**A dual-functional organic–inorganic hybrid (BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$: An Organic–Inorganic Hybrid Conducting Magnet**

Bin Zhang, a, b Yan Zhang, b Zheming Wang, c Zengqiang Gao, d Deliang Yang, e Dongwei Wang, f Yanjun Guo, f and Daoben Zhu* a

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$_5$H$_7$)$_2$N$_2$]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 $^{1,5}$ in a $0\theta$-phase arrangement and Jahn–Teller distorted (4,4) grid anion sheets [Cu$_2$(HCOO)$_5$]$_2$, 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)$_5$]. 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. Chore 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)$_2$Cr($\text{C}_5\text{O}_4$)$_2$]Cl$_2$, BETS$_2$[Cr($\text{C}_5\text{O}_4$)$_2$]Cl and BETS$_2$[Cr($\text{C}_5\text{O}_4$)$_2$]Cl$_2$ (BETS = bis(ethylenedithio)tetrathiafulvalene) have ferromagnetic long-range ordering and antiferromagnetic semiconductors (BEDT-TTF)$_2$Cu$_2$(HCOO)$_5$ composed of BEDT-TTF and two-dimensional antiferromagnetic square copper-formate framework [Cu$_2$(HCOO)$_5$]$_2$.

Brown, thin, plate-like single crystals of 1 were obtained from BEDT-TTF and [(C$_5$H$_7$)$_2$N$_2$]Cu$_2$(HCOO)$_5$ in a mixture of C$_6$H$_5$Cl and C$_2$H$_5$OH through an electrocrystallization method. 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 $\alpha$ 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 $\beta$ axis to form a donor layer as the $\theta$
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 $\pm 0.5$.

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 $\pm 0.5$.

Donor layers are separated by an anion sheet of $[\text{Cu}(\text{HCOO})]_2$, 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.

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.[18] 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$^\circ$ between the donor and anion layer and C7–H7···O4 3.03(1) Å/117$^\circ$ 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 $[\text{Cu}_2(\text{C}_4\text{O}_4)_2]^\text{2+}$, have been observed in ammonium salts and charge-transfer salts with a Cu-oxalate framework.[9,12] Compared with the starting material $[(\text{C}_2\text{H}_3)_2\text{NH}]\text{Cu}_2(\text{HCOO})_2$, the anionic sheet in (BEDT-TTF)$_2\text{Cu}_2(\text{HCOO})_2$ represents a new coordination isomer of $[\text{Cu}_(\text{HCOO})]_2$. In $[(\text{C}_2\text{H}_3)_2\text{NH}]\text{Cu}_2(\text{HCOO})_2$, two Cu atoms were connected by four syn–syn formate ligands to form a binuclear $[\text{Cu}_(\text{HCOO})]_2$ unit. Two $[\text{Cu}_(\text{HCOO})]_2$ units were bridged by two anti–anti formate ligands to form a one-dimensional chain of anions $[\text{Cu}_(\text{HCOO})]_n$. (Figure S7). Thus, a one-dimensional zigzag chain is formed when the cation is a zero-dimensional unit such as $[(\text{C}_2\text{H}_3)_2\text{NH}]^+$. 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: $[(\text{CrMn}(\text{C}_4\text{O}_4)_2)_2]$ anion in β-(BEDT-TTF)$_2[\text{CrMn}(\text{C}_4\text{O}_4)_2]\text{CH}_3\text{Cl}_2$, α-BETS$_2[\text{CrMn}(\text{C}_4\text{O}_4)_2]\text{CH}_3\text{Cl}_2$ and (TM-ET)$_2[\text{CrMn}(\text{C}_4\text{O}_4)_2]\text{CH}_3\text{Cl}_2$. 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 $[(\text{C}_2\text{H}_3)_2\text{NH}]\text{Cu}_2(\text{C}_4\text{O}_4)_2\text{H}_2\text{O}$, a two-dimensional honeycomb compound $[(\text{CH}_3)_2\text{NH}]\text{Cu}_2(\text{C}_4\text{O}_4)_2(\text{H}_2\text{O})_2]$, or a three-dimensional hyper-honeycomb compound $[(\text{C}_2\text{H}_3)_2\text{NH}]\text{Cu}_2(\text{C}_4\text{O}_4)_2$ as the starting materials, the charge-transfer salts $\theta_1$-(BEDT-TTF)$_2[\text{Cu}_2(\text{C}_4\text{O}_4)_2][\text{CH}_3\text{OH}]$, and $\theta_1$-BETS$_2[\text{Cu}_2(\text{C}_4\text{O}_4)_2][\text{CH}_3\text{OH}]$, with honeycomb anions $[\text{Cu}_2(\text{C}_4\text{O}_4)_2]^\text{2+}_n$ were obtained.[10,12] Thus, the 2D, square metal-oxalate framework could be deduced as the most stable coordination isomer in charge-transfer salts with an organic donor layer.

**Figure 1.** The donor and anion arrangement in (BEDT-TTF)$_2\text{Cu}_2(\text{HCOO})_2$, 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)$_2\text{Cu}_2(\text{HCOO})_2$. 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.
The conductivity of 1 at room temperature was \( \sigma_{rt} \approx 0.1 \text{ S cm}^{-1} \). Compound 1 showed semiconducting behavior with \( E_{g} = 0.16 \text{ eV} \) to 150 K (Figure 3). The observed conductivity corresponds with reported charge-transfer salts of \((\text{BEDT-TTF})_2\) such as \((\text{BEDT-TTF})_2\text{RbCo(SCN)}_3\) \(^{(13)}\).

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 \( \chi_T \) value was 0.494 cm\(^3\)Kmol\(^{-1}\) 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 \( g > 2.00 \) \(^{(5,10)}\). The \( \chi_T \) 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 cm\(^3\)Kmol\(^{-1}\) at 2 K. The susceptibility data above 120 K fit the Curie–Weiss law well, giving Curie and Weiss constants of \( C = 0.633(3) \text{ cm}^3 \text{Kmol}^{-1} \), \( \theta = -90(1) \text{ K} \), and \( R = 5.03 \times 10^{-5} \) (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 \( J = -55.9(3) \text{ K} \), \( g = 2.592(2) \), and \( R = 7.83 \times 10^{-5} \) \(^{(14)}\).

At 2 K, the magnetization increased sharply and reached 0.006 N\( \mu \) at 400 Oe, before increasing more smoothly and reaching 0.063 N\( \mu \) 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 N\( \mu \) in \((\text{BEDT-TTF})_2\text{Cu}_2(\text{OC} = \text{O})_2(\text{CH}_2\text{OH})_2\) and 0.075 N\( \mu \) in \((\text{BEDT-TTF})_2\text{Cu}_2(\text{OC} = \text{O})_2(\text{CH}_2\text{OH})_2\) \(^{(2)}\).

To compare the difference between two coordination isomers of \((\text{Cu}_2\text{H}_2\text{NHCu})_2(\text{HCOO})_3\) the magnetization of \((\text{Cu}_2\text{H}_2\text{NHCu})_2(\text{HCOO})_3\) was studied. The magnetization of \((\text{Cu}_2\text{H}_2\text{NHCu})_2(\text{HCOO})_3\) 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 \( \lambda \)-peak was observed around 8 K (Figure S10). The isothermal magnetization at 2 K increased quickly and reached 0.0038 N\( \mu \) at 500 Oe (Figure S11). At 65 kOe, the magnetization reached 0.0059 N\( \mu \) 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. \(^{(10)}\) Changing the counter ions that intercalate between the square antiferromagnetic anions in the insulating compound \( \text{La}_2\text{CuO}_4 \) results in hole doping as charge-transfer salts, which can lead to an antiferromagnetic semiconductor, an antiferromagnetic metal, or a diamagnetic superconductor. \(^{(11)}\) The modulation of Na\(^+\) and H\(_2\)O intercalated between square antiferromagnetic anions of \([\text{CoO}_2\text{M}^2+]\) gave a NaH\(_2\)O–CoO\(_2\) superconductor. \(^{(17)}\) An iron-based superconductor has also been reported that is composed of a La–Fe 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 H₂O between antiferromagnetic square copper-formate frameworks in Cu(H-COO₂)₂(H₂O), to obtain dual-functional molecular crystals. The charge-transfer salt (BEDT-TTF)₄Cu₂(HCOO)₂ shows that this is possible by replacing the intercalated H₂O 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.[13]

In summary, the first organic–inorganic hybrid composed of a semiconducting organic donor BEDT-TTF layer and a square antiferromagnetic carbon has been obtained. The square lattice is formed with Jahn-Teller distorted Cu²⁺ 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.

[(C₅H₅)₃NH]₂Cu₂(HCOO)₄ 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-TTF]₄Cu₂(HCOO)₄ was synthesized by dissolving BEDT-TTF (5.0 mg) and [(C₅H₅)₃NH]₂Cu₂(HCOO)₄ (20.0 mg) in a mixture of distilled C₅H₅Cl (25.0 mL) and C₅H₅OH (5.0 mL), which was then placed in an electrocrystallization cell. The cell was subjected to a constant source of 0.20 mA 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-TTF]₄Cu₂(HCOO)₄ 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, α = β = γ = 90°, V = 1929.3(5) Å³, space group C222, 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 obtained for diamagnetism of sample by using Pascal constants [−243×10⁻⁴ cm³ mol⁻¹ per Cu²⁺ for [BEDT-TTF]₄Cu₂(HCOO)₄, −97×10⁻⁴ cm³ mol⁻¹ per Cu²⁺ for [(C₅H₅)₃NH]₂Cu₂(HCOO)₄] and background-corrected through experimental measurements on the sample holder. The conductivity measurement of [BEDT-TTF]₄Cu₂(HCOO)₄ was performed on the best developed surface of the single crystal with a four-probe method on a Quantum Design MPMS 9XL system from 2 to 300 K.

Acknowledgements

This work was supported by the NSFC (Grants 21573242, 21173230), the National Basic Research Program of China (Grant 2013CB933402), and XDB12030100.

[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.

Received: February 28, 2017
Version of record online April 19, 2017