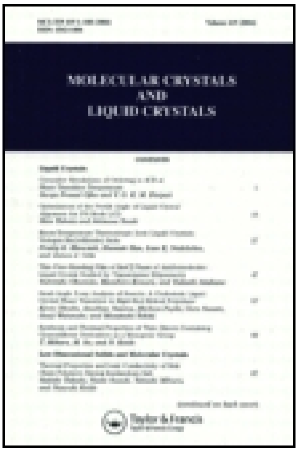

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ESR Studies of Two BEDT-TTF Based Organic Superconductors, θ-(BEDT-TTF)$_2$I$_3$ and ι-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$

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ESR STUDIES OF TWO BEDT-TTF BASED ORGANIC SUPERCONDUCTORS, θ-(BEDT-TTF)$_2$I$_3$ AND κ-(BEDT-TTF)$_4$Hg$_{2.89}$Br$_8$

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Abstract Variable temperature ESR measurements were carried out on two BEDT-TTF, or ET based organic superconductors, θ-(ET)$_2$I$_3$ and κ-(ET)$_4$Hg$_{2.89}$ Br$_8$. The line widths of the former salt range from 60 to 80 G at room temperature and decrease with decreasing temperature. The line widths of the latter salt range from 69 to 83 G and increase with decreasing temperature. The spin susceptibilities of both salts are temperature independent. The ESR properties of these two salts are compared with those of other ET based materials.

INTRODUCTION

Electron spin resonance (ESR) spectroscopy has been an ideal tool for the study of synthetic metals due to its high sensitivity to free radicals, which enables one to characterize small, individual single crystals. Different structural phases formed during electrocrystallization can usually be distinguished based on their room temperature peak-to-peak line widths. Phase transitions at high or low temperature can also be identified by use of this technique. However, ESR measurements are carried out in microwave region (1–100 GHz) so that the microwave conductivities are not required to be identical to that of the dc or low frequency ac conductivities. As part of our research, we intend to establish a structure-ESR property correlation for organic metals. In contrast to the well-known superconductors β-(ET)$_2$X (X$^-$=I$_3^-$, AuI$_2^-$, IBr$_2^-$) and κ-(ET)$_2$Cu(NCS)$_2$, no ESR properties have been published for the title compounds. In this article, we report ESR studies of these less-known BEDT-TTF [bis(ethylenedithia)tetrathiafulvalene) or ET] based organic superconductors, θ-(ET)$_2$I$_3$ and κ-(ET)$_4$Hg$_{2.89}$Br$_8$.

The θ-(ET)$_2$I$_3$ compound was obtained as a minor phase when electrocrystallization was carried out in pure (n-Bu)$_4$NI$_3$ (n-Bu=n-C$_4$H$_9$) or a mixture of (n-Bu)$_4$NI$_3$ and (n-Bu)$_4$NX (X$^-$=AuI$_2^-$ and I$_2$Br$^-$).[1-4] The structure of the θ-phase is similar to that of α-(ET)$_2$I$_3$ in that ET molecules located on adjacent stacks are non-parallel, except that the θ-phase has two nonequivalent donor layers so that the c-axis is doubled. The θ-phase salt is the first α-like structure which remains metallic to very low temperature (below 10 K). Some θ-$(ET)_2I_3$ crystals have been reported to be superconducting below 3.6 K.[1,3]

The procedure used to prepare κ-$(ET)_4Hg_{2.89}Br_8$ has not been reported.[5,6] The salt is isostructural to κ-$(ET)_4Hg_3Cl_8$[7] and also has two nonequivalent donor molecule layers which double the *c*-axis in comparison to κ-$(ET)_2Cu(NCS)_2$.[8] The κ-$(ET)_4Hg_{2.89}Br_8$ salt is an ambient pressure superconductor with T_c around 4.3 K, and very recently a positive pressure dependence of T_c has been reported.[9] The maximum T_c under 3.5 kbar is 6.7 K which is the highest in an organic material after κ-$(ET)_2Cu(NCS)_2$ (10.4 K)[8] and β*-$(ET)_2I_3$ (8 K).[10,11]

EXPERIMENTAL

The θ-$(ET)_2I_3$ crystals were grown by electrocrystallization of ET (1.54 mM) with a mixture of CdI_2 (16.0 mM) and $(n\text{-Bu})_4NI$ (15.3 mM) as supporting electrolytes in tetrahydrofuran and a current density of 4.0 μA/cm^2. The θ-phase was a minor product from this electrocrystallization, α-$(ET)_2I_3$ being the major product. No Cd-containing products normally form with THF as a solvent. The θ-$(ET)_2I_3$ crystals were characterized by use of single crystal X-ray diffraction. The structure is consistent with that of the published,[2,4] and details will be reported elsewhere. Four probe conductivity measurements were carried out from 300 to 12 K indicating metallic behavior over the entire temperature range. However, our θ-$(ET)_2I_3$ crystals did not show any signal of superconductivity by use of RF penetration depth measurements[12] at 0.6 K.

The κ-$(ET)_4Hg_{2.89}Br_8$ crystals were also grown by use of electrocrystallization with ET (1.51 mM) and $(n\text{-Bu})_4NHgBr_3$ (22.7 mM) in trichloroethane (TCE) at 0.5 μA/cm^2. It forms as a *very* minor phase under these conditions. The major phases are $(ET)_2(HgBr_3)(TCE)$ and $(ET)_4(Hg_2Br_6)(TCE)$.[13] One crystal was characterized by its unit cell parameters by use of X-ray diffraction. RF penetration depth measurements revealed that it is an ambient pressure superconductor with a T_c of 3.9 K.

ESR measurements were performed by use of an IBM ER-200 spectrometer with a TE_{102} rectangular cavity and either a VT-4111 temperature controller (300–100 K) or an Oxford Instrument EPR-900 flow cryostat (300–4.2 K).

RESULTS AND DISCUSSION

θ-$(ET)_2I_3$

The room temperature *g*-value (circle) and ESR peak-to-peak line width (triangle) of θ-$(ET)_2I_3$ with respect to rotation angle are shown in Figure 1. Three platelet single crystals were oriented vertically in an ESR cavity with 0° indicating that crystal planes were parallel to the static magnetic field. The solid lines are the simulated angular dependence by use of the following equations:[14,15,16]

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

where l_i and l_j are the direction cosines of the principal axes. The line width ranges from 60 to 80 G at room temperature, which overlaps with that of α-$(ET)_2I_3$ (70 to 110 G). The minimum g-value and ΔH occur near 90° at which angle the static magnetic field is approximately parallel to the c-axis and to the central C=C bond of BEDT-TTF molecule. This result is *opposite* to that found for most of the $(ET)_2X$ compounds, where g and ΔH usually show the maximum values at 90°.[15,16] This unusual observation could be related to the two nonequivalent ET donor layers in θ-$(ET)_2I_3$. The direction of the central C=C bonds of the ET molecules in each layer are tilted away from the c-axis but in opposite directions. This unique linewidth behavior at 90° can be used to differentiate α-$(ET)_2I_3$ (110G) versus θ-$(ET)_2I_3$ (60G).

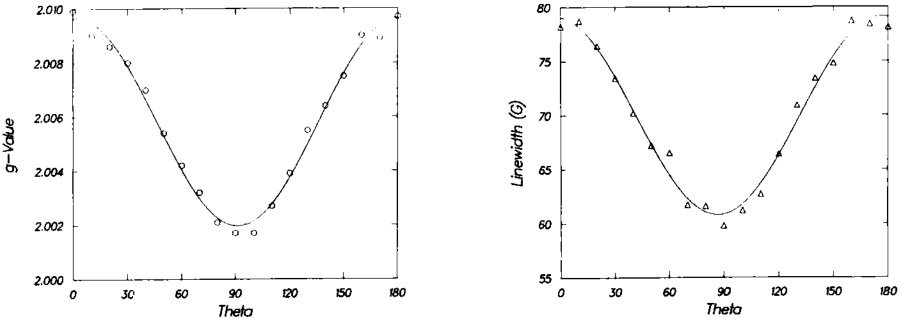

FIGURE 1 Orientation dependence of g-values and line width of θ-$(ET)_2I_3$ at room temperature.

The temperature dependence of the ESR line width (ΔH, triangles) and the relative spin susceptibility (χ, solid squares) of θ-$(ET)_2I_3$ are shown in Figure 2. The variable temperature measurements were carried out at a fixed orientation near 90°, as described above.

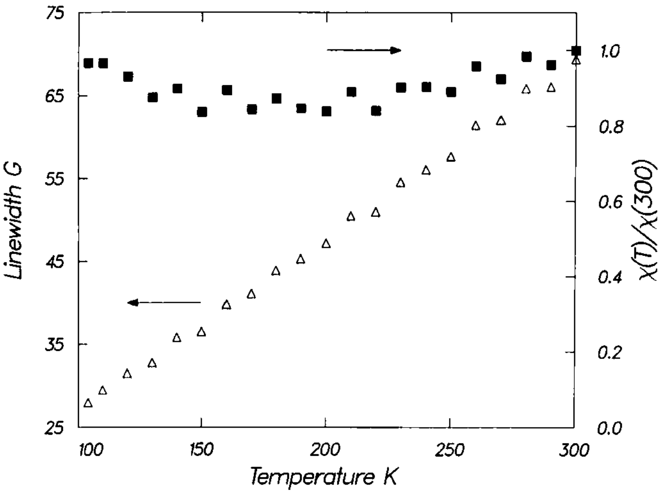

FIGURE 2 Temperature dependence of line width and relative spin susceptibility of θ-$(ET)_2I_3$.

As shown in Figure 2, χ remains constant in the temperature range measured. The behavior is consistent with Pauli paramagnetism of a metal. ΔH decreases monotonically with decreasing temperature from 69 G at 300 K to 28 G at 104 K. The spin susceptibility as well as the linewidth behavior is in contrast to that of α-$(ET)_2I_3$ although both compounds have similar structure within the donor molecule layer.[17,18,19] The ESR line width behavior can be qualitatively understood by use of the Elliott formula:[20,21]

$$\Delta H \sim (\Delta g)^2/\tau \qquad \text{and} \qquad \sigma = ne^2\tau/m \tag{2}$$

where $\Delta g = g_{obs}-2.0023$ (constant within our experimental accuracy), τ is the relaxation time for the conduction electrons, m is mass, and n is the number of carriers. Since the conductivity (σ) increases with decreasing temperature in θ-$(ET)_2I_3$, the linewidth is expected to decrease with decreasing temperature. In summary, the temperature dependence of χ and ΔH of the θ-phase is similar to that of the β-$(ET)_2X$ organic metals, where $X^- = I_3^-$, IBr_2^-, and AuI_2^-.[15,16,18,22]

κ-$(ET)_4Hg_{2.89}Br_8$

The room temperature g-value (circle) and line width (triangle) of κ-$(ET)_4Hg_{2.89}Br_8$ with respect to rotation angle are shown in Figure 3. One platelet single crystal was oriented vertically in the cavity with 0° indicating that the crystal plane is parallel to the static

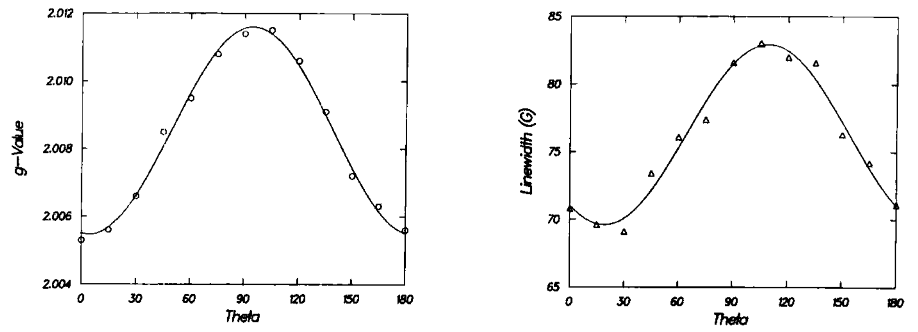

FIGURE 3 Orientation dependence of *g*-value and line width of κ-$(ET)_4Hg_{2.89}Br_8$ at room temperature.

magnetic field. The solid lines are the simulated angular dependence by use of equation 1 (vide supra). The principal axes of the *g* tensor, and the line width tensor, apparently do not coincide. The line width scatters slightly due to limited sample size (~0.2 mg) and broad signal. It ranges from 69 to 83 G, which is similar to the previously reported κ-$(ET)_2Cu(NCS)_2$ (~59–73 G),[23] κ-$(ET)_4Hg_3Cl_8$ (80–110 G),[24] and κ-$(ET)_2Ag(CN)_2 \cdot H_2O$ (70 G).[25] The maximum *g*-value and line width occur near 90° at which angle the static magnetic field is approximately parallel to the *c*-axis and the central C=C bond of ET molecule. This behavior is commonly observed in other ET salts,[15,16] and opposite to that described in the previous section for θ-$(ET)_2I_3$.

The variable temperature experiment was carried from 300 K to 4.2 K with the crystal *ab*-plane parallel to the microwave electric field; i.e., the platelet crystal was at a horizontal orientation. A strongly Dysonian lineshape was observed for all temperatures measured. The temperature dependence of the spin susceptibility, χ (solid square), and the line width, ΔH (triangle), are shown in Figure 4. At 4.2 K, the broad signal due to κ-$(ET)_4Hg_{2.89}Br_8$ disappeared upon the onset of superconductivity, which is consistent with the previously reported value of T_c near 4 K.[5,6] The spin susceptibility is

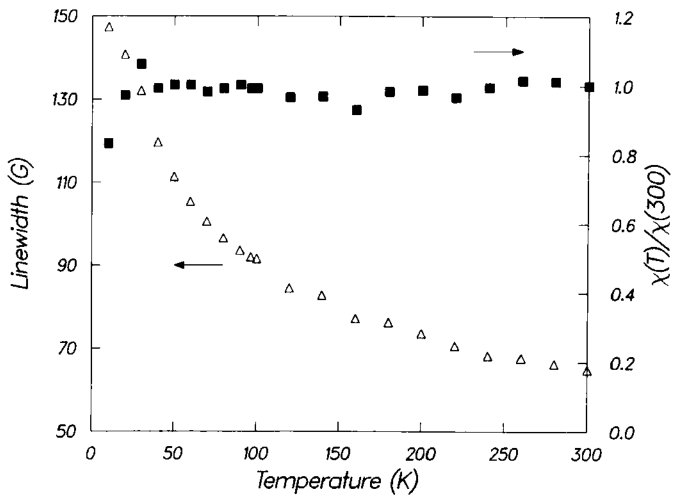

FIGURE 4 Temperature dependence of line width and relative spin susceptibility of κ-$(ET)_4Hg_{2.89}Br_8$.

approximately constant from 300 to 50 K. A slight decrease is observed below 40 K, which is likely related to microwave skin effects and not an intrinsic property.[26] The line width increases with decreasing temperature. This behavior has been reported in other κ-phase salts: κ-$(ET)_2Cu(NCS)_2$,[23,27] κ-$(ET)_2Ag(CN)_2{\cdot}H_2O$,[25] and κ-$(MDT\text{-}TTF)_2AuI_2$,[28] except that of $(BMDT\text{-}TTF)_2Au(CN)_2$,[29] where a different molecule dimer unit has been noted.[30] In the case of κ-phase salts, Elliott 's formula (equation 2) alone cannot explain the line width behavior.

For comparison purposes, we plot the log(line width) versus log(T) for both κ-$(ET)_4Hg_{2.89}Br_8$ and κ-$(ET)_2Cu(NCS)_2$[27] in Figure 5. The line width is fit with a $T^{-0.30}$ power function in κ-$(ET)_4Hg_{2.89}Br_8$ for almost the entire temperature region. A slight deviation is observed below 20 K. In contrast, two notable slope changes are observed in κ-$(ET)_2Cu(NCS)_2$ at 100 and 30 K. The change in slope at 100K corresponds to a resistance maximum in the 4-probe measurement. The slope change at 30K in κ-$(ET)_2Cu(NCS)_2$ might be associated with a structural instability as has been measured in preliminary low temperature X-ray diffraction experiments.[31] At present, there is no low temperature structural data for κ-$(ET)_4H_{2.89}Br_8$.

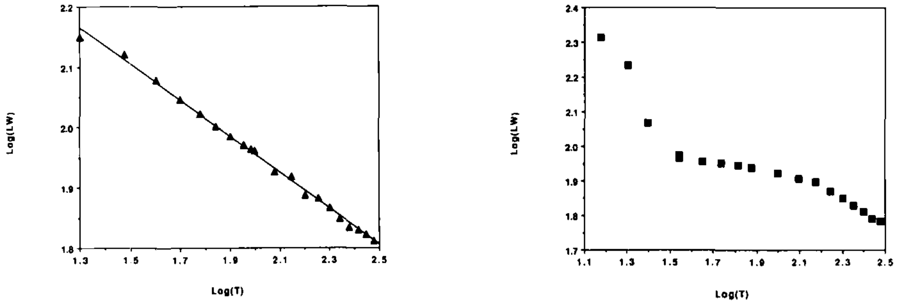

FIGURE 5 Log(line width) vs log(temperature) plot for κ-$(ET)_4Hg_{2.89}Br_8$ and κ-$(ET)_2Cu(NCS)_2$.

An interesting point worth noting is that the line width vs. temperature correlations in the two aforementioned κ-salts correspond to a different pressure dependence of T_c. The κ-$(ET)_2Cu(NCS)_2$ and κ-$(ET)_4Hg_{2.89}Br_8$ salts have shown a negative[32] (- 3 *K/kbar*) and a positive[9] (+ 1 *K/kbar*) pressure dependence on T_c, respectively. A fundamental understanding of the origin of ESR linewidths is clearly needed as has been pointed out previously in the ESR studies of TMTSF complexes.[33]

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