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(BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$: An Organic–Inorganic Hybrid Conducting Magnet

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A dual-functional organic–inorganic hybrid (BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$ (**1**) (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene) was obtained through the electrochemical oxidation of neutral BEDT-TTF in the presence of an ammonium salt of the one-dimensional copper-formate framework [(C$_2$H$_5$)$_3$NH]Cu$_2$(HCOO)$_5$ in a C$_6$H$_5$Cl–C$_2$H$_5$OH solution. Compound **1** was composed of organic donor BEDT-TTF$^{+0.5}$· in a θ-phase arrangement and Jahn–Teller distorted (4,4) grid anion sheets [Cu$_2$(HCOO)$_5^-$]$_n$ with $S=1/2$. We identified the material as a semiconductor with values of $\sigma_{300K}=10^{-1}$ S cm^{-1}. The anion sheet is a coordination isomer of [Cu$_2$(HCOO)$_5^-$]$_n$ and, compared with the starting material, shows antiferromagnetic behavior as the well-known inorganic Cu–O, Co–O square layers for creating inorganic conducting magnets. Long-range antiferromagnetic ordering was observed at 8.0 K.

Dual-functional molecular crystals show a range of conductivity behaviors from semiconducting to metallic and even superconducting properties. These crystals can also display a variety of magnetic behaviors including antiferromagnetic, ferromagnetic long-range magnetic ordering, and spin frustration. The materials have drawn considerable interest in materials science for their potential uses in molecular spintronics.[1] Charge-transfer salts are a powerful route for obtaining dual-functional molecular crystals by combining an organic conducting unit and an inorganic magnetic unit in organic–inorganic hybrids. Three notable ferromagnetic metals [(BEDT-TTF)$_3$[CrMn(C$_2$O$_4$)$_3$]CH$_2$Cl$_2$, BETS$_3$[CrMn(C$_2$O$_4$)$_3$]CH$_2$Cl$_2$ (BETS = bis(ethylenedithio)tetraselenafulvalene), and (TM-ET)$_3$[CrMn(C$_2$O$_4$)$_3$]CH$_2$Cl$_2$ (TM-ET = (S,S,S,S-tetramethylbis(ethylenedithio)tetrathiafulvalene)] with ferromagnetic long-range ordering (LRO), the antiferromagnetic semiconductor (BEDT-TTF)$_3$[Cu$_2$(C$_2$O$_4$)$_3$](CH$_3$OH)$_2$, and the antiferromagnetic metal BETS$_3$[Cu$_2$(C$_2$O$_4$)$_3$](CH$_3$OH)$_2$, which features spin frustration, have previously been reported.[2,3] The formate (HCOO$^-$) ion, as the smallest carboxylate, is one of the best short bridging ligands to mediate the magnetic coupling between transition-metal atoms with the local spin. Two-dimensional metal-formate frameworks have been extensively studied as dual-functional materials, offering dielectric properties and long-range magnetic ordering.[4] Three-dimensional metal-formate frameworks are important building blocks of multifunctional materials, and there is great interest in the relationship between their structure and their magnetic, dielectric, and ferroelectric properties.[5] However, the electrical conductivity of dual-functional materials composed of a metal-formate framework has not yet been reported. Here, we present the synthesis and characterization of a charge-transfer salt (BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$ composed of BEDT-TTF and a two-dimensional antiferromagnetic square copper-formate framework [Cu$_2$(HCOO)$_5^-$]$_n$.

Brown, thin, plate-like single crystals of **1** were obtained from BEDT-TTF and [(C$_2$H$_5$)$_3$NH]Cu$_2$(HCOO)$_5$ in a mixture of C$_6$H$_5$Cl and C$_2$H$_5$OH through an electrocrystallization method.[6] The crystal structure was determined from single-crystal X-ray diffraction data. The independent unit cell contained half a BEDT-TTF molecule, half a Cu^{2+} cation, and one and a quarter formate anions. Four BEDT-TTF molecules, four Cu^{2+} cations, and ten formate anions were present in a unit cell with the formula (BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$ and $Z=2$. The conformation of the two ethylene groups on one BEDT-TTF molecule was eclipsed. Expect for the two ethylene groups, all of the atoms on one BEDT-TTF molecule were co-planar with a maximum deviation of 0.026 Å. The donors stacked face-to-face to form a donor column along the *a* axis. Hydrogen bonds formed between donor molecules: C5–H5B···S3 3.689(6) Å/154°, C6–H6B···S4 3.682(6) Å/153° (Figure 1). Columns are arranged side-by-side along the *c* axis to form a donor layer as the θ

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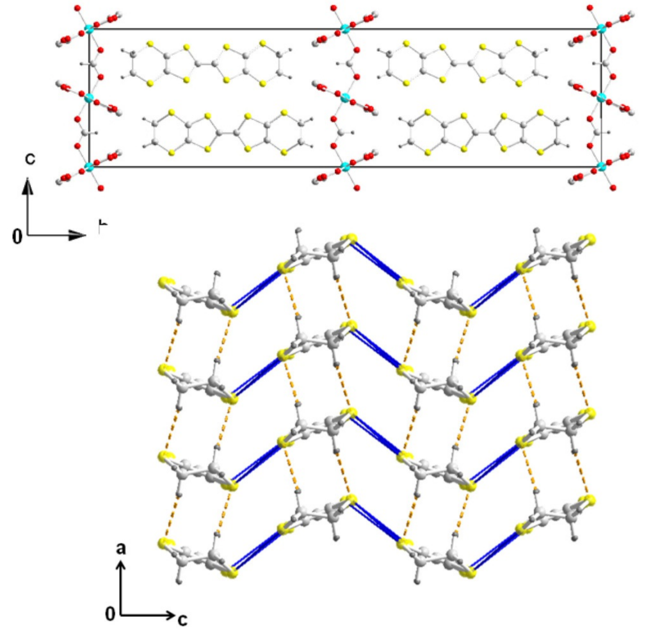

Figure 1. The donor and anion arrangement in (BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$ viewed along the *a* axis (top). Color code: S, yellow; C, dark grey; O, red; Cu, blue; H, grey. Donor arrangement on the *a*–*c* plane (bottom). Color code: solid blue lines are S⋯S contacts; dashed orange lines are hydrogen bonds.

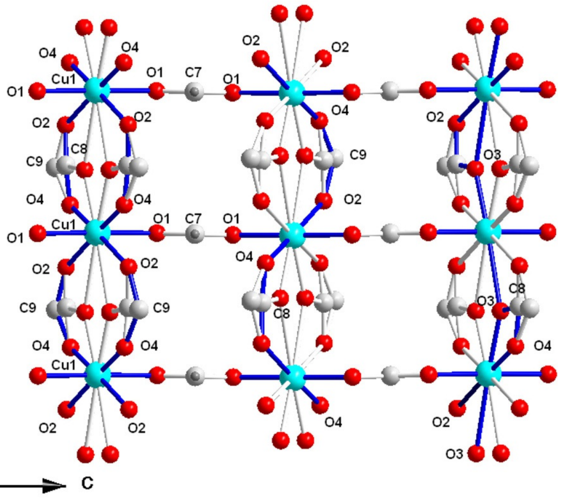

Figure 2. Structure of the anion sheet in (BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$. Along the *c* axis, Cu is bridged by formate in an *anti*–*anti* mode. Along the *a* axis, formate bridges two metal atoms in *syn*–*syn* and chelating–*anti* modes, as highlighted by solid blue lines.

phase.[7] The dihedral angle between neighboring BEDT-TTF molecules along the *c* axis was 47.42(3)°. S⋯S contacts existed between donor columns. Depending on the bond lengths of the TTF core, the formal charge on BEDT-TTF was assigned as +0.5.[8]

In the Raman spectrum (Figure S5), two strong bands were observed at 1458 and 1484 cm^{-1}, which were also found for 2:1 BEDT-TTF salts, thereby confirming the oxidation state of the donor molecule as +0.5.[9]

Donor layers are separated by an anion sheet of [Cu$_2$(HCOO)$_5^-$]$_n$ along the *b* axis. In the anionic sheet, the Cu^{2+} cations are coordinated by O atoms from two and half formate anions with square and octahedral configurations, as highlighted by blue solid lines in Figure 2. Along the *c* axis, one formate ligand bridges two metal atoms in an *anti*–*anti* mode with a Cu–O (Cu1–O1) distance of 1.966(4) Å. Along the *a* axis, one and a half formate ligands bridge two metal atoms with the C atoms disordered in two positions: C8, C9, and O atoms disorder in three positions: O2, O3, and O4. So, the O atoms are coordinated to Cu^{2+} with a *syn*–*syn* relationship and with chelating–*anti* modes, as observed in α-Cu(HCOO)$_2$, with Cu–O distances ranging from 1.95(2) to 2.41(2) Å (Figure 2) along the *a* axis.[10] Atoms on the main plane (Cu1, O2, O3, O4, C8, C9) were co-planar with a deviation of 0.05 Å. Thus, the metal atom is coordinated by formate ligands with Q2 and Q3 Jahn–Teller distortion.[11] The Cu⋯Cu distance is 4.12 Å along the *a* axis and 5.65 Å along the *c* axis. A square lattice is formed on the *a*–*c* plane. There are hydrogen bonds C5–H5A⋯O1 3.31(1) Å/109° between the donor and anion layer and C7–H7⋯O4 3.03(1) Å/117° between the formate ligands inside the anion sheet.

Polytypism and polymorphism are occasionally encountered in molecular crystals, especially in coordination polymers. Isomers, such as two-dimensional (6,3) grid and three-dimensional (10.3) grid [Cu$_2$(C$_2$O$_4$)$_3^{2-}$]$_n$, have been observed in ammonium salts and charge-transfer salts with a Cu-oxalate framework.[3,12] Compared with the starting material [(C$_2$H$_5$)$_3$NH]Cu$_2$(HCOO)$_5$, the anionic sheet in (BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$ represents a new coordination isomer of [Cu$_2$(HCOO)$_5^-$]$_n$.[6] In [(C$_2$H$_5$)$_3$NH]Cu$_2$(HCOO)$_5$, two Cu atoms were connected by four *syn*–*syn* formate ligands to form a binuclear [Cu$_2$(HCOO)$_4$] unit. Two [Cu$_2$(HCOO)$_4$] units were bridged by two *anti*–*anti* formate ligands to form a one-dimensional chain of anions [Cu$_2$(HCOO)$_5^-$]$_n$ (Figure S7). Thus, a one-dimensional zigzag chain is formed when the cation is a zero-dimensional unit such as [(C$_2$H$_5$)$_3$NH$^+$]. When the cation is a two-dimensional unit, a two-dimensional square lattice is formed as the cation template.

The two-dimensional coordination anion should be one of the most stable coordination isomers in a charge-transfer salt when an organic donor layer is present. For example, honeycomb metal-oxalate-framework anions exist in charge-transfer salts with layers of an organic donor: [CrMn(C$_2$O$_4$)$_3^-$]$_n$ anion in β-(BEDT-TTF)$_3$[CrMn(C$_2$O$_4$)$_3$]CH$_2$Cl$_2$, α-BETS$_3$[CrMn(C$_2$O$_4$)$_3$]CH$_2$Cl$_2$ and (TM-ET)$_3$[CrMn(C$_2$O$_4$)$_3$]CH$_2$Cl$_2$. In these cases, mononuclear coordination compounds were used as starting materials.[2] When ammonium salts of various copper-oxalate frameworks, including either a one-dimensional zigzag chain compound [(CH$_4$)$_4$N]$_2$Cu(C$_2$O$_4$)$_2$(H$_2$O), a two-dimensional honeycomb compound [(C$_3$H$_7$)$_3$NH]$_2$Cu$_2$(C$_2$O$_4$)$_3$(H$_2$O)$_{2.2}$, or a three-dimensional hyper-honeycomb compound [(C$_2$H$_5$)$_3$NH]$_2$Cu$_2$(C$_2$O$_4$)$_3$ as the starting materials, the charge-transfer salts θ^{21}-(BEDT-TTF)$_3$[Cu$_2$(C$_2$O$_4$)$_3$](CH$_3$OH)$_2$ and θ^{21}-BETS$_3$[Cu$_2$(C$_2$O$_4$)$_3$](CH$_3$OH)$_2$ with honeycomb anions [Cu$_2$(C$_2$O$_4$)$_3^{2-}$]$_n$ were obtained.[3,12] Thus, the 2D, square metal-formate framework could be deduced as the most stable coordination isomer in charge-transfer salts with an organic donor layer.

The conductivity of **1** at room temperature was $\sigma_{rt} \approx 0.1\ \mathrm{S\,cm^{-1}}$. Compound **1** showed semiconducting behavior with $E_\alpha = 0.16$ eV to 150 K (Figure 3). The observed conductivity corresponds with reported charge-transfer salts of θ-(BEDT-TTF), such as θ-$(BEDT\text{-}TTF)_2RbCo(SCN)_4$.[13]

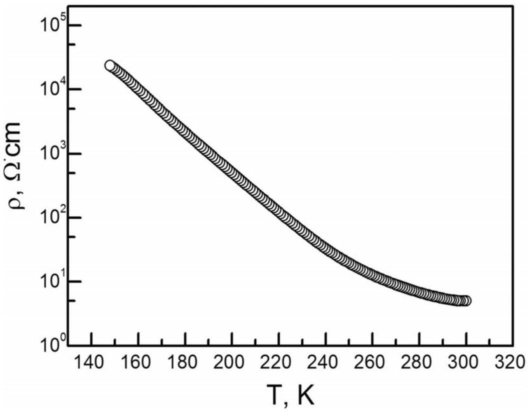

Figure 3. Temperature-dependent resistance on a single crystal of $(BEDT\text{-}TTF)_2Cu_2(HCOO)_5$.

To investigate the magnetism of the two-dimensional copper-formate frameworks with $S = 1/2$, its magnetic properties were studied. The temperature-dependent susceptibility under 1000 Oe increased smoothly upon cooling with a broad peak around 50 K as the low-dimensional magnetism. The χT value was $0.494\ \mathrm{cm^3\,K\,mol^{-1}}$ at room temperature, which was larger than the value expected for isolated spin-only Cu^{2+} with $S = 1/2$ and $g = 2.00$, but is similar to a previously reported value in a copper-oxalate framework with Jahn–Teller distortion and $g > 2.00$.[3,12] The χT value decreased smoothly upon cooling, and reached a minimum at around 10 K. It then increased and reached a maximum at approximately 6.8 K, before decreasing again to $0.105\ \mathrm{cm^3\,K\,mol^{-1}}$ at 2 K. The susceptibility data above 120 K fit the Curie–Weiss law well, giving Curie and Weiss constants of $C = 0.633(3)\ \mathrm{cm^3\,K\,mol^{-1}}$, $\theta = -90(1)$ K, and $R = 5.03\times10^{-5}$ (Figure 4). The negative Weiss value suggests strong antiferromagnetic interactions between the Cu^{2+} ions through the formate bridge. A sudden increase in the magnetization was observed below 9.0 K, which then increased slowly below 7.4 K. The zero-field-cooled and field-cooled magnetization showed a bifurcation at 8.0 K; this means long-range ordering magnetization occurred, as confirmed by remnant magnetization measurements as an antiferromagnet (Figure 4, inset). If interactions between two Cu^{2+} in the anionic sheet along the *a* and *c* axes are considered to be the same, and the interaction between the anionic sheets is neglected; the data above 60 K fit the square lattice antiferromagnetic model with $J = -55.9(3)$ K, $g = 2.592(2)$, and $R = 7.83\times10^{-5}$.[14]

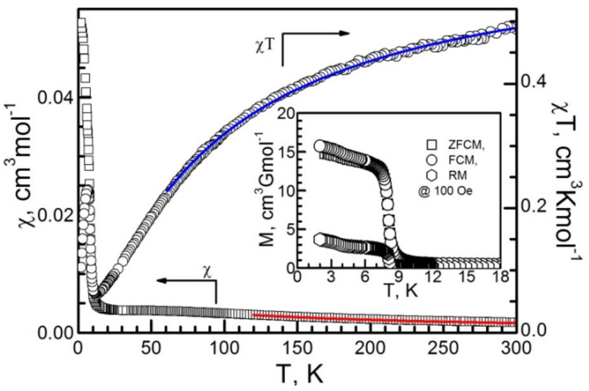

Figure 4. Temperature-dependent magnetization of $(BEDT\text{-}TTF)_2Cu_2(HCOO)_5$ under 1000 Oe from room temperature to 2 K (χ: empty black square; χT: empty black circle). Red line: Curie–Weiss fitting; blue solid line: Heisenberg (4,4) grid fitting. Inset: ZFCM/FCM/RM under 100 Oe from 2 to 20 K (ZFCM: empty black square; FCM: empty black circle; RM: empty black triangle).

At 2 K, the magnetization increased sharply and reached 0.006 Nβ at 400 Oe, before increasing more smoothly and reaching 0.063 Nβ at 65 kOe as a weak ferromagnet. This value is a little lower than a molecular antiferromagnetic conductor with Jahn–Teller distorted oxalate-bridged honeycomb anions: 0.077 Nβ in θ^{21}-$(BEDT\text{-}TTF)_3Cu_2(C_2O_4)_3(CH_3OH)_2$, and 0.075 Nβ in θ^{21}-$BETS_3Cu_2(C_2O_4)_3(CH_3OH)_2$.[3]

To compare the difference between two coordination isomers of $[Cu_2(HCOO)_5^-]_n$, the magnetization of $(C_2H_5)_3NHCu_2(HCOO)_5$ was studied. The magnetization of $(C_2H_5)_3NHCu_2(HCOO)_5$ increased sharply from 8.2 to 7.7 K, according to ZFCM/FCM/RM plots. This result indicated that both isomers show antiferromagnetic LRO around 8 K. To confirm these results, AC susceptibility measurements were performed on the ammonium salt. The real part of the spectrum increased from 9.0 K and reached a maximum at 7.7 K, and a weak peak was observed at 7.7 K in the imaginary spectrum (Figure S9). This corresponded with the specific heat measurement: a λ-peak was observed around 8 K (Figure S10). The isothermal magnetization at 2 K increased quickly and reached 0.0038 Nβ at 500 Oe (Figure S11). At 65 kOe, the magnetization reached 0.0059 Nβ and was one order of magnitude lower than that of a two-dimensional isomer in a charge-transfer salt.

The two-dimensional square lattice is important for inorganic dual-functional materials with magnetism and conductivity, because of its close relationship with high-temperature superconductivity.[15] Changing the counter ions that intercalate between the square antiferromagnetic anions in the insulating compound La_2CuO_4 results in hole doping as charge-transfer salts, which can lead to an antiferromagnetic semiconductor, an antiferromagnetic metal, or a diamagnetic superconductor.[16] The modulation of Na^+ and H_2O intercalated between square antiferromagnetic anions of $[CoO_2^{2-}]_n$ gave a Na/H_2O–CoO_2 superconductor.[17] An iron-based superconductor has also been reported that is composed of a La–F cation layer and a square antiferromagnetic Fe–As anion layer.[18]

Depending on the supramolecular chemistry, the variation in coordination and number of formate ligands in the two-dimensional copper-formate framework may have similar effects to O ligands in the reported Cu–O and Co–O layers of inorganic dual-functional materials. In the 1990s, during a period of intense research into high-temperature superconductors, people proposed replacing the intercalated H_2O between antiferromagnetic square copper-formate frameworks in $Cu(HCOO)_2(H_2O)_4$ to obtain dual-functional molecular crystals. The charge-transfer salt $(BEDT\text{-}TTF)_2Cu_2(HCOO)_5$ shows that this is possible by replacing the intercalated H_2O with the organic donor BEDT-TTF molecules between square antiferromagnetic Cu-formate-framework anionic sheets. It is also possible to construct new molecular metals with a square lattice copper-formate framework when BEDT-TTF is replaced with BETS.[3]

In summary, the first organic–inorganic hybrid composed of a semiconducting organic donor BEDT-TTF layer and a square antiferromagnetic layer has been obtained. The square lattice is formed with Jahn–Teller distorted Cu^{2+} bridged by formate anions. We show the potential for obtaining new molecular conductors and superconductors from a square lattice antiferromagnetic unit with Cu-formate-framework compounds as starting materials.

Experimental Section

Sample Preparation

All reagents were commercially purchased and used as received without further purification.

$[(C_2H_5)_3NH]Cu_2(HCOO)_5$ was synthesized by using a reported method. Elemental analysis: calcd C 29.08, H 4.66, N 3.08; exp C 29.02, 29.01; H 4.65, 4.69; N 3.12, 3.15.

$[BEDT\text{-}TTF]_2Cu_2(HCOO)_5$ was synthesized by dissolving BEDT-TTF (5.0 mg) and $[(C_2H_5)_3NH]Cu_2(HCOO)_5$ (20.0 mg) in a mixture of distilled C_6H_5Cl (25.0 mL) and C_2H_5OH (5.0 mL), which was then placed in an electrocrystallization cell. The cell was subjected to a constant source of 0.20 μA for 3 weeks at room temperature. A small, thin, brown, plate-like single crystal was obtained on the cathode.

Physical Characterization

The single X-ray diffraction data of $[BEDT\text{-}TTF]Cu_2(HCOO)_5$ was collected at Beijing Synchrotron Radiation Facility with radiation of 0.75 Å. The crystal structure was determined from X-ray diffraction data with cell parameters: $a = 4.116(1)$ Å, $b = 41.463(3)$ Å, $c = 11.305(1)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 1929.3(5)$ Å^3, space group $C222_1$ at 110 K. The data remained the same up to room temperature.[19]

Magnetization measurements were performed on a tightly packed polycrystalline sample in a capsule on a Quantum Design MPMS 7XL SQUID system. Susceptibility data were corrected for diamagnetism of sample by using Pascal constants [-243×10^{-6} cm^3 mol^{-1} per Cu^{2+} for $[BEDT\text{-}TTF]Cu_2(HCOO)_5$, -97×10^{-6} cm^3 mol^{-1} per Cu^{2+} for $[(C_2H_5)_3NH]Cu_2(HCOO)_5$] and background-corrected through experimental measurements on the sample holder. The conductivity measurement of $(BEDT\text{-}TTF)_2Cu_2(HCOO)_5$ was performed on the best developed surface of the single crystal with a four-probe method on a Quantum Design PPMS 9XL system from 2 to 300 K.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: antiferromagnetism · cation templates · charge-transfer salts · Jahn–Teller distortion · square lattices

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[19] CCDC 1439058 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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