is considerably larger than the corresponding value for BEDO-TTF (BEDO-TTF = bis(ethylenedioxo)tetrathiafulvalene) in the composite structure $(BEDO\text{-}TTF)_{2.4}I_3$,[48] in which S···S intermolecular contacts are as short as 3.40 Å, compared with 3.53 Å in the present case (Table IV). The effect of the modulation on the band structure is discussed in the following section.

Band Electronic Structure. To examine how the incommensurate structural modulation affects the electronic structure, we have performed tight binding band calculations[49–52] on the basis of two different models for the donor layers. The first model corresponds to the average structure and ignores the modulation of the lattice;

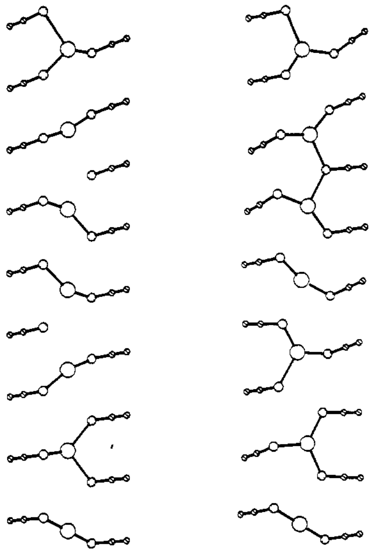

Figure 5. Left: coordination of Hg and SCN in the *average structure* of $ETHg_{0.776}(SCN)_2$ as projected on the *ab* plane. The *b* axes of the two sublattices are vertical. The lack of commensurability leads to a continuously varying coordination. Connected atoms are at distances less than 3.0 Å. Large circles, Hg; intermediate size circles, S. Right: as at the left, *including the modulation.*

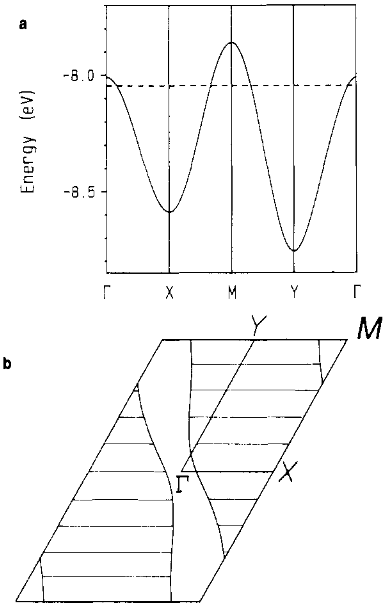

Figure 6. (a) Dispersion relation of the highest occupied band calculated for model A, where $G = (0,0)$, $x = (a^*/2,0)$, $Y = (0,b^*/2)$, and $M = (a^*/2,b^*/2)$. (b) Fermi surface associated with the partially filled band in Figure 6a, where the parallelogram represents a primitive cell in reciprocal space. The wave vectors in the shaded and unshaded regions lead to the occupied and unoccupied band levels, respectively.

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(47) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(48) Wudl, F.; Yamochi, H.; Suzuki, T.; Isotalo, H.; Fite, C.; Kasmai, H.; Liou, K.; Srdanov, G.; Coppens, P.; Maly, K.; Frost-Jensen, A. *J. Am. Chem. Soc.* **1990**, *112*, 2461.

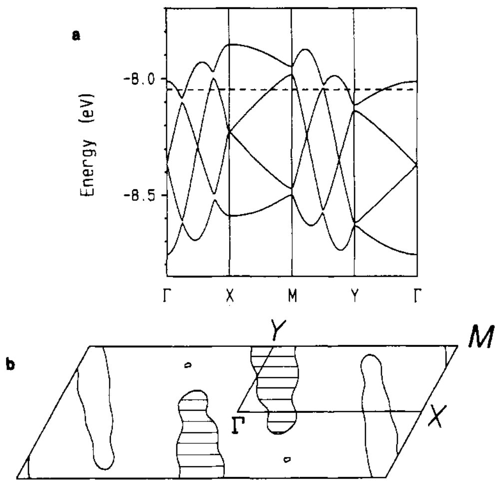

Figure 7. (a) Dispersion relations of the highest four occupied bands calculated for model B, where $G = (0,0)$, $x = (a^*/2,0)$, $Y = (0,b^*/2)$ and $M = (a^*/2,b^*/2)$. (b) Hole Fermi surfaces (unshaded) and electron Fermi surface (shaded) associated with the partially filled bands of Figure 7a.

the second is a commensurate 4-fold superstructure, which is an approximation to the incommensurately modulated lattice of the ET cations, the true q vector being $0.006a^* + 0.224b^* - 0.704c^*$ rather than $0.25b^*$. In this approximation, the second and the fourth molecule in the supercell are displaced in opposite directions from the average position, by amounts equal to the amplitude of the modulation as determined in the X-ray analysis.

Figure 6a shows the dispersion relation of the highest occupied band for the average structure, where the dashed line is the Fermi level corresponding to the approximate formal oxidation state $(ET)^{+0.5}$. The Fermi surface associated with this band, shown in Figure 6b, is not closed, so that on the basis of the *average* structure $(ET)Hg_{0.776}(SCN)_2$ is predicted to be a pseudo-one-dimensional metal, which would be expected to show a Peierls-type metal–insulator transition on cooling.

For the 4-fold modulated structure the calculations lead to the bands shown in Figure 7a. Two of the four bands penetrate the Fermi level. Figure 7b shows that the corresponding Fermi surfaces are all closed; the salt is therefore expected to be a two-dimensional metal.

Our results suggest that the incommensurate structural modulation of the donor–molecule layer has the effect of enhancing the interactions between the donor molecule stacks and hence to increase the dimensionality of the electrical properties. Thus, the modulation, induced by the interaction between the two sublattices appears to be responsible for the solid remaining metallic down to at least 13 K.

Conclusion

The title compound, $(ET)HG_{0.776}(SCN)_2$, has a few structural characteristics that are similar to those of κ-$(ET)_4Hg_3X_8$ (X^- = Cl^- and Br^-). All three salts contain two incommensurate sublattices. The ET molecule and the halide or pseudohalide are in one sublattice, and the mercury atoms are in another. The Hg–X (X^- = Cl^-, Br^-, or SCN^-) bond lengths vary from one unit cell to another. One major difference is that the title compound contains a β-like ET donor molecule network. Another point worth noting is that the choice of cation, i.e., $(n\text{-}Bu)_4N^+Hg(SCN)_3^-$ versus (K-18-crown-6)$^+SCN^-$ and $Hg(SCN)_2$ in the electrocrystallization, leads to two totally different products (vide supra). This unique aspect certainly adds a new dimension to the synthesis of organic metals. In summary, $(ET)Hg_{0.776}(SCN)_2$ is a new two-dimensional synmetal that is metallic to at least 13 K. No superconductivity is observed either under ambient pressure or up to 5 kbar hydrostatic pressure. The incommensurate structural modulation appears to be responsible for the metallic character of this salt.

Acknowledgment. Work at Argonne National Laboratory, North Carolina State University, and Sandia National Laboratories is sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-109-ENG-38 and Grants DE-FG05-86ER45259 and DE-04-76DP00789, respectively. The part of the work done at SUNY/Buffalo has been supported by the National Science Foundation (CHE8711736) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. A.M. is a student research participant from San Jose State University, San Jose, CA, in a program coordinated by the Argonne Division of Educational Programs.

Registry No. (BEDT-TTF)$Hg_{0.776}(SCN)_2$, 133495-42-8.

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(49) Details of our tight binding band electronic structure calculations, based upon the extended Hückel method,[50] are described in refs 51 and 52.

(50) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(51) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.

(52) Whangbo, M.-H.; Williams, J. M.; Leung, P. C. W.; Beno, M. A.; Emge, T. J.; Wang, H. H.; Carlson, K. D.; Crabtree, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 5815.

(53) Geiser, U.; Schultz, A. J.; Wang, H. H.; Watkins, D.; Stupka, D. L.; Williams, J. M.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Novoa, J. J.; Whangbo, M.-H. *Physica C*, submitted.