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# Nonelectrochemical Synthesis, Crystal Structure, and Physical Properties of the Radical Salt $[ET]_2[CuCl_4]$ (ET = Bis(ethylenedithio)tetrathiafulvalene)

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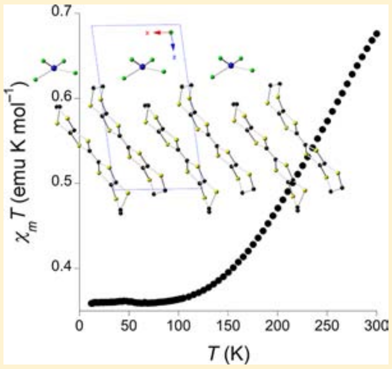
Supporting Information

**ABSTRACT:** The radical salt $[ET]_2[CuCl_4]$ was obtained by chemical oxidation of bis(ethylenedithio)tetrathiafulvalene (ET) with the tetranuclear copper(II) halide cluster $[Cu_4OCl_{10}]^{4-}$. Although a complex mixture of anions forms in solution during the redox reaction, only this product is obtained as large (>3 mm) single crystals. X-ray diffraction analysis determined that the ET molecules stack in the solid state forming dimerized 1D chains along the *a* axis, interleaved by $[CuCl_4]^{2-}$ anions. The ET dimers show very short S···S contacts (<3.41 Å). The physical properties are dominated by these intradimer ET interactions. The magnetic behavior shows antiferromagnetic coupling with a singlet−triplet gap >620 K (430 cm$^{-1}$). The $Cu^{2+}$ ($S = {}^1/_2$) centers are magnetically isolated and yield a narrow EPR line in the X-band at $g = 2.01$. The ET moieties are EPR silent.



## INTRODUCTION

Crystalline molecular conductors are a versatile type of molecular materials. Their essential building blocks are electroactive organic molecules able to give rise to charge delocalization through supramolecular interactions in the solid state.[1] Through self-assembly, the organic radicals typically form mixed valence segregated stacks with electron delocalization. Examples of charge transfer or radical salts with metallic and even superconducting transport properties have been reported in the last decades. The organic radicals are combined with anions to balance the charge of the segregated stacks in the solid state through self-assembly.

The most remarkable family of crystalline organic conductors are those obtained from tetrathiafulvalene (TTF) and its derivatives (Figure 1).[2] TTFs have yielded the largest number of organic metals and superconductors. And they have been used to prepare some of the most unique hybrid materials when combined with electroactive anions, to yield magnetic organic metals[3] and superconductors,[4] ferromagnetic metals,[5] chiral conductors,[6] ferromagnetic chiral metals,[7] or switchable conductors.[8]

Metal halides have been typically used as the magnetic component in these hybrid conductors.[9] The combination of ET with tetracoordinated $[MX_4]^{n-}$ anions was particularly successful. $[ET]_3[CuCl_4]$ represented the first TTF-based organic metal exhibiting coexistence of localized and conduction electrons.[10] $[BETS]_2[Fe_xGa_{(1-x)}Cl_4]$ ($x \approx 0.4$) was just the second magnetic superconductor reported.[11] And $[BETS]_2[FeBr_4]$ was the first organic antiferromagnetic superconductor.[12]

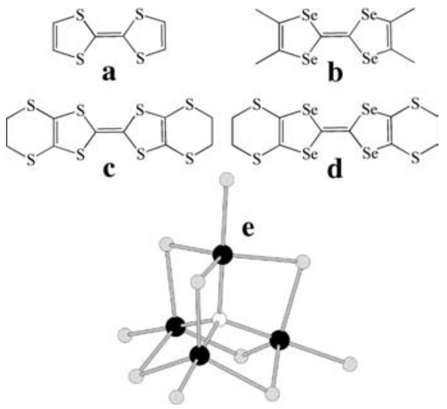


**Figure 1.** Representation of the molecular structure of (a) tetrathiafulvalene (TTF); (b) tetra(methyl)tetraselenafulvalene; (c) bis(ethylendithio)tetrathiafulvalene (ET); (d) bis(ethylendithio)-tetraselenafulvalene (BETS); (e) $[Cu_4OCl_{10}]^{4-}$ (Cu, black; Cl, gray; O, white).

Copper halides chemistry is very rich and diverse, with many different oligomeric and polymeric architectures reported.[13] Among them, $[Cu_4OCl_{10}]^{4-}$ (**1**, Figure 1e), first prepared by Bertrand and Kelley in 1969,[14] is stable in solution and a

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common building block.[15] While attempting the electrochemical synthesis of a hybrid salt of this polyanion with ET, we discovered that **1** readily oxidizes ET to yield good quality single crystals of $[\mathrm{ET}]_2[\mathrm{CuCl}_4]$ (**2**). Although the $[\mathrm{Cu}_4(\mu_4\text{-}\mathrm{O})]^{n-}$ core is a well-known oxidation catalyst,[16] it is the first time it is reported as an oxidant. Furthermore, chemical oxidation of ET, instead of the classical electrocrystallization technique, is very rare to yield crystalline radical salts.[9d,17] Here we report the synthesis, structure, and physical properties of **2**.

## ■ EXPERIMENTAL SECTION

All chemicals and solvents were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N, and S) were carried out by the CAI Microanálisis Elemental (Universidad Complutense, Madrid). Magnetic susceptibility measurements on grained single crystals were performed on a Quantum Design MPMS-XL-7 SQUID magnetometer in the 2−300 K range under an applied direct current (dc) magnetic field of 1 T. EPR measurements in the solid state were registered at the X-band (9.4 GHz) frequency using a Bruker ESP-300E spectrometer, from room temperature to 5 K at the Unitat de Mesures Magnètiques (Universitat de Barcelona). Electrical transport measurements were carried out with Keithley sourcemeter (2400 series) and nanovoltmeter (2182A model) with a 4-probe measurement at room temperature. Contacts were made with copper wires (0.05 mm diameter) and silver epoxy. The current−voltage curve was measured with a voltage sweep, but resistance exceeded the limit of the setup to be quantified.

**Synthesis.** *$[\mathrm{N(CH_3)_4}]_4[\mathrm{Cu_4OCl_{10}}]$ (1).* A solution of tetra(methyl)-ammonium hydroxide (3.68 g, 20.3 mmol) in 100 mL of ethanol was added dropwise to a solution of $\mathrm{CuCl_2{\cdot}H_2O}$ (4.74 g, 27.8 mmol) in 200 mL of ethanol. After 1 h, the abundant orange precipitate was filtered to vacuum, washed thoroughly with ethyl acetate and ether, and dried in air. Yield: 60%. Calcd for $\mathrm{Cu_4OCl_{10}N_4C_{16}H_{48}}$ C 20.86, H 5.25, N 6.08; found C 20.97, H 5.18, N 6.01. This product can be conveniently recrystallized from ethanol or acetonitrile to yield good quality single crystals.

*$[\mathrm{ET}]_2[\mathrm{CuCl}_4]$ (2).* **1** (200 mg) and ET (10 mg) were placed as solids in each compartment of a two compartment U cell, with a frit separating both compartments. Acetonitrile (40 mL) was used as solvent. After several days single crystals of **2** were obtained as long black needles. Single crystals were hand collected and washed with water, acetone, acetonitrile, and dichloromethane to remove unreacted ET and any excess of copper halide products. Calcd for $\mathrm{C_{20}H_{16}Cl_4CuS_{16}}$: C 24.65, H 1.65, S 52.64; found C 24.82, H 1.66, S 52.47.

**X-ray Diffraction.** Crystal structure determination for **1** was carried out using a Apex DUO Kappa 4-axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 IuS using Mo K$\alpha$ radiation, Quazar MX multilayer Optics as monochromator, and a Oxford Cryosystems low temperature device Cryostream 700 plus ($T = -173$ °C). Full-sphere data collection was used with $\omega$ and $\varphi$ scans. *Programs used:* Data collection APEX-2,[18] data reduction Bruker Saint,[19] and absorption correction TWINABS.[20] *Structure Solution and Refinement*: Crystal structure solution was achieved using direct methods as implemented in SHELXTL[21] and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on $F^2$ using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters. The asymmetric unit contains two independent ET molecules and one $\mathrm{CuCl_4}$ anion. The $\mathrm{CuCl_4}$ anion is disordered in two orientations (ratio 74:26). The measured sample was formed by two crystals with a ratio of 53:47. The collected data for both crystals were processed with TWINABS, taking into account overlapping reflections.[20] The crystal data were treated for absorption correction as a strong absorber (absorption coefficient 2.09 mm$^{-1}$). Crystal data collection, refinement parameters, and bond distances and angles are given in Tables 1−3.

### Table 1. Crystallographic Data for $[\mathrm{ET}]_2[\mathrm{CuCl}_4]$ (2)

| | |
|---|---|
| chemical formula | $\mathrm{C_{20}H_{16}Cl_4CuS_{16}}$ |
| formula weight | 974.63 |
| $T$ (K) | 100(2) |
| wavelength (Å) | 0.71073 |
| crystal size (mm$^3$) | 0.50 × 0.05 × 0.02 |
| crystal system | triclinic |
| space group | $P\bar{1}$ |
| $a$ (Å) | 8.7978(10) |
| $b$ (Å) | 12.193(2) |
| $c$ (Å) | 15.7667(18) |
| $\alpha$ (deg) | 95.334(5) |
| $\beta$ (deg) | 95.042(6) |
| $\gamma$ (deg) | 107.352(5) |
| $V$ (Å$^3$) | 1595.4(4) |
| $Z$ | 2 |
| $\rho_{\mathrm{calcd}}$ (g cm$^{-3}$) | 2.029 |
| $\mu$ (mm$^{-1}$) | 2.086 |
| $F$ (000) | 978 |
| $\theta$ range (deg) | 1.31−29.13 |
| index ranges | $-12 \le h \le 11$ |
| | $-16 \le k \le 16$ |
| | $0 \le l \le 21$ |
| data/restraints/parameters | 8254/270/408 |
| goodness-of-fit on $F^2$ | 1.068 |
| $R_1$ ($I > 2\sigma(I)$)/$wR_2$ ($I > 2\sigma(I)$) | 0.0633/0.1600 |
| $R_1$ (all data)/$wR_2$ (all data) | 0.0787/0.1675 |
| largest diff peak and hole (e Å$^{-3}$) | 1.890 and −1.537 |

### Table 2. Bond Lengths (Å) for $[\mathrm{ET}]_2[\mathrm{CuCl}_4]$ (2)

| | | | |
|---|---|---|---|
| Cu−Cl1 | 2.2760(18) | S8−C6 | 1.752(6) |
| Cu−Cl2 | 2.2966(17) | S8−C10 | 1.783(7) |
| Cu−Cl3 | 2.2416(16) | C9−C10 | 1.464(10) |
| Cu−Cl4 | 2.2038(18) | S4−C6 | 1.716(6) |
| Cu−Cl1′ | 2.068(8) | S11−C11 | 1.726(5) |
| Cu−Cl2′ | 2.184(7) | S11−C13 | 1.733(5) |
| Cu−Cl3′ | 2.474(7) | C11−C12 | 1.387(7) |
| Cu−Cl4′ | 2.363(7) | C11−S12 | 1.736(5) |
| S1−C1 | 1.730(5) | S15−C13 | 1.755(5) |
| S1−C3 | 1.755(5) | S15−C17 | 1.826(6) |
| C1−C2 | 1.372(7) | C13−C14 | 1.352(7) |
| C1−S2 | 1.742(5) | S16−C14 | 1.740(5) |
| C3−C4 | 1.360(7) | S16−C18 | 1.798(6) |
| C3−S5 | 1.715(5) | C17−C18 | 1.463(8) |
| S5−C7 | 1.815(6) | S12−C14 | 1.748(5) |
| S6−C4 | 1.746(5) | S13−C15 | 1.728(5) |
| S6−C8 | 1.845(6) | S13−C12 | 1.739(5) |
| C7−C8 | 1.478(9) | S17−C15 | 1.737(5) |
| S2−C4 | 1.744(5) | S17−C19 | 1.802(7) |
| S3−C2 | 1.709(5) | C12−S14 | 1.708(5) |
| S3−C5 | 1.756(5) | C15−C16 | 1.360(8) |
| C2−S4 | 1.739(5) | S18−C16 | 1.753(6) |
| S7−C5 | 1.744(5) | S18−C20 | 1.875(7) |
| S7−C9 | 1.824(7) | S14−C16 | 1.754(6) |
| C5−C6 | 1.371(7) | C19−C20 | 1.488(9) |

CCDC-937784 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif.

**Table 3. Selected Bond Angles (deg) for $[ET]_2[CuCl_4]$ (2)**

| | | | |
|---|---|---|---|
| Cl1−Cu−Cl2 | 94.85(6) | C10−C9−S7 | 117.7(5) |
| Cl1−Cu−Cl3 | 96.80(6) | C6−S4−C2 | 95.3(3) |
| Cl1−Cu−Cl4 | 144.18(8) | C9−C10−S8 | 114.8(5) |
| Cl2−Cu−Cl3 | 139.93(7) | C5−C6−S4 | 117.8(4) |
| Cl2−Cu−Cl4 | 96.01(6) | C5−C6−S8 | 124.3(4) |
| Cl3−Cu−Cl4 | 96.52(7) | S4−C6−S8 | 117.9(3) |
| Cl1′−Cu−Cl2′ | 102.5(3) | C11−S11−C13 | 95.3(2) |
| Cl1′−Cu−Cl3′ | 94.7(3) | C12−C11−S11 | 121.6(4) |
| Cl1′−Cu−Cl4′ | 152.0(3) | C12−C11−S12 | 122.7(4) |
| Cl2′−Cu−Cl3′ | 133.1(2) | S11−C11−S12 | 115.7(3) |
| Cl2′−Cu−Cl4′ | 95.6(3) | C13−S15−C17 | 102.6(3) |
| Cl4′−Cu−Cl3′ | 88.1(2) | C14−C13−S11 | 117.6(4) |
| C1−S1−C3 | 96.2(2) | C14−C13−S15 | 125.9(4) |
| C2−C1−S1 | 121.8(4) | S11−C13−S15 | 116.6(3) |
| C2−C1−S2 | 122.5(4) | C14−S16−C18 | 95.6(3) |
| S1−C1−S2 | 115.4(3) | C18−C17−S15 | 118.8(4) |
| C4−C3−S5 | 125.8(4) | C17−C18−S16 | 116.7(5) |
| C4−C3−S1 | 115.2(4) | C11−S12−C14 | 95.1(2) |
| S5−C3−S1 | 119.0(3) | C15−S13−C12 | 95.5(2) |
| C3−S5−C7 | 97.1(3) | C13−C14−S16 | 124.1(4) |
| C4−S6−C8 | 105.3(3) | C13−C14−S12 | 116.4(4) |
| C8−C7−S5 | 117.0(5) | S16−C14−S12 | 119.5(3) |
| C1−S2−C4 | 94.9(2) | C15−S17−C19 | 99.2(3) |
| C7−C8−S6 | 117.1(4) | C11−C12−S14 | 124.3(4) |
| C3−C4−S2 | 118.3(4) | C11−C12−S13 | 119.7(4) |
| C3−C4−S6 | 124.6(4) | S14−C12−S13 | 115.9(3) |
| S2−C4−S6 | 117.1(3) | C16−C15−S13 | 116.5(4) |
| C2−S3−C5 | 95.8(3) | C16−C15−S17 | 126.2(4) |
| C1−C2−S3 | 123.9(4) | S13−C15−S17 | 117.4(3) |
| C1−C2−S4 | 120.4(4) | C16−S18−C20 | 103.9(3) |
| S3−C2−S4 | 115.7(3) | C12−S14−C16 | 95.1(3) |
| C5−S7−C9 | 101.8(3) | C20−C19−S17 | 113.6(5) |
| C6−C5−S7 | 130.1(4) | C19−C20−S18 | 115.4(5) |
| C6−C5−S3 | 115.2(4) | C15−C16−S18 | 128.1(4) |
| S7−C5−S3 | 114.8(3) | C15−C16−S14 | 116.9(4) |
| C6−S8−C10 | 97.5(3) | S18−C16−S14 | 115.0(3) |

## RESULTS AND DISCUSSION

**Synthesis and Crystal Structure of $[ET]_2[CuCl_4]$ (2).** We prepared the salt $[N(CH_3)_4]_4[Cu_4OCl_{10}]$ with a new synthetic procedure, different from the classic synthesis using CuO as starting material.[14,22] Direct reaction of $CuCl_2$ with $[N(CH_3)_4]$-OH in ethanol yields **1** in high yield and purity. The compound was recrystallized from ethanol as single, red, cubic shaped crystals. Its purity was confirmed by powder X-ray diffraction (Supporting Information Figure S1) and elemental analysis.

Slow diffusion of **1** and ET in a dichloromethane/acetonitrile solution yielded long black needles of the compound $[ET]_2[CuCl_4]$ (**2**, Figure 2). The nature of the oxidant during this reaction is unclear. The most plausible hypothesis is the reduction of some of the $Cu^{2+}$ centers in the tetra-copper cluster to $Cu^+$, yielding the formation of $[CuCl_2]^-$, $[CuCl_4]^{2-}$, and, possibly, other species from cluster decomposition. This would be an analogous redox process to that reported in the preparation of the radical salt $[ET][CuCl_2]$, obtained by diffusion of ET and $CuCl_2$ in an organic solvent.[9d] However, the outcome of the reaction is different, since **2** does not contain a $Cu^+$ species. Although a variety of anions coexist in solution, including the starting material, $[ET]_2[CuCl_4]$ is the only product of this reaction, controlled by the preferential self-assembly of anions and cations.

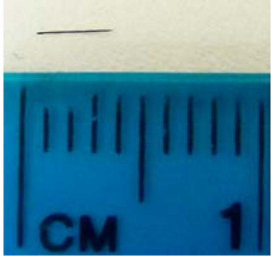

**Figure 2.** Single crystal of $[ET]_2[CuCl_4]$.

$[ET]_2[CuCl_4]$ crystallizes in the triclinic $P\overline{1}$ space group. The unit cell contains two crystallographically independent ET molecules and one $[CuCl_4]$ anion. The ET molecules form one-dimensional stacks along the *a* axis (Figure 3) following a regular ABAB pattern. These chains are strongly dimerized, with multiple very short intradimer S···S contacts between the core TTF sulfur atoms: S1−S14, 3.399(9) Å; S3−S12, 3.440(9) Å; S4−S11, 3.420(9) Å. The interdimer shortest contacts are above 3.8 Å along the chains. There are also close contacts between chains, with a minimum 3.48(1) Å distance for S8−S15 and S5−S18. These short contacts are mediated by strong cation−anion interactions, with very short S8−Cl and S18−Cl distances below 3.0 Å. The anions are surrounded by ET molecules imposing long Cu···Cu distances (9.342 Å). It is important to note that the terminal ethylenic groups from the ET molecules are not crystallographically disordered between both possible configurations, as usually found in ET salts.

Copper halides can appear in multiple oxidation states, and even delocalized mixed valence has been invoked in some ET hybrid radical salts with $CuX_n$ counterions.[23] For example, it was concluded that $[ET][CuCl_2]$ is a mixed valence compound. The crystal structure revealed a mixture of $CuCl_2$ and $CuCl_2^-$ (estimated from the Cu−Cl bonding distances), resulting in formal noninteger oxidation state of $+^2/_3$ for the ET molecules.[9d] The coordination geometry of the $CuCl_4$ moieties in **2** shows a strong Jahn−Teller distortion with the chloride positions disordered between two different orientations with a 3:1 crystallographic occupancy. Both coordination modes are analogous. The average Cu−Cl distance is 2.5 Å with Cl−Cu−Cl angles of 140°. This coordination geometry with pseudo-4-fold symmetry is typical of $Cu^{2+}$ chlorides.[24] $Cu^+$ chlorides exhibit significantly shorter bond distances and regular coordination.[25]

With divalent $[CuCl_4]^{2-}$ anions, the stoichiometry of the $[ET]_2[CuCl_4]$ salt suggests that each $[ET]_2$ dimer in the 1D chains should possess an overall 2+ charge. The charge of an ET molecule can be estimated from the bond lengths. Guionneau et al.[26] established a good correlation between the C−S distances in the ET core skeleton and the overall charge. Following this approximation we found charges of +0.9 and +1 for molecules A and B, respectively. Therefore, the 2+ charge appears equally distributed between the two ET molecules, both completely oxidized by 1 $e^-$. The lack of mixed valence in the ET stacks, and the strong dimerization suggest no electron delocalization.

**Magnetic and Transport Properties.** The EPR spectra of **2** in the solid state show only one Lorentzian signal that appears around $g \approx 2$ (Figure 4). At room temperature this signal shows the typical shape of a spin doublet with $g = 2.00$ and 50 G line width. The line becomes narrower as temperature is decreased, reaching 29 G line width at 5 K,

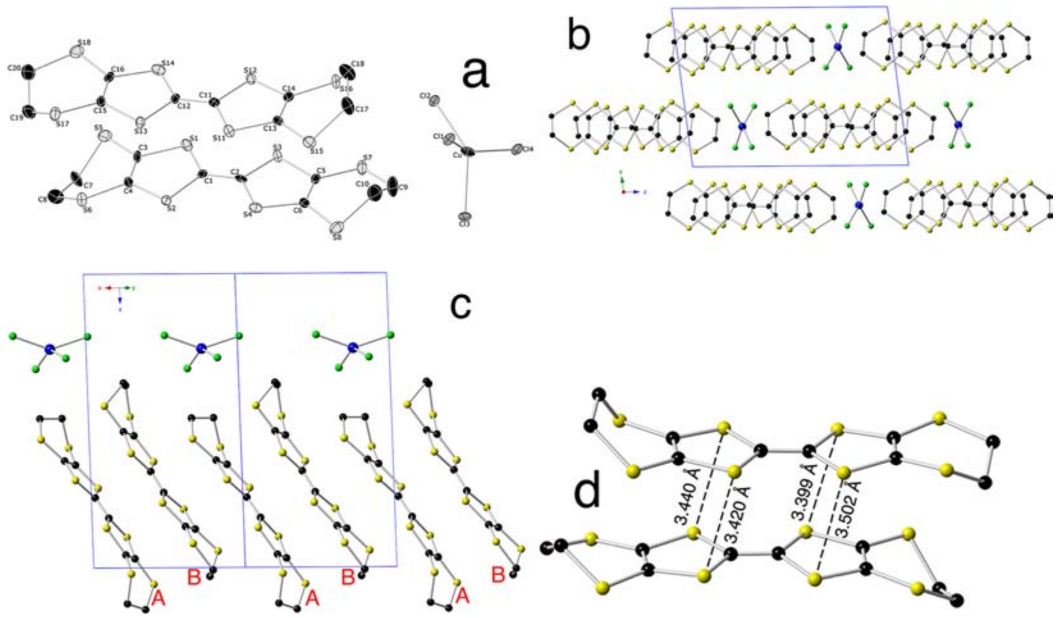

**Figure 3.** (a) ORTEP (50% probability) representation of the asymmetric unit in the crystal structure of **2**. The disordered Cl atoms with minor occupancy factors and H atoms were omitted for clarity. (b) Representation of the crystal structure on the *bc* plane. (c) Side view of the dimerized ET chains running along the *a* axis. (d) Intradimer ET short contacts.

for a $g = 2.01$. Such a small temperature dependence indicates that this signal should be assigned to the metal centers. The absence of a signal coming from the ET molecules at any temperature indicates strong intradimer coupling and the absence of paramagnetic impurities in the organic network.

Magnetic measurements of **2** were performed under an applied dc field of 1 T (Figure 5). The room temperature $\chi_m T$ product is 0.6 emu K mol$^{-1}$, much lower than the value expected for three magnetically diluted unpaired electrons from the three spin carriers ($Cu^{2+}$ and the two fully oxidized ET molecules). This indicates strong intradimer antiferromagnetic coupling between the ET molecules, as expected since they appear strongly dimerized in the crystal structure. $\chi_m T$ decreases as the temperature is decreased, reaching a plateau below 100 K. This plateau at 0.37 emu K mol$^{-1}$ corresponds to the magnetically isolated $Cu^{2+}$ $S = {}^1/_2$ centers, for $g = 2$ as derived from the EPR data. Below 5 K there is an additional small decrease that should correspond to intermolecular dipolar interactions (Supporting Information Figure S2).

The magnetic data in the 5−300 K range can be modeled to a $S_1 = S_2 = {}^1/_2$ dimer with the Hamiltonian:

$$\mathcal{H} = -2j(S_1 \times S_2)$$

plus an isolated $S = {}^1/_2$ center, corresponding to the $[ET]^{2+}$ dimer and the $[CuCl_4]^{2-}$ moieties, respectively. We fixed the same $g$ factor for all spin carriers to avoid overparametrization. The best fit for the experimental data was found for $\overline{g} = 2.00$ and $J = -216$ cm$^{-1}$ (Figure 5). The $g$ value is in perfect agreement with the EPR data. The magnetization data at 2 K (Supporting Information Figure S3) shows saturation at very high fields (>5 T), reaching 0.95 $\mu_B$, as expected for only one unpaired electron. Since the triplet in the ET dimer is far away from the singlet ground state, no contribution from the organic layer appears in the magnetization data at low temperatures.

We also performed transport measurements with the four probe technique on single crystals of **2**. The resistance of the single crystals was too high to be measured with our experimental setup (>100 MΩ). Thus, this material is an insulator, as expected from the charge localization in the packing of the organic radicals.

## CONCLUSIONS

We have obtained a new radical salt of ET by its direct oxidation with a polynuclear copper(II) chloride complex. The product forms through self-assembly in solution of $[ET]^{2+}$ dimers and $[CuCl_4]^{2-}$ anions. This is just the second ET salt reported obtained as single crystals from a direct oxidation procedure, with the additional novelty that the counteranion is not the product of the redox process. From a solution containing a variety of anions, we obtained exclusively compound **2** as large single crystals. This is surprising, since the presence of different anion types in the electrochemical synthesis of hybrid TTF-based materials usually yields mixtures of products. Thus, this strategy could be useful for the preparation of new ET hybrid materials, not accessible through electrocrystallization.

It is worthy to note that, in the report of the related $[ET]_3[CuCl_4]\cdot H_2O$ conductor,[11] the authors mentioned that a second phase of $[ET]_2[CuCl_4]$ stoichiometry was also obtained during electrocrystallization. Both phases were easily recognized because of the different shape of the single crystals. The 3:1 phase crystallized as hexagonal plates, and it was fully characterized. The 2:1 phase was described as multifaceted needles, and its poor crystallinity did not allow for further characterization. It is plausible to think that this phase corresponds to compound **2**, since stoichiometry and crystal shape are identical. We were able to characterize this material, finding insulating behavior and an antiferromagnetic magnetic exchange parameter of $J = -216$ cm$^{-1}$ for the ET dimer. The insulating nature of this material would also explain why good quality single crystals could not be obtained by electrocrystallization. Poor conductors do not typically yield good quality single crystals since electrical conductivity is needed for crystal growth. Indeed, few ET salts with strongly dimerized

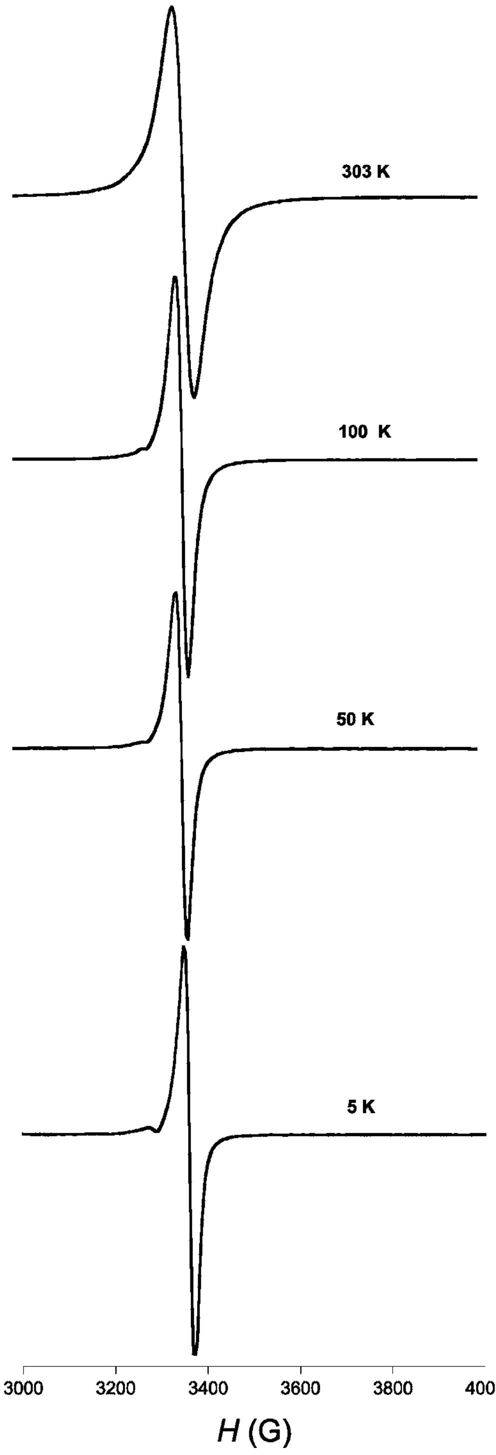

**Figure 4.** EPR spectra for **2** in the solid state at different temperatures.

and/or completely oxidized cationic structure have been reported,[27] and they showed semiconducting behavior.

Although in this case the material obtained shows low conductivity, the same synthetic procedure could yield better conductors. The synthetic procedure is kinetically controlled by the low solubility of the product. Therefore, the use of additional anions able to form better conducting but highly insoluble radical salts is a possibility that deserves further study.

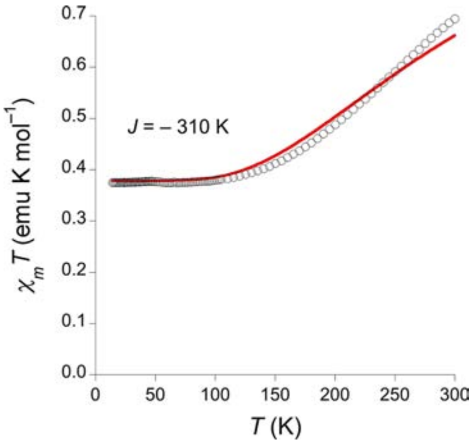

**Figure 5.** Thermal dependence of the $\chi_m T$ product of **2** (empty circles) and best fitting to a $[ET_2]^+$ and $Cu^{2+}$ ($S = {}^1/_2$) (red line). A temperature independent paramagnetism (TIP) was subtracted from the experimental data (≈$1.18 \times 10^{-4}$ emu mol$^{-1}$).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

PXRD pattern for **1**and additional magnetic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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