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An Organic-Inorganic Hybrid Semiconducting Quantum Spin Liquid Candidate: $(BEDT\text{-}TTF)_3[Cu_2(\mu\text{-}C_2O_4)_3]\cdot 2CH_3CH_2OH$

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Abstract: The organic-inorganic hybrid $(BEDT\text{-}TTF)_3[Cu_2(\mu\text{-}C_2O_4)_3]\cdot 2CH_3CH_2OH$ (**I**) was synthesized using the electrocrystallization method. It composes θ_{21}-phase organic donor layer and an inorganic antiferromagnetic honeycomb lattice with the Jahn-Teller distortion. The disordered solvent molecules CH_3CH_2OH are present within the cavities of the honeycomb lattice. The formal charge of donor molecules was assigned to +2/3 based on bond lengths in TTF core and corresponded to Raman spectra. Jahn-Teller effect on conductivity and magnetization is studied. It is a semiconductor with σ_{rt} = 0.04 S/cm and $E\alpha$ = 40 meV. No long-range ordering is observed above 2 K from zero-field cooling/field cooling magnetization and confirmed by specific heat measurement. The spin frustration with f > 10 from the antiferromagnetic copper-oxalate-framework was observed. It is a candidate for quantum spin liquid.

Keywords: Jahn-Teller effect; Cu(II); oxalate; single crystal; conductivity; spin frustration; quantum spin liquid candidate

1. Introduction

In 1973, P. W. Anderson suggested that in a *S* = 1/2 antiferromagnetic interaction triangular lattice, the magnetic ordering or freezing is not observed due to spin frustration leading to a quantum spin liquid [1]. In 1987, he proposed that the insulating antiferromagnet La_2CuO_4 serves as the parent compound of the cuprate superconductor after hole doping [2,3]. Quantum spin liquids with two-dimensional lattice are suggested in the triangular lattice, Kagome lattice and the honeycomb lattice [4,5]. Quantum spin liquid has become one of the core goals of condensed matter physics due to its close relationship with magnetism and superconductivity. The organic-inorganic hybrid charge-transfer complex hosts most of the organic superconductor [5]. It also provides solid support for research into quantum spin liquid candidates. The quantum spin liquid behavior was discovered in organic-inorganic hybrid charge-transfer salts κ-$(BEDT\text{-}TTF)_2[Cu_2(CN)_3]$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene), κ-$(BEDT\text{-}TTF)_2[Ag_2(CN)_3]$, $EtMe_3Sb[Pd(dmit)_2]_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate), and κ-H_3(cat-EDT-TTF)$_2$. κ-$(BEDT\text{-}TTF)_2[Cu_2(CN)_3]$ [6-11]. The

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oxalate ($C_2O_4^{2-}$) anion, as one of the most commonly used short connectors, plays a key role in superconductor and molecular magnets. The first superconductor cotaining paramagnetic metal ion β''-(BEDT-TTF)$_3$[Fe(C_2O_4)$_3$(H_3O)·C_6H_5CN] [12,13]. The Jahn-Teller effect plays an important role in inorganic cuprate superconductor and copper-oxalate-framework [2,14,15]. Quantum spin liquid candidate was discovered in organic-inorganic hybrid antiferromagnetic copper-oxalate-framework. Their conductivity varies based on organic donor (cation), which can act as an insulator, semiconductor or metal [16,17,18,19]. Further research on organic-inorganic hybrid containing copper-oxalate-framework will aid in identifying molecular conductor/superconductor and quantum spin liquid candidate. An organic-inorganic hybrid θ^{21}-(BEDT-TTF)$_3$[Cu_2(μ-C_2O_4)$_3$·2CH_3CH_2OH] (**I**) was obtained and related work is presented here.

2. Experiment and Discussion

BEDT-TTF was purchased by TCI company. [(C_2H_5)$_3$NH]$_2$$Cu_2$(m-$C_2O_4$)$_3$ was synthesized from $Cu(NO_3)_2$·6H_2O, $H_2C_2O_4$·2H_2O, and (C_2H_5)$_3$N from CH_3OH. A total of 5.0 mg of BEDT-TTF and 30.0 mg of [(C_2H_5)$_3$NH]$_2$$Cu_2$(μ-$C_2O_4$)$_3$ were dissolved in a mixture of 25.0 mL of distilled C_6H_5Cl and 5.0 mL of distilled C_2H_5OH, then placed in an electrocrystallization cell. The cell was subjected to a constant source of 0.20 μA at room temperature. Shiny black, thin plate crystals were obtained on the cathode after two weeks.

A piece of single crystal was selected for single crystal X-ray diffraction experiments at the Beijing Radiation Synchrony Facility using λ = 0.70 Å and a Rigaku SuperNova diffractometer with Mo radiation (λ = 0.71073 Å). Data was collected at 290 K, 180 K and 120 K. The crystal structure was solved using the direct method and refined with the full-matrix least-square of F^2 using the SHELX program for nonhydrogen atoms on BEDT-TTF, Cu and oxalate anisotropically [20]. The hydrogen atoms on C and N of ammonia were found from difference Fourier map, and refined isotropically. The non-hydrogen atoms of C_2H_5OH were disordered and refined isotropically. It remains stable from 290 K to 120 K. The crystallographic data is listed in Table 1. The discussion is based on data collected at 120 K.

Table 1. Crystallographic data of **I.**

T, K	**290**	**180**	**120**
Cell parameters	8.8661(5)	8.7230(8)	8.6836(4)
	16.7819(8)	16.7838(7)	16.8123(7)
	19.4803(9)	19.3844(4)	19.3959(7)
	74.271(4)	74.312(4)	74.329(3)
	88.962(4)	89.053(3)	88.991(4)
	88.022(4)	88.347(4)	88.420(4)
	2788.2(2)	2731.0(3)	2725.2(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\ \bar{1}$	$P\ \bar{1}$	$P\ \bar{1}$
Z	2	2	21.986
Dc. g/cm^3	1.945	1.986	1.990
μ mm^{-1}	1.726	1.762	1.766
θ °	3.428, 27.877	3.446, 27.878	3.401, 27.878
Completeness, %	99.7	99.7	99.7
no. total reflns	45474	45148	44834
no. unique reflns (R_{int})	13222(0.048)	12961(0.0373)	12934(0.0375)
no. obs. [$I \geq 2\sigma(I_0)$]	8829	10020	10328
no. params	759	759	759
R_1, wR_2 [$I \geq 2\ \sigma(I_0)$]	0.0610, 0.1488	0.0475, 0.1182	0.0469, 0.1163
R_1, wR_2 (all data)	0.0973, 0.1762	0.0669, 0.1325	0.0629, 0.1280
GOF	1.030	1.070	1.067
Shift/error	0.001/0.000	0.001/0.000	0.001/0.000

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$\Delta\rho$, e/Å^3	1.361(-0.849)	1.017(-1.033)	1.194(-1.156)
CCDC	1431596	1431595	1431594

There are two and two of a half of BEDT-TTF, two Cu, three oxalate and two ethanol in an independent unit (Figure 1). It is different from θ^{21}-(BEDT-TTF)$_3$[Cu$_2$(m-C$_2$O$_4$)$_3$]·2CH$_3$OH and θ^{21}-(BETS-TTF)$_3$[Cu$_2$(m-C$_2$O$_4$)$_3$]·2CH$_3$OH, three donor molecules, two Cu, three oxalate and two methanol coexist in an independent unit.

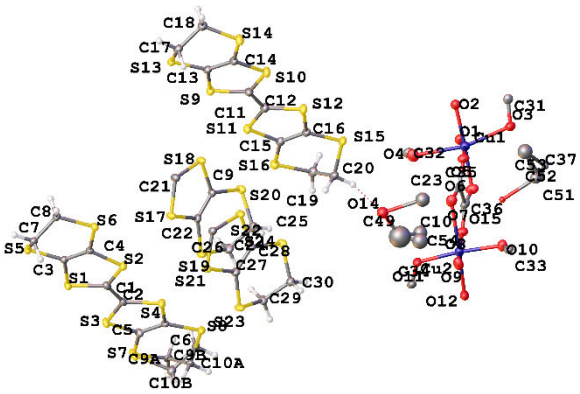

Figure 1. Atoms in an independent unit of **I**.

The donor molecules are stacked face-to-face along the *a* axis to form a donor column. Donor columns are arranged side-by-side along the *b* axis to form a donor layer as θ^{21}-phase, which is observed in θ^{21}-(BEDT-TTF)$_3$[Cu$_2$(m-C$_2$O$_4$)$_3$]·2CH$_3$OH and θ^{21}-(BETS-TTF)$_3$[Cu$_2$(m-C$_2$O$_4$)$_3$]·2CH$_3$OH (Figure 2) [16,17]. There are S···S contacts between donor molecules. One of the ethylene groups on BEDT-TTF is disorder at 290 K and order below 180 K. It is similar to [(C$_2$H$_5$)$_3$NH]$_2$[Cu$_2$(μ-C$_2$O$_4$)$_3$] with a disorder to order transition of ethylene group at 170 K [20]. There are S···S contacts between donor molecules.

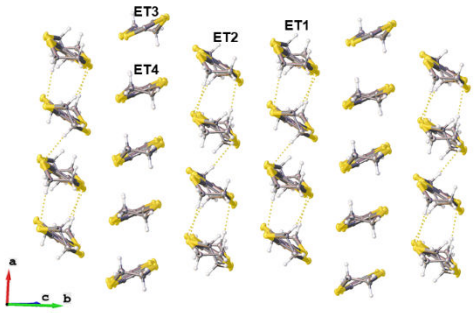

Figure 2. Donor arrangement of **I** on the ab plane. Dashed yellow lines are S···S contacts. ET is an abbreviation for BEDT-TTF.

Cu^{2+} is octahedrally coordinated by six O atoms from three bisbidentate oxalate ligands. The Cu1-O distances are 1.960(3)~2.002(3) Å in the equatorial plane, 2.239(2) Å and 2.373(3) Å from the apex. The Cu2-O distances are 1.952(2)~1.988(3) Å in the equatorial plane, 2.266(3) Å and 2.383(3) Å from the apex (Table 2). The elongated bonds on the Jahn-Teller distorted octahedron around the Cu are highlighted with blue solid lines (Figure 3). Cu1 and Cu2 are neighboring to each other. A honeycomb lattice is formed in the *ab* plane as observed in [(C$_3$H$_7$)$_3$NH]$_2$[Cu$_2$(m-C$_2$O$_4$)$_3$]·2.2H$_2$O, θ^{21}-(BEDT-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)$_3$]·2CH$_3$OH and θ^{21}-(BETS-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)$_3$]·2CH$_3$OH (Figure 3 [16,17,21]). Solvent molecules occupy the cavities of the honeycomb lattice. Hydrogen bonds exist between the donor and anion, as well as between the anion and solvent molecules (Figure 4).

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Table 2. Bond lengths of Cu-O in **I.**

T, K	290	180	120
Cu1-O, Å	1.970, 1.976, 1.993	1.958, 1.967, 1.985	1.960, 1.971, 1.985
	2.008, 2.259, 2.387	1.997, 2.239, 2.378	2.002, 2.239, 2.373
Cu2-O, Å	1.962, 1.964, 1.979	1.953, 1.953, 1.974	1.952, 1.956, 1.975
	2.010, 2.282, 2.378	1.991, 2.268, 2.383	1.988, 2.266, 2.382

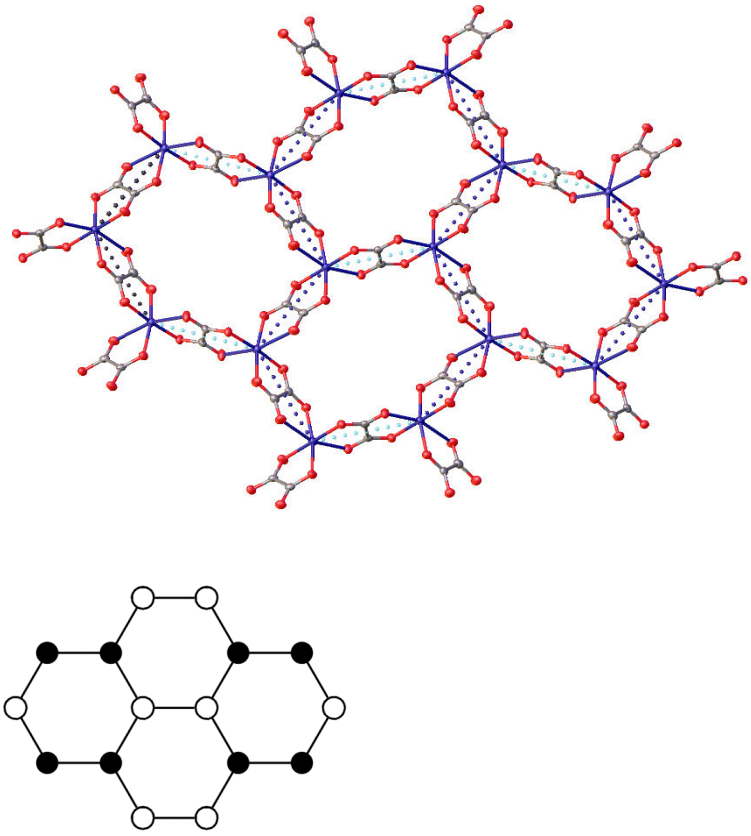

Figure 3. Anion layer of I viewed along the *c* axis.

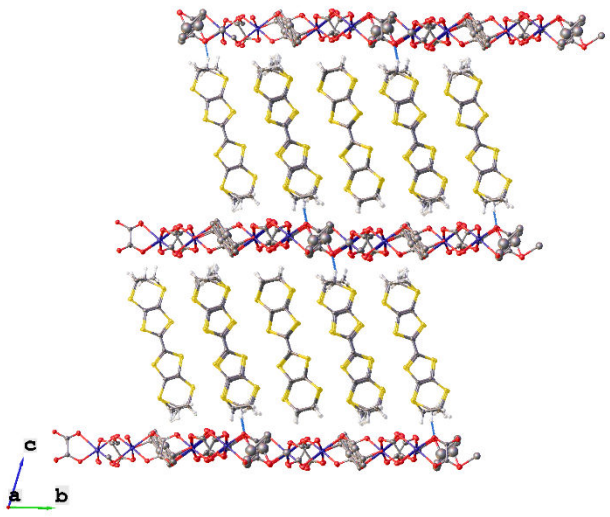

Figure 4. Packing diagram of **I** viewed along the a axis. Color code: Cu, blue; O red: S, yellow; C grey. Hydrogen bond, dashed blue line.

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Considering the bond length of the TTF core with a standard deviation of 0.1 of δ, the oxidation state of BEDT-TTF aligns well with the +2/3 average charge (Table S1), remaining consistent at both 180 K and 290 K [22].

The C=C stretching frequency of the charge-transfer complexes of BEDT-TTF serves as a robust method for determining the oxidation state of BEDT-TTF [23]. In the Raman spectra (λ = 514.5 nm), the υ_2 mode is at 1470~1485 cm^{-1} (Figure 5). This is the same as that of charge-transfer complexes with $BEDT\text{-}TTF^{+2/3}$. The formal charge is deduced to be +0.66.

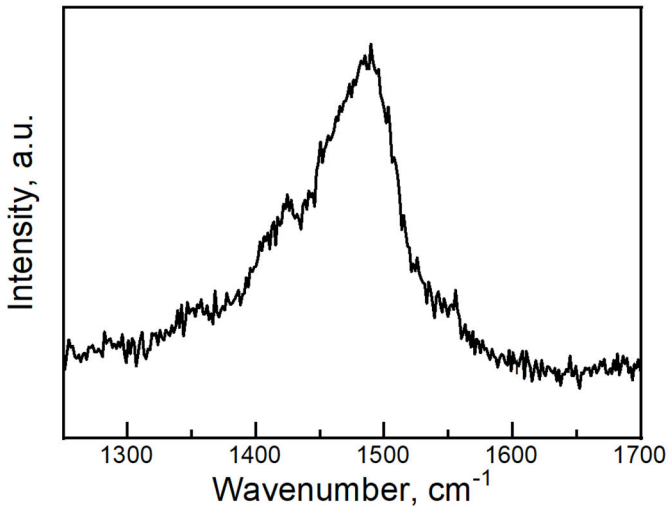

Figure 5. Raman spectrum of **I** with λ = 514.5 nm.

The conductivity measurement was conducted using a four-probe method in a Quantum Design PPMS 9 system. Gold wire was affixed to the best developed surface of a single crystal with gold paste. The room-temperature conductivity is σ_{rt} = 0.02 S/cm. This value lower than σ_{rt} = 4 S/cm of θ^{21}-$(BEDT\text{-}TTF)_3[Cu_2(\mu\text{-}C_2O_4)_3]\cdot 2CH_3OH$, but lower than σ_{rt} = 140 S/cm of θ^{21}-$(BETS\text{-}TTF)_3[Cu_2(\mu\text{-}C_2O_4)_3]\cdot 2CH_3OH$. The conductivity decreased when temperature dropped, with Eα = 40 meV as a semiconductor (Figure 6). It differs β''-$(BEDT\text{-}TTF)_3[Fe(C_2O_4)_3\cdot H_3O\cdot solvent]$, where the conductivity is primarily influenced by the organ donor [24].

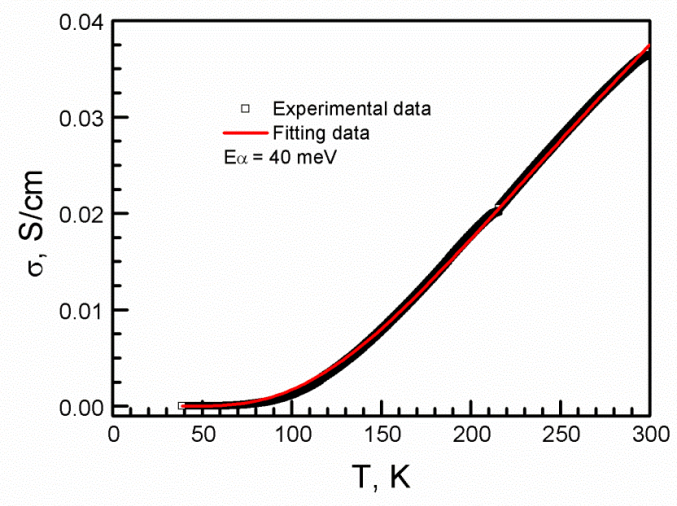

Figure 6. Temperature-dependence resistance of **I**.

The unpaired electron of Cu(II) resides in the magnetic orbital $dx^2\text{-}y^2$ on the equatorial plane. The orbital along the elongated octahedral Cu(II) is the dz^2 orbital, as highlighted by blue solid line in Figure 3. The magnetic configuration is a stripy arrangement based on orbital analysis [25]. Since

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the antiferromagnetic interaction is stronger than the ferromagnetic interaction between oxalate-bridged Cu(II) atoms, antiferromagnetic behavior is anticipated[26].

The magnetic susceptibility measurement was carried out on Quantum Design MPMS 7XL system. Susceptibility data was corrected by the Pascal constant of sample and sample holder [27].

At 300 K, the χT value was 0.389 cm^3 K mol^{-1} and g was 2.04. It is the same as an isolated, spin only Cu(II) ion with S = 1/2 and g = 2.00. As the temperature decreased, the χ increased smoothly, exhibiting a bend around 230 K, followed by an upturning at 22 K. The data with fits to the Curie-Weiss law yielded C = 0.503(2) cm^3 mol^{-1}, θ = –87(2) K and $R = 9.6 \times 10^{-7}$ above 230 K, while C = 0.405(1) cm^3 mol^{-1}, θ = –25.2(7) K and R = 1.3◊10^{-5} from 100 K to 230 K (Figure 7). No bifurcation is observed from zero-field-cool magnetization and field-cool magnetization (ZFCM/FCM) measurement above 2 K under 100 G. No long rang ordering is detected above 2 K. It is a spin frustrated complex with f > 12 [28].

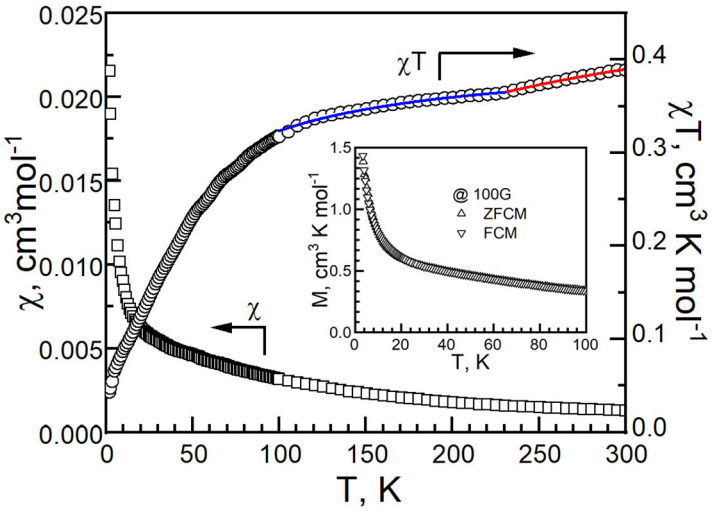

Figure 7. χ vs. T (empty black square), χT vs. T (empty black circle) of **I**. The red and solid lines are fits to the Curie-Weiss law. Insert: ZFCM/FCM of polycrystal under 100 G.

Specific heat measurements were conducted from 2 to 120 K under 0 T and 8 T, using a Quantum Design PPMS9 system (Figure 8). No λ-peak was observed in the range of 2 to 120 K. Combining with the X-ray diffraction experiment from 280 K to 120 K, there is no long range order above 2 K.

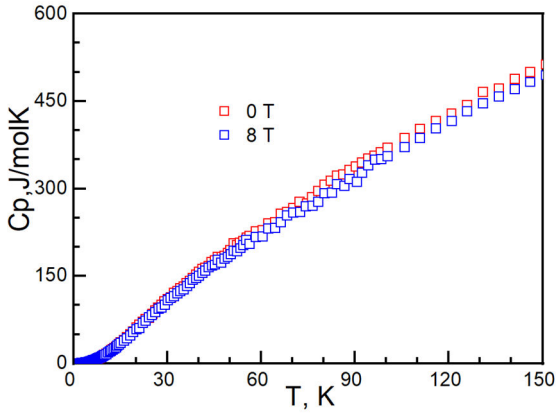

Figure 8. Specific heat of **I** from 2 K to 120 K.

Isothermal magnetization at 2 K displayed a S-shaped curve, reaching 0.162 $N\beta$ at 65 kG (Figure 9). This value exceeds 0.077 $N\beta$ for θ^{21}-(BEDT-TTF)$_3$[Cu_2(m-C_2O_4)$_3$]·2CH_3OH, 0.076 $N\beta$ of θ^{21}-(BETS-TTF)$_3$[Cu_2(μ-C_2O_4)$_3$]·2CH_3OH, and 0.040 $N\beta$ of [(C_3H_7)$_3$NH]$_2$[Cu_2(μ-C_2O_4)$_3$]·2.2H_2O at 2 K and 65 kG [16,17,18]. The solvent molecules in the honeycomb lattice play a crucial role in the magnetism of organic-inorganic hybrids.

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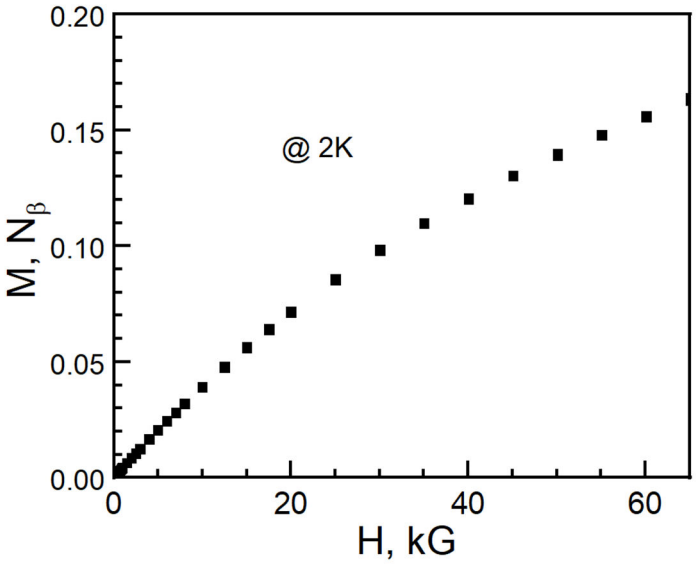

Figure 8. Isotheromal magnetizaion of **I** at 2 K.

3. Conclusions

It is an organic-inorganic hybrid charge-transfer salt made up of a θ^{21}-phase organic donor layer and an inorganic sheet featuring a honeycomb lattice. The Jahn-Teller effect on magnetism of organic-inorganic hybrid charge-transfer salts from solvent molecules hosted in honeycomb Cu-oxalate-framework was studied. It shows semiconducting behavior with $E\alpha$ = 40 meV. An antiferromagnetic interaction with the spin frustration as f > 10, and no long range order observed above 2 K. It is a semiconducting quantum spin liquid candidate.

Supplementary Materials: Table S1: The crystallography data of θ^{21}-(BEDT-TTF)$_3$[Cu$_2$(m-C$_2$O$_4$)$_3$]·2CH$_3$OH and θ^{21}-(BETS-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)$_3$]·2CH$_3$OH at 290 K. Table S2: The bond lengths of the TTF core in BEDT-TTF of **I**.

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Conflicts of Interest: The authors declare no conflict of interest.

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