Electrochemical Synthesis and Crystallization of a Novel Tetraarylaurate Anion: Synthesis, Structure, and Physical Properties of (BEDT-TTF)Au(C_6Cl_5)$_4$

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Received March 7, 1997[⊗]

The homoleptic tetraarylaurate anion, Au(C_6Cl_5)$_4^-$, which has never been prepared via traditional chemical methods, has been synthesized by use of an electrochemical technique and crystallized *in situ* with the bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF, or ET) electron-donor molecule. This salt, ($C_{10}H_8S_8$)Au(C_6Cl_5)$_4$, crystallizes having the monoclinic space group $P2_1/c$, with $a = 14.7835(9)$ Å, $b = 20.2270(12)$ Å, $c = 16.7303(10)$ Å, $\beta = 101.396(1)°$, $Z = 4$. The crystal structure of this (ET)Au(C_6Cl_5)$_4$ salt contains the Au(C_6Cl_5)$_4^-$ anion in an essentially square-planar coordination with the pentachlorophenyl groups arranged in a propeller-like D_4 symmetry, consistent with the formal oxidation state +3 of the central metal atom. The ET$^+$ cations are completely surrounded by the pentachlorophenyl rings of the anions, thereby precluding the formation of a S···S network with concomitant conducting properties. Analysis of the Raman spectrum of (ET)Au(C_6Cl_5)$_4$ confirms that the ET molecule in this salt is in the +1 oxidation state. The variable temperature spin susceptibility data obtained from ESR spectroscopy indicate a weak ferromagnetic coupling between the radical ET$^+$ cations. This salt provides the unique opportunity to investigate the properties of a highly isolated ET$^+$ cation in the solid state.

Introduction

Homoleptic tetraarylaurates are quite rare, with only the TBA[Au(C_6F_5)$_4$][1,2] (TBA = tetrabutylammonium), TBA[Au($C_6F_3H_2$)$_4$],[3] and TBA[Au(C_6F_4H)$_4$][4] salts currently characterized. Two mixed tetraarylaurates have also been reported: TBA[Au(C_6F_5)$_2$($C_6F_3H_2$)$_2$][2] and PPN[Au(C_6Cl_5)$_3$(C_6F_5)].[5] To date, it has not been possible to synthesize the tetrakis(pentachlorophenyl)aurate(III) anion through traditional chemical methods, such as through the reaction of PPN[Au(C_6Cl_5)$_3$Cl] and Ag(C_6Cl_5).

The electron-donor molecule BEDT-TTF [bis(ethylenedithio)-tetrathiofulvalene, or ET] has been widely used for the preparation of charge transfer salts containing a large variety of charge-compensating anions.[6] These complexes exhibit a wide range of electrical properties, including semiconductive, metallic, and superconducting. We have found that large organometallic anions of the M(CF_3)$_4^-$ (M = Cu, Ag, and Au) type produce a remarkable series of superconducting charge transfer salts with superconducting transition temperatures (T_cs) ranging from 2 to 11 K.[7−11] Recently, we have shown that the large, organic $SF_5CH_2CF_2SO_3^-$ anion also yields a superconducting salt (T_c = 5 K) when crystallized with ET.[12]

It is possible that higher T_cs can be obtained in organic charge transfer salts if the donor molecule S···S contact lattice can be expanded through the use of large counteranions. Following this reasoning, we strove to crystallize the large bis(pentachlorophenyl)aurate(I) anion, Au(C_6Cl_5)$_2^-$, with ET. However, the

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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previously unknown homoleptic, square-planar, gold(III) tetrakis(pentachlorophenyl)aurate(III) anion, $Au(C_6Cl_5)_4^-$, was generated in the electrochemical cell and crystallized with the radical cation of ET. Herein, we report that the crystal structure of this $(ET)Au(C_6Cl_5)_4$ salt contains ET^+ cations surrounded by the pentachlorophenyl rings of the $Au(C_6Cl_5)_4^-$ anion. This salt provides the unique opportunity to investigate the properties of a highly isolated ET^+ cation in the solid state.

Experimental Section

Preparations. Bis(ethylenedithio)tetrathiafulvalene (ET, Strem Chemicals, Inc.) was recrystallized from chloroform (Aldrich) prior to use. Elemental analyses were performed at Galbraith Laboratories (Knoxville, TN) or Midwest Microlab (Indianapolis, IN). 1,1,2-Trichloroethane (TCE, Fluka) was distilled from P_2O_5 (Aldrich) and filtered through a column containing neutral alumina prior to use. $TBA[Au(C_6Cl_5)_2]$ was prepared as described previously.[1] (Calcd for $C_{28}H_{36}N_1AuCl_{10}$: C, 35.85; H, 3.87; N, 1.49; Au, 21.00; Cl, 37.79. Found: C, 35.79; H, 3.88; N, 1.49; Cl, 37.58. Mp: 180−183 °C.) $TBA[Au(C_6F_5)_2]$ was prepared as previously described.[1] (Mp: 113−115 °C.) The $Au(C_6F_5)_4^-$ anion was prepared by combining $Cd(C_6F_5)_2$[13] with $AuCl_3$ in a molar ratio of 6:1 in diethyl ether at room temperature. A gold(I) compound initially formed which immediately disproportionated into $Au(C_6F_5)_4^-$ and elemental gold. PPh_4Cl was added, and the yellowish solution was chromatographed over silica. $PPh_4[Au(C_6F_5)_4]$ was isolated as a nearly colorless polycrystalline solid. Yield: 26%. Mp: 175 °C. ^{19}F-NMR: −121.9 (d, *o*-F), −161.7 (t, *p*-F), and −164.4 ppm (t, *m*-F).

$(ET)Au(C_6Cl_5)_4$ via Electrocrystallization. Single crystals of the title compound were grown by use of electrocrystallization techniques.[14,15] The electrochemical cell was assembled in an argon-filled drybox. $TBA[Au(C_6Cl_5)_2]$ (95.15 mg, 0.10 mmol) was divided between the two chambers of an H-cell. ET (10.31 mg, 0.03 mmol) was loaded into the anode chamber. The crystallization solvent, TCE (7.5 mL), was then added to each chamber of the H-cell. A current density of 0.2 $\mu A/cm^2$ was initially applied and gradually increased over a period of 2 weeks to 3.7 $\mu A/cm^2$, at which time crystallization of black rods commenced. Crystals were grown at 25°C on platinum wire electrodes for a period of 21 days. A similar electrocrystallization procedure with THF as the solvent failed to produce any crystals.

Instrumentation. A. Raman Spectroscopy. Raman spectra were recorded with use of a Raman microscope spectrometer (Renishaw, Ltd.) equipped with a He:Ne ($\lambda_0 = 6328$ Å) laser. Low laser power of 0.06 mW focused on a 1 μm^2 area was applied. The spectra were averaged over 20 scans.

B. ESR Spectroscopy. ESR measurements were performed 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.

C. X-ray Analysis. The crystal structure of the title compound was determined at 296 K with use of a Siemens SMART single-crystal X-ray diffractometer equipped with a CCD-based area detector and a sealed-tube X-ray source. The following constraints were applied during the refinement of the disordered ET molecule: occupation factor 0.5 for all atoms, a common isotropic thermal parameter for atoms C11−C18, and a different common isotropic thermal parameter for atoms C19 and C20. All positional parameters were refined independently without any further constraints or restraints. Further details have been deposited as Supporting Information.

Results and Discussion

Synthesis. Interest in aryl−gold chemistry has been rising steadily recently.[16] The use of polyhalophenyl groups as ligands has greatly increased the number of known aryl−gold complexes because the electron-withdrawing character of the halogen atoms stabilizes the Au^{3+} metal center. More research has been performed on pentafluorophenyl complexes than on the analogous pentachlorophenyl molecules, because their increased stability renders them easier to isolate. While tris- and tetrakis(pentafluorophenyl)gold derivatives have been synthesized, only a few tris(pentachlorophenyl)gold(III) complexes have been prepared.[5] Until now, it has not been possible to synthesize the $Au(C_6Cl_5)_4^-$ anion, although attempts have been made by reacting $PPN[Au(C_6Cl_5)_3Cl]$ and $Ag(C_6Cl_5)$, and by refluxing toluene solutions of $TBA[Au(C_6Cl_5)_2]$ and $Tl(C_6Cl_5)_2Cl$.[5] The related $Au(C_6F_5)_4^-$ anion has previously been synthesized and isolated as a salt with the tetrabutylammonium[1] and tetraphenylphosphonium cations.[17]

At Argonne, we have recently initiated a new effort to include large, discrete anions as the charge-compensating entities in conducting charge transfer salts. This approach allows for expansion of the electron-donor lattice and modification of the solid state properties of these salts. The $Au(C_6Cl_5)_2^-$ anion was chosen as a promising candidate for forming interesting charge transfer salts with ET because of its large size, the possibility that its electronegative Cl atoms could interact with the ethylene group hydrogen atoms of the ET molecule and expand the S···S networks, and its ability to be chemically modified.

To date, it has not been possible to crystallize this $Au(C_6Cl_5)_2^-$ anion with ET. However, when the electrochemical potential applied during the electrocrystallization step was increased to a high enough level, both oxidation of ET to ET^+ and disproportionation of $Au(C_6Cl_5)_2^-$ to $Au(C_6Cl_5)_4^-$ occurred and led to the crystallization of the $(ET)Au(C_6Cl_5)_4$ salt. During the course of the electrocrystallization process, black crystals of $(ET)Au(C_6Cl_5)_4$ formed on the anode surface while a shiny brown solid deposited on the bottom of the anode compartment. Although an analysis of the mechanism of electrochemical formation of the $Au(C_6Cl_5)_4^-$ anion is beyond the scope of this paper, a simplistic representation consistent with experimental observations is described by the following equation:

$$2Au(C_6Cl_5)_2^- \rightarrow Au(C_6Cl_5)_4^- + Au + e^-$$

Attempts to electrocrystallize the related, chemically synthesized $Au(C_6F_5)_4^-$ anion with ET failed to produce crystals when TCE or benzonitrile was used as the solvent. This is potentially a result of the smaller size of the $Au(C_6F_5)_4^-$ anion, or the harder fluorine atoms. Attempts to crystallize the $(ET)Au(C_6F_5)_4$ salt through electrochemical oxidation of the $Au(C_6F_5)_2^-$ anion in a manner identical to that used to form $(ET)Au(C_6Cl_5)_4$ were also unsuccessful.

Crystal and Molecular Structure. The crystal structure (Table 1) of $(ET)Au(C_6Cl_5)_4$ comprises discrete $Au(C_6Cl_5)_4^-$ anions and $BEDT\text{-}TTF^+$ cations. The crystal packing is dominated by the large $Au(C_6Cl_5)_4^-$ anion, see Figure 1. The bulky pentachlorophenyl substituents arrange themselves in such a way as to leave two crystallographically inequivalent box-like cavities (located at the inversion centers 0.5,0,0 and 0,0,0) that hold the $BEDT\text{-}TTF^+$ cations (molecules 1 and 2), respectively. The two molecules are shown in more detail in Figure 2. Molecule 1 is crystallographically ordered and adopts inversion symmetry, whereas the cavity surrounding molecule 2 is larger and allows the $BEDT\text{-}TTF^+$ cation to move off-center. A disordered model of two complete BEDT-TTF molecules of occupancy 0.5 and related to each other by the center of inversion at 0,0,0 was adopted for site 2. Unlike in

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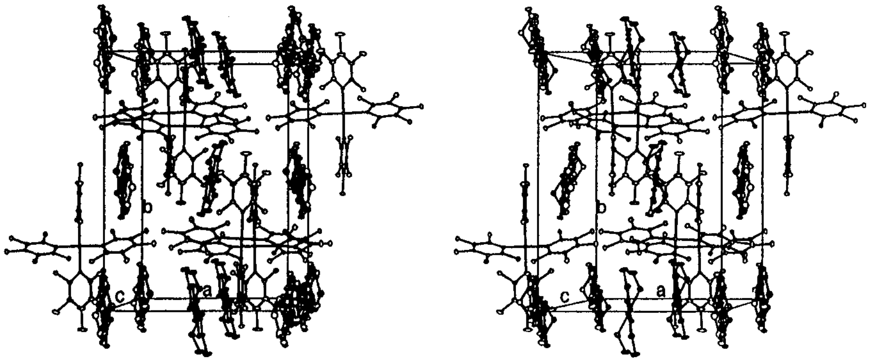

Figure 1. Stereo packing diagram of the crystal structure of (BEDT-TTF)Au(C_6Cl_5)$_4$.

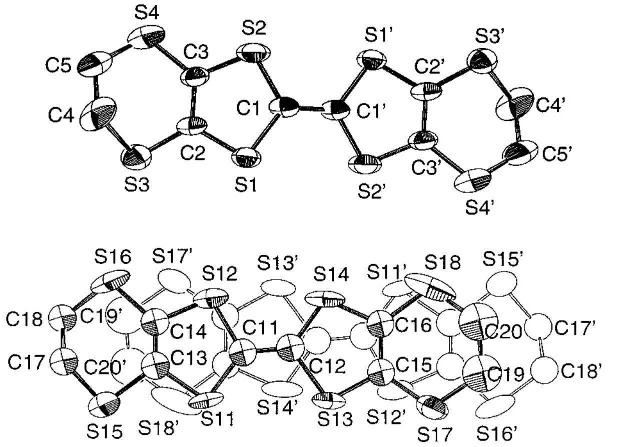

Figure 2. The BEDT-TTF radical cations 1 (top) and 2 (bottom) in (BEDT-TTF)Au(C_6Cl_5)$_4$. Site 2 (disordered) is randomly occupied by a molecule in either the shaded or the unshaded position, these positions being related to each other by a center of inversion. Hydrogen atoms and some atomic labels have been omitted for clarity. Thermal ellipsoids are drawn at the 33% probability level.

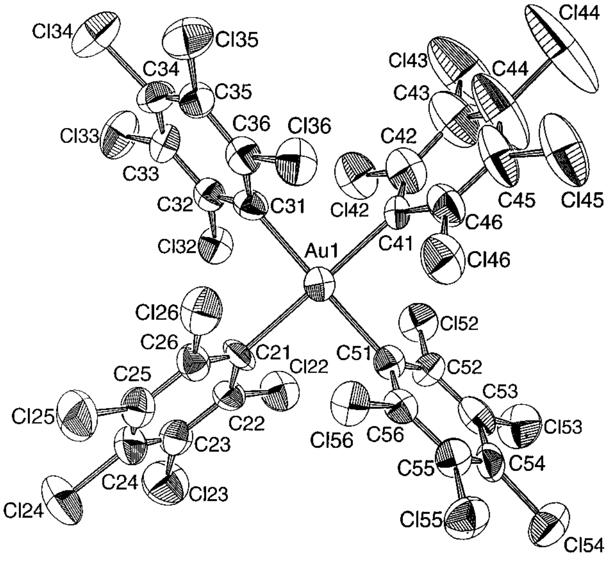

Figure 3. Thermal ellipsoid plot (50% probability level) of the Au(C_6Cl_5)$_4^-$ anion.

most salts of BEDT-TTF and related electron-donor molecules, all interactions between neighboring BEDT-TTF$^+$ radical cations are through the bulky anion ligands; thus the title compound represents an example of extremely isolated BEDT-TTF$^+$ cations.

Table 1. Summary of Crystallographic Data for (ET)Au(C_6Cl_5)$_4$[a]

chem formula	($C_{10}H_8S_8$)Au(C_6Cl_5)$_4$
formula weight, g mol^{-1}	1578.94
a, Å	14.7835(9)
b, Å	20.2270(12)
c, Å	16.7303(10)
β, deg	101.396(1)
V, Å^3	4904.2(5)
Z	4
space group	$P2_1/c$ (No. 14)
temp, K	296
λ, Å	0.710 73 (Mo Kα)
ρ_{calcd}, g cm^{-3}	2.139
μ, cm^{-1}	44.51
$R(F_o)$	0.065
$R_w(F_o)$	0.061

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) in (ET)Au(C_6Cl_5)$_4$

Au1−C21	2.126(9)	S3−C2	1.723(14)
Au1−C31	2.101(10)	S3−C4	1.82(2)
Au1−C41	2.104(9)	S4−C3	1.72(2)
Au1−C51	2.103(10)	S4−C5	1.69(2)
S1−C1	1.717(13)	C1−C1[a]	1.38(3)
S1−C2	1.731(14)	C2−C3	1.35(2)
S2−C1	1.704(13)	C4−C5	1.45(3)
S2−C3	1.73(2)		

[a] $1 - x, -y, -z$.

Table 3. Selected Bond Angles (deg) in (ET)Au(C_6Cl_5)$_4$

C11−Au1−C21	89.6(4)	C1−C1−S2	122.1(13)
C11−Au1−C41	178.8(4)	S1−C1−S2	114.9(8)
C21−Au1−C51	91.3(4)	C3−C2−S1	116.5(12)
C31−Au1−C41	89.3(4)	C3−C2−S3	123.5(12)
C31−Au1−C51	179.0(4)	S1−C2−S3	119.9(7)
C41−Au1−C51	89.8(4)	C2−C3−S2	115.9(12)
C1−S1−C2	96.0(6)	C2−C3−S4	126.2(13)
C1−S2−C3	96.4(7)	S2−C3−S4	117.9(8)
C2−S3−C4	98.1(8)	C5−C4−S3	117.6(15)
C3−S4−C5	106.1(9)	C4−C5−S4	120.6(15)
C1−C1−S1	122.9(13)		

As illustrated in Figure 3, the coordination geometry of the gold complex anion is essentially square-planar, consistent with the formal oxidation state +3 of the central metal atom. While not imposed by crystallographic symmetry, the anion adopts an approximate propeller-like D_4 symmetry. The Au−C bond lengths, 2.101(10)−2.126(9) Å (Table 2), are comparable to those found in Au(III)−C_6F_5 complexes.[2,17−19] Steric constraints (avoidance of repulsive Cl···Cl interactions) force the planes of the phenyl rings to be twisted with respect to the central coordination square. The average torsion angle of 65.1° is the maximal value allowed by the nonbonded Cl···Cl interactions, as shown by molecular modeling. In contrast, the smaller van der Waals radius of the fluorine atom and the shorter C−F bond lengths in the Au(III)−C_6F_5 analogue do not impose

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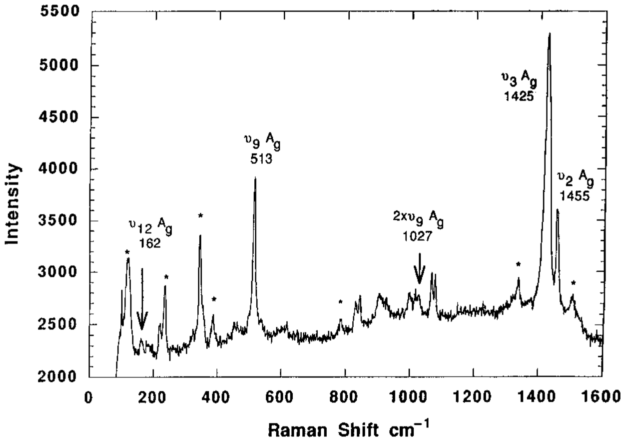

Figure 4. Raman spectrum of a (BEDT-TTF)Au(C_6Cl_5)$_4$ single crystal. The bands marked with stars are associated with the Au(C_6Cl_5)$_4^-$ anion.

an upper limit on the torsion angle. In Au(C_6F_5)$_4^-$ the observed values are more than 70°.[17]

Selected geometric results are listed in Tables 2 and 3. Those of BEDT-TTF molecule 2 (not listed) are of limited use due to the crystallographic disorder, but the bond distances found in molecule 1 are typical of the fully oxidized (+1) radical cation.[20]

Raman Spectroscopy. Raman spectra of the charge transfer salts are known to reveal essential information on the oxidation state of the donor BEDT-TTF molecules. The vibrational frequencies of the C=C and C−S bonds in the BEDT-TTF molecule are sensitive probes for the oxidation state of the molecule. When electrons are removed from the HOMO which has bonding characteristics with respect to the C=C double bonds, the effect is weakening of the C=C bond and reduction of the C=C vibration frequencies. Since the HOMO has antibonding characteristics with respect to the C−S bonds, the effect of oxidation is strengthening of the C−S bonds and increase of the C−S frequencies.

The Raman spectrum of a (BEDT-TTF)Au(C_6Cl_5)$_4$ crystal is shown in Figure 4. The strong bands can be readily assigned to the totally symmetric Raman-active ν_2, ν_3, and ν_9 A$_g$ modes. The bands marked with stars are associated with the Au(C_6Cl_5)$_4^-$ anion by comparison with the Raman spectrum of the starting material, TBA[Au(C_6Cl_5)$_2$]. The ν_2 and ν_3 modes are associated with the C=C double bonds in the two outer six-membered rings and the central C=C double bond, respectively. The charge (Z) on the BEDT-TTF molecule was calculated by use of eq 1, as previously described.[21]

$$Z = 0.5\frac{1539 - \nu_2}{86.0} + 0.5\frac{1508 - \nu_3}{88.4} = 0.96 \qquad (1)$$

The resulting charge, +0.96, on the BEDT-TTF molecule is in excellent agreement with that determined from the X-ray structural analysis. The ν_9 A$_g$ mode is derived from the C−S stretching vibrations, and the observed value of 513 cm^{-1} is also consistent with the values for other 1:1 salts, such as (BEDT-TTF)Br (511 cm^{-1})[22] and (BEDT-TTF)Cu[N(CN)$_2$]$_2$ (508 cm^{-1}). The value 513 cm^{-1} fits well with the trend for the ν_9 frequencies of the neutral BEDT-TTF (486 cm^{-1}) and the +2 salt, BEDT-TTF(ClO_4)$_2$ (534 cm^{-1}).[23]

ESR Spectroscopy. A small rod-like crystal of (BEDT-TTF)Au(C_6Cl_5)$_4$ was used for ESR measurements. For the orientation dependence studies, the crystal was oriented in the cavity with its needle axis (a-axis) vertical and the static magnetic field parallel to the bc plane. The angular dependent g-values and peak-to-peak line widths have been plotted and deposited as Supporting Information. The observed g-values were fitted with eq 2, with minimum and maximum g-values at 2.0048 and 2.0122, respectively. Since there is negligible

$$g_{\mathrm{obs}}{}^2 = g_{||}{}^2 \sin^2\theta + g_x{}^2 \sin 2\theta + g_\perp{}^2 \cos^2\theta \qquad (2)$$

orbital overlap between neighboring BEDT-TTF molecules, and the two nonequivalent BEDT-TTF molecules are not parallel but form an angle between the two long molecular axes (see crystal structure section), the maximum g-value is approximately along the resultant vector directions of the two long molecular axes. The maximum g-value is quite consistent with that of the other BEDT-TTF salts (2.011−2.014). The minimum g-value is 90° away from the maximum value and corresponds to the direction between the directions of the short molecular axis and the normal to the molecular plane.

The peak-to-peak line widths are narrow, between 2.8 and 3.5 G, even when compared to other 1:1 BEDT-TTF salts, such as (BEDT-TTF)($Re_6Se_5Cl_9$)[(CH_3)$_2$NCOH]$_2$ (3.7−4.3 G),[24] (BEDT-TTF)Cu[N(CN)$_2$]$_2$ (8−10 G),[25] and (BEDT-TTF)Ag$_4$(CN)$_5$ (12−14 G).[26] The sharp line width is likely associated with the well-isolated spins in the crystal lattice. The angle-dependent line widths show double periodicity with respect to the g-values. In order to test if this was an artifact due to sample twinning, three independent measurements were carried out on three different crystalline samples, and reproducible results were observed each time. Although the possibility of twinned samples can not be ruled out, it is likely that the double periodicity is an intrinsic effect and caused by the packing motif with two nonequivalent and crossed BEDT-TTF molecules (1 and 2, see above).

To probe the low-temperature behavior of (ET)Au(C_6Cl_5)$_4$, an ESR measurement was carried out between 4 and 300 K, and the results have been deposited as Supporting Information.

The peak-to-peak line widths showed a small increase with decreasing temperature from 2.7 G at room temperature to 3.2 G at 4 K, while the spin susceptibility (χ) followed the Curie−Weiss law. The spin susceptibility was fit to the Curie−Weiss equation:

$$\frac{1}{\chi} = \frac{1}{C}(T - \Theta) \qquad (3)$$

where C is the Curie constant and Θ is the Weiss temperature. The value of Θ (=15 K) suggested a weak ferromagnetic coupling between the ET$^+$ radical cations. The closest donor···donor distances between molecule centers along the $a + c$, b, and $a - c$ directions are 10.0, 10.1, and 12.2 Å,

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respectively. The ESR results are in good agreement with those of the X-ray structure and Raman measurements.

Conclusions

We have illustrated that electrochemical techniques can be used to prepare novel anions in solution which cannot be synthesized through conventional chemical methods. These anions can then be crystallized *in situ* with organic electron-donor molecules such as ET. This method can potentially be used to prepare charge transfer salts containing unique anions and possessing novel electrical and magnetic properties.

Specifically, we have electrocrystallized the electrochemically synthesized Au(C_6Cl_5)$_4^-$ anion with ET to form the (ET)Au(C_6Cl_5)$_4$ salt. The crystal structure of this salt contains highly isolated ET^+ cations that are completely surrounded by the bulky pentachlorophenyl substituents of the anion. The analysis of the ν_2 and ν_3 Raman-active modes of the ET molecule in (ET)Au(C_6Cl_5)$_4$ confirms that the donor molecule is oxidized to the integral +1 oxidation state. Spin susceptibility data obtained from variable temperature ESR spectroscopy indicate that this salt has a weak ferromagnetic coupling between the ET^+ radical cations.

Acknowledgment. Work at Argonne National Laboratory is sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under Contract W-31-139-ENG-38. M.L.V. and S.B.F. are undergraduate student research participants sponsored by the Argonne Division of Educational Programs from Michigan Technological University, Houghton, MI, and the University of North Carolina, Asheville, NC, respectively. Research at the University of Zaragoza was suppported by the Direccion General de Investigacion Cientifica y Tecnica (No. PB94-0079). Research at the University of Cologne was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Figures illustrating both the angular and temperature dependence of the ESR line width (2 pages). An X-ray crystallographic file, in CIF format, has been deposited. Ordering and access information is given on any current masthead page.

IC970274W