

Communication



Two One-Dimensional Copper-Oxalate Frameworks with the Jahn–Teller Effect: $[(CH_3)_3NH]_2[Cu(\mu-C_2O_4)(C_2O_4)]\cdot 2.5H_2O$ (I) and $[(C_2H_5)_3NH]_2[Cu(\mu-C_2O_4)(C_2O_4)]\cdot H_2O$ (II)

Bin Zhang ^{1,*}, Yan Zhang ², Zheming Wang ^{3,*}, Yang Sun ⁴, Tongling Liang ⁴, Mei Liu ⁴ and Daoben Zhu ^{1,*}

- ¹ Organic Solid Laboratory, BNLMS, CMS & Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
- ² Department of Physics, Institute of Condensed Material Physics, Peking University, Beijing 100871, China; zhang_yan@pku.edu.cn
- ³ State Key Laboratory of Rare Earth Materials Chemistry and Applications, BNLMS, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China
- ⁴ BNLMS, CMS & Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
- * Correspondence: zhangbin@iccas.ac.cn (B.Z.); zmw@pku.edu.cn (Z.W.); zhudb@iccas.ac.cn (D.Z.)

Abstract: Two one-dimensional oxalate-bridged Cu(II) ammonium salts, $[(CH_3)_3NH]_2[Cu(\mu-C_2O_4)(C_2O_4)]\cdot 2.5H_2O$ (I) and $[(C_2H_5)_3NH]_2[Cu(\mu-C_2O_4)(C_2O_4)]\cdot H_2O$ (II) were obtained and characterized. They were composed of ammonium: $(CH_3)_3NH^+$ in (I), $(C_2H_5)_3NH^+$ in (II), $[Cu(\mu-C_2O_4)(C_2O_4)^{2-}]_n$ and H_2O . The Jahn–Teller-distorted Cu(II) is octahedrally coordinated by six O atoms from three oxalates and forms a one-dimensional zigzag chain. The hydrogen bonds between ammonium, the anion and H_2O form a three-dimensional network. There is no hydrogen bond between the anion chains. They were insulated at 20 °C with a relative humidity of 40%. Ferromagnetic and weak-ferromagnetic behaviors were observed in I and II, separately. No long-range ordering was observed above 2 K.

Keywords: Jahn-Teller effect; Cu(II); oxalate; crystal structure; conductivity; magnetism

1. Introduction

The Jahn–Teller effect plays an important role in inorganic superconductors and colossal magneto-resistance materials [1–9]. Interesting conductivity and magnetic behaviors are expected when the Jahn–Teller effect exists in molecular crystals, such as metal–organic frameworks. Oxalate $(C_2O_4^{2-})$, as one of the most commonly used short connectors, plays a key role in molecular-based magnets [10–12]. Long-range ordering has been reported in metal–oxalate framework compounds from one-dimensional zigzag chains (K₂Fe(μ -C₂O₄)(C₂O₄), K₂Co(μ -C₂O₄)(C₂O₄), Co(μ -C₂O₄)(μ -HOC₃H₆OH), TTF[Fe(μ -C₂O₄)Cl₂] and κ -BETS₂[Fe(μ -C₂O₄)(Cl₂O₄)] to two-dimensional honeycomb lattices ([(C₄H₉)₄N][CrMn(μ -C₂O₄)₃], A[M^{II}Fe^{III}(μ -C₂O₄)₃] (A = ammonium; M = Mn, Fe), [C₅H₁₀N₃O]₂[Fe₂(μ -C₂O₄)(H₂O)_{0.25}, [Z^{II}(bpy)₃][M^{II}Cr^{III}(μ -C₂O₄)₃][ClO₄] (M = Mn, Fe, Co, Ni) and (Me₄N)₆[Mn₃Cr₄(μ -C₂O₄)₁₂] ·6H₂O), while a single chain magnet [C₁₂H₂₄O₆K]_{0.5}[(C₁₂H₂₄O₆)(FC₆H₄NH₃)]_{0.5}[Co(H₂O)₂ Cr(μ -C₂O₄)(C₂O₄)₂] has been reported [13–29].

Quantum spin liquid is an intriguing magnetic state, where spin ordering or freezing prevents spin frustration in a resonating valence bond (RVB) state. In 1979, P. W. Anderson proposed the RVB state in S = 1/2, a two-dimensional triangular lattice [30]. In 1987, he proposed that La₂CuO₄ is a parent compound of cuprate superconductors. The antiferromagnetic insulator La₂CuO₄ turns into a diamagnetic superconductor after hole doping,



Citation: Zhang, B.; Zhang, Y.; Wang, Z.; Sun, Y.; Liang, T.; Liu, M.; Zhu, D. Two One-Dimensional Copper-Oxalate Frameworks with the Jahn–Teller Effect: $[(CH_3)_3NH]_2$ $[Cu(\mu-C_2O_4)(C_2O_4)]\cdot 2.5H_2O$ (I) and $[(C_2H_5)_3NH]_2[Cu(\mu-C_2O_4)$ $(C_2O_4)]\cdot H_2O$ (II). *Magnetochemistry* **2023**, *9*, 120. https://doi.org/ 10.3390/magnetochemistry9050120

Academic Editor: Carlos J. Gómez García

Received: 20 March 2023 Revised: 27 April 2023 Accepted: 27 April 2023 Published: 29 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). and a quantum spin liquid with Jahn–Teller distortion on Cu(II) is an indispensable magnetic state [31]. The spin-frustrated copper-oxalate framework with Jahn–Teller distortion supports a platform for molecular-based quantum spin liquids [32,33]. Strong antiferromagnetic interactions without a long-range ordering above 2 K with spin frustration were observed in two-dimensional honeycomb lattices: θ^{21} -(BEDT-TTF)₃[Cu₂(μ -C₂O₄)₃]·2CH₃OH, θ^{21} -(BETS-TTF)₃[Cu₂(µ-C₂O₄)₃]·2CH₃OH, [(C₃H₇)₃NH]₂[Cu₂(µ-C₂O₄)₃]·2.2H₂O, hydrogenbonded square lattice β'' -(BEDT-TTF)₃[Cu₂(μ -C₂O₄)(C₂O₄)₂(CH₃OH)(H₂O)], and threedimensional hyperhoneycomb lattice $[(C_2H_5)_3NH]_2[Cu_2(\mu-C_2O_4)_3][34-38]$. $[(C_2H_5)_3NH]_2$ $[Cu_2(\mu-C_2O_4)_3]$, which is a quantum spin liquid with no long-range ordering was observed until 60 mK [39]. In these compounds, the antiferromagnetic behavior depends on the antiferromagnetic interaction between the ferromagnetic couple. The magnetic structure of $[(C_2H_5)_3NH]_2[Cu_2(\mu-C_2O_4)_3]$ is lower than the three-dimensional, with the coexistence of ferromagnetic and antiferromagnetic interactions between Jahn-Teller distorted Cu(II) [37,39]. Researching the magnetic properties of Jahn–Teller distorted onedimensional copper-oxalate frameworks $[Cu(\mu-C_2O_4)(C_2O_4)_2^{2-}]_n$ without the hydrogen bond between anions will help us to quantitatively analyze the magnetic interaction in Jahn-Teller-distorted two-dimensional and three-dimensional copper-oxalate frameworks and design new candidate quantum spin liquids. Two one-dimensional copper-oxalate framework compounds, $[(CH_3)_3NH]_2[Cu(\mu-C_2O_4)(C_2O_4)] \cdot 2.5H_2O(I)$ and $[(C_2H_5)_3NH]_2[Cu(\mu-C_2O_4)(C_2O_4)] \cdot 2.5H_2O(I)$ $(C_2O_4)(C_2O_4)$]·H₂O (II), have been obtained and characterized. The related work is presented here.

2. Experiment

[(CH₃)₃NH]₂[Cu(μ -C₂O₄)(C₂O₄)]·2.5H₂O (I) and [(C₂H₅)₃NH]₂[Cu(μ -C₂O₄)(C₂O₄)]·H₂O (II) were obtained from a methanol solution of Cu(NO₃)₂·3H₂O and H₂C₂O₄·2H₂O with (CH₃)₃N for I and (C₂H₅)₃N for II in a 1:3:5 ratio at room temperature. Bulk blue plateful crystals of I and II were obtained after four weeks. The crystal was washed with CH₃COOC₂H₅ and dried. Elemental analysis calculated (%) for C₁₀H₂₅CuN₂O_{10.50} (I): C 29.67, H 6.22 and N 6.92 and found C 29.87, H, 6.08 and N 6.97. For C₁₆H₃₄CuN₂O₉ (II): C 41.60, H 7.42, N 6.06 and found C 42.03, H 7.46 and N 6.11.

Elemental analyses of carbon, hydrogen and nitrogen were performed using the Flash EA 1112 elemental analyzer. The IR spectra were recorded on a Bio-rad FTS6000/UMA500 spectrometer (Figure S1). Thermogravimeter analysis was carried out on a Shimadzu DTG-60 analyzer at a 10 °C/min heating rate from room temperature to 550 °C under N₂ gas with an Al bag. I remains stable until 40 °C, and II remains stable until 80 °C.

X-ray powder diffraction was carried out using a Rigaku RINT2000 diffractometer at room temperature with Cu K α radiation (λ = 1.54056 Å) in a flat-plate geometry (Figures S2 and S3).

Single-crystal X-ray diffraction was carried out on an Enraf-Nonius KappaCCD diffractometer at room temperature. The crystal structure was solved using the direct method and refined using the full-matrix least square on F^2 using the SHELX program, with anisotropic thermal parameters for all non-hydrogen atoms [40]. The hydrogen atoms on C and N were located through calculation, and on H₂O they were located through a difference Fourier map. All of the H were refined isotropically. The crystallographic data are listed in Table S1.

The resistance measurement was performed on a single crystal at Tonghui TH2828. Gold wires were attached to the best developed surfaces of a single crystal with a size of 0.40 * 0.30 * 0.11 mm (I) and 0.71 * 0.60 * 0.17 mm (II) using gold paste. The two-probe conductivity was measured at 20 °C and a relative humidity (RH) of 40%.

Magnetization measurements were performed on a polycrystalline sample tightly packed into a capsule on a Quantum Design MPMS 7XL SQUID system above 2 K. Susceptibility data were corrected for the diamagnetism of the sample by Pascal constants and background by experimental measurement of the sample holder [41]. Temperaturedependent magnetization was performed under an applied field of 1000 G. Isothermal magnetization was measured at 2 K from 0 to 65 kG.

3. Result and Discussion

I crystallizes in a triclinic system with space group $P \overline{1}$. There are two (CH₃)₃NH⁺, one Cu²⁺, one oxalate anion, two half-oxalate anions and one-and-a-half H₂O coexisting in an independent unit (Figure 1). Cu²⁺ is coordinated to two O atoms from one bidentate oxalate (O1 and O2) and four O atoms from two disbidentate oxalates in the Q₃ Jahn–Teller distortion mode of a CuO₆ octahedron [8].



Figure 1. Atomic structure of **I** in an independent unit with scheme label and 50% ellipsoids. Asymmetry code for C3A, O5A, O6A: 2 - x, 2 - y, -z; C4A, O7A, O8A: 1 - x, 1 - y, -z; H15A: -x, 2 - y, -z.

The Cu–O distances are 1.954(2)~1.992(2) Å on the equatorial plane and 2.292(2) Å, 2.329(2) Å from the apex as a result of the Jahn–Teller distortion. The elongated Cu–O bonds (Cu1–O6, Cu1–O8) on the Jahn–Teller-distorted octahedron around Cu²⁺ are highlighted with solid black lines (Figure 2). The cis O–Cu–O angles are 77.73° and 77.12° for the bridged oxalate, 83.56° for the terminal oxalate, and 90.70°, 98.89°, 90.31°, 96.85°, 93.12° and 100.68° among the terminal and bridged oxalate. The trans O–Cu–O angles are in the range of 161.01(6)~171.46(6)°. The axial Cu to oxalate-oxygen angles are 109.17° (Cu1–O6–C3) and 108.27° (Cu1–O8–C4). A one-dimensional zigzag [Cu(μ -C₂O₄)(C₂O₄)^{2–}]_n is formed along the *b* axis.



Figure 2. The zigzag anionic chain in I.

The one-dimensional $[Cu(\mu-C_2O_4)(C_2O_4)^{2-}]_n$ zigzag chain running along the *b* axis is separated by $(CH_3)_3NH^+$ (N1) along the *c* axis, and there are hydrogen bonds N–H···O, C–H···O between the cation and the out O atom in the oxalate. The anionic sheets composed of a $[Cu(\mu-C_2O_4)(C_2O_4)^{2-}]_n$ chain and $(CH_3)_3NH^+$ in a 1:1 ratio are separated by a cation layer composed of a zigzag $(CH_3)_3NH^+$ (N2) chain and a zigzag H_2O chain along the *c* axis. There are hydrogen bonds between neighboring H_2O molecules. Five H_2O molecules formed a hydrogen-bond $[H_2O]_5$ linear cluster along the *c* axis (Figure 3).



Figure 3. Arrangement of $(CH_3)_3NH^+$ and H_2O in cation layer of **I**. Dashed yellow lines are hydrogen bonds between H_2O in $[H_2O]_5$.

At last, the hydrogen bonds N–H···O and C–H···O between the ammonium and the inner O of the terminal and bridged oxalate, the O–H···O between H₂O and the oxalate, and the O–H···O between the H₂O molecules form a three-dimensional hydrogen-bonded network in crystal (Figure 4). There is no hydrogen bond between the anions.



Figure 4. Packing diagram of I viewed along the *b* axis. Dash yellow lines are hydrogen bonds. Color code: Cu, cyan; O, red; C, white; N, blue; H, light grey.

II crystallizes in a monoclinic system with the space group $P2_1/c$. There are two $(C_2H_5)_3NH^+$, one Cu^{2+} , one and two half oxalates, and one H_2O in an independent unit (Figure 5). The Cu^{2+} is octahedrally coordinated by six O atoms from two bisbidentate oxalates and one bidentate oxalate, as in I, with Cu–O distances of 1.960(2)~1.999(2) Å on the equatorial plane, and Cu1–O8: 2.314(2) Å and Cu1–O7: 2.368(2) Å from the apex. The Cu–O distances of II in the equatorial plane are shorter than the direction of the apex as a result of the Q₃ Jahn–Teller distortion mode, as in I. The cis–O–Cu–O angles are 75.93° and 77.79° for the bridged oxalate, 88.31° for the terminal oxalate and 92.34°, 93.72°, 95.98°, 89.66°, 95.48° and 102.48° between the terminal and bridged oxalate. The trans-O–Cu–O angles are in the range of 160.21(7)~172.64(7)°. The axial Cu to oxalate-oxygen angles are 108.09° (Cu1–O1–C3) and 108.53° (Cu1–O8–C4). The Cu–O distances and O–Cu–O angles in I and II are in the same range of the Cu–oxalate coordination polymer [29,30,34,35,37,38]. A one-dimensional oxalate-bridged zigzag [Cu(μ -C₂O₄)(C₂O₄)^{2–}]_n chain is formed along the *b* axis.



Figure 5. ORTEP drawing of **II** in an independent unit with scheme label and 50% ellipsoids. Asymmetry code for C3A, O5, O7: -x, -y, 1 - z; C4A, C6A, C8A: -x, 1 - y, 1 - z.

The zigzag chain in **I** and **II** is centrosymmetric with the inversion center located at the middle point of the oxalate bridge; thus, the metal sites have a $\Delta \Lambda \Delta \Lambda$ configuration along the *b* axis in **I** and **II** (Figure 6). It is similar to $[(CH_3)_4N]_2Cu(C_2O_4)_2(H_2O)$ [42,43]. The hydrogen bonds between ammonium and the anion and H₂O and the anion influence the bond length of the CuO₆ octahedron due to the Jahn–Teller distortion. Due to the magnetic orbitals of dx² – y² on Cu(II) with the unpaired electrons parallel to each other and the axial Cu to oxalate-oxygen angles, which are sensitive to magnetic interaction and smaller than 109.5°, a ferromagnetic interaction was expected [43,44].



Figure 6. The zigzag anionic chain in II.

In II, the $[Cu(\mu-C_2O_4)(C_2O_4)^{2-}]_n$ chain is surrounded by zigzag chains of $(C_2H_5)_3NH^+$ and H₂O. A pair $(C_2H_5)_3NH^+$ column separates two zigzag chains along the *c* axis. There are hydrogen bonds between the N of the ammonium and the O on the bridged oxalate: N1– H1···O5 2.10 Å/146.9°, N1–H1···O8 2.44 Å/131.7°. There are hydrogen bonds between the N of the ammonium and the O on the terminal oxalate: N2–H2···O3 2.20 Å/139°, N2–H2···O4 2.21 Å/143.1°. There are hydrogen bonds between H₂O and the terminal oxalate: O9–H4···O3 2.11 Å/159°, O9–H3···O4 2.20 Å/164°. There are hydrogen bonds between ammonium and H₂O: C8–H8C···O1 2.45 Å/174°; C15–H15A···O8 2.40 Å/155°. The hydrogen bond forms a two-dimensional (2D) network on the (201) plane (Figure 7). There is no hydrogen bond between the one-dimensional [Cu(μ -C₂O₄)(C₂O₄)^{2–})]_n chains.

On the basis of the hydrogen bonded cation layer, the resistance, as the proton conductivity under different relative humidities (RH), was measured. Depending on the thermal dynamic analysis, I and II dehydrate at 40 °C (I) and 76 °C (II), losing H₂O, with a relative weight of 11.2% in I and 4% in II; therefore, the experiment should be carried out below 40 °C (Figure 8). When the RH increased, the conductivity of I and II increased. Under a relatively high RH, the surfaces of the crystal were covered with debris at first, which was solvable in gel. Although the sample was restored to a solid state when the RH decreased and reached the same value as the beginning, the sample turned out to be in a polycrystalline state but not a single crystal. When a single crystal of I or II was exposed to air under a low relative humidity, such as when the relative humidity was lower than 35%, guest molecules, such as H₂O, in I and II would escape from the crystal, leading to crystalline collapse. The crystal surface remained transparent and clear after measurements at 20 °C and an RH of 40%. The resistance comes from the intrinsic behavior of the crystal. The resistance is $1 \times 10^9 \ \Omega$ ·cm in I and $1 \times 10^7 \ \Omega$ ·cm in II. They are insulators.



Figure 7. Arrangement of $(C_2H_5)_3NH^+$, zigzag $[Cu(\mu-C_2O_4)(C_2O_4)^{2-}]_n$ chain and H_2O on twodimensional hydrogen-bond network viewed along the *b* axis in **II**. Dashed yellow lines are hydrogen bonds. Color code: Cu, cyan; O, red; C, white; N, blue; H, light grey.



Figure 8. Schematic TGA curves of I and II. Above 300 °C, the final residue is CuO.

On the basis of the oxalate-bridging and Jahn–Teller distortion of the Cu(II) ion, Cu(II) in an independent unit, and the magnetic properties were studied per Cu²⁺/mol.

At 300 K, the χT value of I was 0.473 cm³ K mol⁻¹ and g = 2.25. It is higher than 0.375 cm³ K mol⁻¹ for an isolated, spin only Cu(II) ion with S = 1/2, g = 2.00 and in the range of Cu²⁺ compounds [34–37,45,46]. The χT value remained stable at 0.478 cm³ K mol⁻¹ at 40 K and increased slowly, reaching 0.71 cm³ K mol⁻¹ at 2 K. No bifurcation is observed from zero-field-cool magnetization and field-cooled magnetization (ZFCM/FCM) measurements from 2 K to 100 K under 100 G (Figure S4). The magnetic data were fitted with the Curie–Weiss law from 2 to 300 K: C = 0.4711(2) cm⁻¹·K/mol, $\theta = 0.61(6)$ K and $R = 1.37 \times 10^{-5}$. It suggests a ferromagnetic interaction in I (Figure 9) [47,48].

A one-dimensional Baker–Rushbrooke–Gilbert model was used to fit the temperaturedependent magnetization above 2 K, yielding J = 0.60(2) cm⁻¹, g = 2.31(1) and $R = 9.2 \times 10^{-4}$ (Figure 10) [49]. It shows an intrachain ferromagnetic interaction and corresponds with the Curie–Weiss fitting.

At 2 K, the isothermal magnetization (M) saturated at 1.11 N β (N is Avogadro's number and β is the Bohn magneton, 1 N β = 5585 cm⁻¹ G mol⁻¹) at 65 kG (Figure 11). The average anisotropic *g*-factor calculated from isothermal magnetization at 2 K is 2.22. It is in the range of 2.25 from χT at 300 K and 2.31 from Baker–Rushbrooke–Gilbert model fitting.



Figure 9. χT vs. *T* (left, black empty square), $1/\chi$ vs. *T* (right, black empty circle) and Curie–Weiss fitting data (red solid) of **I**.



Figure 10. Temperature-dependent susceptibility of **I**. Black empty square is experimental data. Red solid curve is the best fit from the Baker–Rushbrooke–Gilbert model.



Figure 11. Isothermal magnetization of I at 2 K.

In **II**, the χT value was 0.443 cm³ K mol⁻¹ at 300 K with a *g*-factor of 2.13. It is higher than the 0.375 cm³ K mol⁻¹ of an isolated, spin only Cu(II) ion with S = 1/2, g = 2.00. It is in the range of Cu²⁺ compounds, as in **I** [34–37,45,46]. As the temperature decreased, the

 χT value decreased slowly to 0.393 cm³ K mol⁻¹ around 30 K, and then increased, reaching 0.446 cm³ K mol⁻¹ at 2 K (Figure 12). No bifurcation was observed in the ZFCM/FCM measurement from 2 K to 100 K under 100 G (Figure S5). The magnetic data were fitted with Curie–Weiss law from 80 to 300 K with C = 0.462(1)) cm⁻¹·K/mol, g = -14.2(4) K and $R = 3.8 \times 10^{-5}$ (Figure 12).



Figure 12. *cT* vs. *T* (left, black empty square), 1/*c* vs. *T* (right, black empty circle) and Curie–Weiss fitting data (red solid) of **II**.

A one-dimensional Baker–Rushbrooke–Gilbert model combined with exchange coupling was used to fit the temperature-dependent magnetization from 2 to 300 K with $J = 0.87(2) \text{ cm}^{-1}$, g = 2.035(3), $zJ = -0.65(2) \text{ cm}^{-1}$ and $R = 6.76 \times 10^{-5}$ (Figure 13) [50]. It shows that intrachain ferromagnetic interaction is stronger than intrachain antiferromagnetic interaction. The *g*-factor is in the range of 2.13 from χT at 300 K.



Figure 13. Temperature-dependent susceptibility of **II**. Empty solid square, is experimental data. Red solid curve is best fit from the Baker–Rushbrooke–Gilbert model with exchange coupling.

At 2 K, the magnetization increases with increasing field and is saturated at 0.89 N β at 65 kG (Figure 14). The average anisotropic *g*-factor calculated from isothermal magnetization at 2 K is 1.78. Its magnetic behavior is not the same as expected. This means the Jahn–Teller effect is important to the magnetic property of the copper-oxalate framework. This is different from the compounds [CrMn(C₂O₄)₃⁻]_n, where in the ferromagnetic order, temperature and isothermal magnetization at 2 K are the same as those taken from ammonium salts to charge-transfer salts [19,51,52]. Depending on the difference in magnetic

behaviors between I and II, the Jahn–Teller effect will help us to obtain molecular-based candidate quantum spin liquid and to look for a new superconductor and colossal magnetoresistance material from copper-oxalate frameworks as cuprate superconductors and colossal magnetoresistance material.



Figure 14. Isothermal magnetization of II at 2 K.

4. Conclusions

Two one-dimensional copper-oxalate framework compounds were obtained and characterized. The hydrogen bonds among ammonium, H₂O and the copper-oxalate framework form a three-dimensional hydrogen-bond network, and there is no hydrogen bond between the one-dimensional $[Cu(\mu-C_2O_4)(C_2O_4)^{2-}]_n$ chains. The Q₃-mode Jahn–Teller distortion of elongated CuO₆ octahedrons is observed. They are insulators. The Jahn–Teller effect results the ferromagnetic and weak-ferromagnetic interaction between Cu(II) in I and II. No long-range ordering is observed above 2 K.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/magnetochemistry9050120/s1, Table S1. Crystallographic data of I and II; Figure S1. IR spectra on crystalline I (top) and II (bottom); Figure S2. Experimental X-ray powder diffraction pattern of crystalline sample and simulated one based on single crystal structure of I. I shows preferred orientation; Figure S3. Experimental X-ray powder diffraction pattern of crystalline sample and simulated one based on single crystal structure of II; Figure S4. ZFCM/FCM of polycrystal of I under 100 G; Figure S5. ZFCM/FCM of polycrystal of II under 100 G.

Author Contributions: The manuscript was written with the contributions of all authors. Funding acquisition: B.Z., D.Z. and Y.Z. Synthesized the sample: Y.Z. Performed the magnetic measurements: Z.W. Performed the single-crystal X-ray diffraction experiments: T.L., Y.S. and M.L. Performed the X-ray experiments and data analysis: B.Z. Conducted experiments: B.Z. and Z.W. Analyzed the data: B.Z., Y.Z. and Z.W. Wrote the main manuscript text. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China: 22273109, 22073106, 21573242 and 21173230 and the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (Grant No. XDB12030100).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The IR spectra, powder X-ray diffraction pattern and ZFCM/FCM of I and II are available in the Supplementary Materials.

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

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