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Article

An Uneven Chain-like Ferromagnetic Copper(II) Coordination Polymer Displaying Metamagnetic Behavior and Long-Range Magnetic Ordering

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Abstract: Ferromagnetic coupling exists in an uneven chain-like copper(II) complex with both end-on azido and *syn-syn* carboxylato bridges, $(Cu_3(L)_2(N_3)_4(H_2O)_3)_n$ (**1**, HL = 6-hydroxynicotinic acid). It is the first example of one-dimensional (1D) chain-like copper(II) coordination polymer showing both metamagnetic behavior and long-range magnetic ordering (T_c = 6.7 K), thanks to the interchain hydrogen bonds, which make a three-dimensional (3D) supramolecular array of the entire molecular structure and mediate the interchain antiferromagnetic interaction.

Keywords: copper(II) coordination polymer; azido; ferromagnetic interaction; chain-like complex; magnetic ordering

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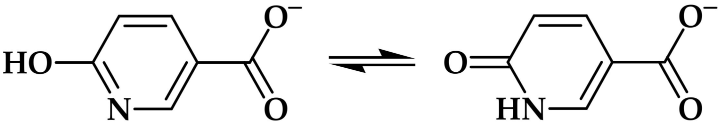
1. Introduction

Molecular magnets have attracted considerable attention during the past decades by virtue of their novel properties and promising applications in fields such as information storage [1–5]. One of the great challenges is the rational design of molecular-based materials exhibiting spontaneous magnetization. Though a pure one-dimension (1D) system cannot create long-range magnetic ordering at $T > 0$ K [1], many essentially 1D compounds exhibiting the spontaneous magnetization have been explored through elaborate control of both intra- and interchain interactions, which include quasi-1D donor-acceptor stack compounds $(Fe(C_5Me_5)_2)(TCNE)$ [6] and $(Mn(C_5Me_5)_2)(TCNQ)$ [7], Mn(II)-Cu(II) [8–10] and Co(II)-Cu(II) [11] chain-like complexes, Mn(II)-nitronyl nitroxide chain complexes [12,13], and 1D radical complex $\{Mn^{III}(porphyrin)\}^+(TCNE)^{\bullet-}$ [14]. However, most 1D coordination polymer molecular magnets [8–14] belong to heterospin systems; few structurally characterized 1D homospin coordination polymers can exhibit magnetic ordering [15–18].

To date, it is still quite difficult to obtain 1D copper(II) coordination polymer molecular magnet due to its small local spin value ($S_{Cu} = 1/2$). Obviously, enlarging the spin ground state through the ferromagnetic interaction is a promising approach to obtaining such a molecular magnet. One strategy involves the rational design of an uneven copper(II) chain, in which several copper(II) atoms are linked to each other by mixed bridges to form polynuclear copper(II) subunit, yielding a larger spin ground state through the ferromagnetic interaction, then the subunits are carefully assembled together. To achieve such a design, a reasonable choice of bridging ligands is of ultimate importance, because they can determine the strength and type of the magnetic coupling. Furthermore, a suitable complementary organic ligand is also necessary to handpick. The azido in the end-on (EO) coordination mode is an ideal inorganic bridge to connect with two neighboring metal (M) cations. The reason is that the M-N-M bond angle is less than 108° [19–32], or this angle is greater than 108° but the EO- azido bridge works synchronously with the *syn-syn* carboxylato bridge [33–36], in both cases it can mediate ferromagnetic coupling; while 6-hydroxynicotinate (Scheme 1) was utilized as the organic bridge: the proton in its hydroxyl group can be automatically transferred to the nitrogen atom of the pyridine ring (that is, autoisomerization), which avoids the latter taking part in the coordination role to form high dimensional networks, as those pyridine rings in nicotinate and isonicotinate do [37,38], furthermore, the dehydrogenated hydroxyl group can generate interchain hydrogen-bonds, mediating the interchain magnetic interactions. As a result of our attempts, such an uneven chain-like copper(II) complex, $(Cu_3(L)_2(N_3)_4(H_2O)_3)_n$ (HL = 6-hydroxynicotinic acid) (**1**) was obtained by self-assembly process. To the best of our knowledge, this is the first 1D chain azido-bridged copper(II) coordination polymer showing not only metamagnetic behavior but also long-range magnetic ordering.



Scheme 1. Autoisomerization of the single deprotonated 6-hydroxynicotinate anion.

2. Results

2.1. Crystal Structure

Complex **1** was self-assembled by the solution slow diffusion method in an *H*-shaped tube. Its structure and composition are different from the 1D chain-like product $(Cu_{1.5}(L)(N_3)_2(\mu^2\text{-}H_2O))_n$ and the trinuclear copper(II) product $Cu_3(L)_4(N_3)_2(H_2O)_3$ obtained by hydrothermal method [39]. A crystal structure determination revealed that complex **1** is a 1D chain-like complex crystallizing in the *P*-1 space group, which is composed of double EO-azido bridges connecting $(Cu_3(L)_2(N_3)_2(H_2O)_3)$ trinuclear units (Figure 1). The adjacent Cu^{2+} ions within the trinuclear unit are linked by one EO azido bridge and one *syn-syn* carboxylato bridge. There are two types of crystallographically independent copper(II) cations (Figure 1a): the Cu1 ion is located at the crystallographic inversion center, adopting a distorted octahedral (CuO_4N_2) coordination geometry, in which two equivalent carboxylato oxygen atoms (O2 and $O2^{\#1}$, $^{\#1}$ −x, −y + 1, −z + 1) from two L^- ligands (Cu1-$O_{carboxylato}$, 1.9659(18) Å, Table 1) and two equivalent nitrogen atoms (N2 and $N2^{\#1}$) from two EO-azido ligands (Cu1-N_{azido}, 2.009(2) Å, Table 1) generate the basal plane; while two equivalent water molecules (O1w and $O1w^{\#1}$) occupy two axial positions (Cu1-O_{water}, 2.307(3) Å, Table 1), showing a prominent Jahn–Teller elongation effect. The Cu2 ion exhibits a distorted square pyramid (CuO_3N_2) configuration, which is formed with one carboxylato oxygen atom ($O3^{\#1}$) from one L^- ligand (Cu2-$O_{carboxylato}$, 1.9346(19) Å, Table 1) and three nitrogen atoms (N2, N5 and $N5^{\#2}$, $^{\#2}$ −x + 1, −y + 2, −z + 1) from three EO-azido ligands (Cu2-N_{azido}, 1.981(2)–2.015(2) Å, Table 1) as the base, and the oxygen atom of the water molecule (O2w) occupying the apical site.

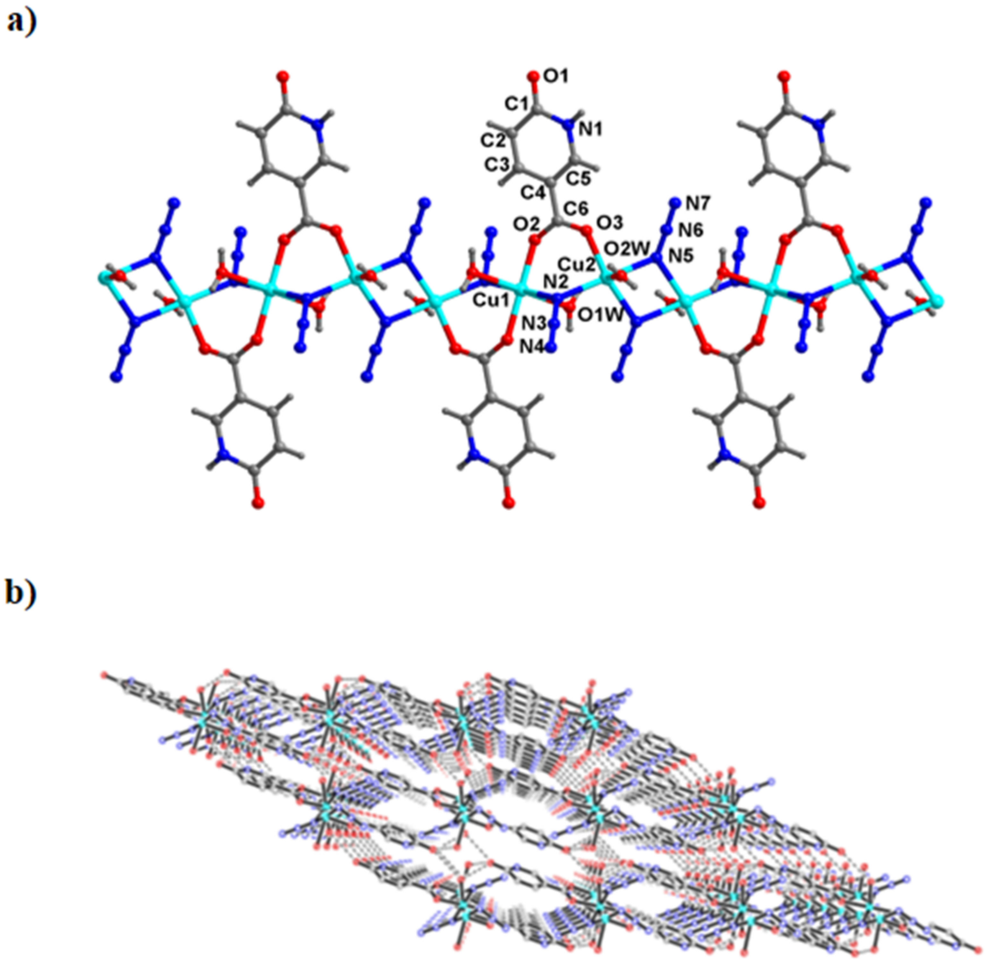


Figure 1. Section of the uneven chain of **1** (**a**) and the 3D supramolecular network formed by interchain hydrogen bonds (viewed down the 110 direction) (**b**).

Table 1. Selected bond lengths (Å) and angles (°) of **1**.

Cu1-N2	**2.009(2)**	**Cu1-N2 $^{\#1}$**	**2.009(2)**
Cu1-O1W	2.307(3)	Cu1-O1W $^{\#1}$	2.307(3)
Cu1-O2	1.9659(18)	Cu1-O2 $^{\#1}$	1.9659(18)
Cu2-N2	1.981(2)	Cu2-N5	2.015(2)
Cu2-N5 $^{\#1}$	2.015(2)	Cu2-O2W	2.246(2)
Cu2-O3 $^{\#1}$	1.9346(19)		
O2-Cu1-N2	87.50(9)	N2-Cu1-O1W	85.00(10)
O2-Cu1-O1W	87.32(10)	N2-Cu1-N2 $^{\#1}$	180.00(14)
O1W-Cu1-O1W $^{\#1}$	180.00(15)	N2-Cu2-N5	172.90(9)
N2-Cu2-O2W	92.56(10)	N5-Cu2-O2W	94.50(10)
Cu2-N2-Cu1	112.67(11)	Cu2-N5-Cu2 $^{\#2}$	100.19(9)

$^{\#1}$ −x, −y + 1, −z + 1; $^{\#2}$ −x + 1, −y + 2, −z + 1.

The trinuclear units ($Cu_3(L)_2(N_3)_2(H_2O)_3$) are connected with each other through double EO-azido bridges to generate a 1D copper(II) chain along the 110 direction (Figure 1b). The bond angle Cu(2)-N(5)-Cu(2)$^{\#2}$ involved with the double EO-azido bridges is 100.19(9)° (Table 1), smaller than the bond angle Cu(1)-N(2)-Cu(2) involved with the EO-azido/*syn-syn* carboxylato mixed bridges (112.67(11)°, Table 1), the latter is smaller than the Cu-N$_{\text{azido}}$-Cu angle in the trinuclear complex $Cu_3(L)_4(N_3)_2(H_2O)_3$ also containing the EO-azido/*syn-syn* carboxylato mixed bridges (116.2°) [39]. The intrachain Cu … Cu separations secluded by the double EO-azido bridges and the EO-azido/*syn-syn* carboxylato mixed bridges are

3.070 Å and 3.321 Å, respectively. It is noteworthy that **1** is a rare uneven chain copper(II) coordination polymer containing simultaneous azido/carboxylato bridges, because these two mixed bridges generally link to metal ions to form 1D uniform metal chains [33–38]. Another uneven chain-like copper(II) coordination polymer containing azido/carboxylato mixed bridges is $(Cu_{1.5}(L)(N_3)_2(\mu^2\text{-}H_2O))_n$ [39], which is formed by double EO-azido ligands bridging the trinuclear units $(Cu_3(L)_2\ (N_3)_2(\mu^2\text{–}H_2O)_2)$. In addition, uneven chain-like compounds containing other 3d metal clusters have also been used to construct single chain magnets [40].

There are two types of intermolecular hydrogen bonds between the dehydrogenated hydroxyl oxygen atom of the L^- ligand and two coordination water molecules from two neighboring chains (O2W ... O1$^{\#1}$, 2.759(3) Å and O1W ... O1$^{\#2}$, 2.907(3) Å, $^{\#1}$: x + 1, y + 2, z + 2; $^{\#2}$: x + 1, y + 1, z + 2) (Figure 1b), extending the structure into a 3D supramolecular array, with the separations between parallel chains of 7.75 Å and 10.10 Å, respectively. These weak interactions play important roles not only in stabilizing the crystal structure of **1** but also in mediating the interchain antiferromagnetic interaction.

2.2. Magnetic Properties

The thermal variation of χ and χT for **1** under a 1 kOe dc field in the temperature range of 2–300 K is shown in Figure 2. The value of χT at room temperature is 1.73 cm^3 K mol^{-1}, which is somewhat larger than that expected for three magnetically isolated copper(II) ions (1.24 cm^3 K mol^{-1} for g = 2.1). From room temperature down to 13 K, the χT product increases continuously to 3.83 cm^3 K mol^{-1} and then suddenly decreases to 0.77 cm^3 K mol^{-1} at 2 K. This suggests an overall intrachain ferromagnetic interaction with the presence of interchain antiferromagnetic interactions and/or zero-field splitting (ZFS) effect prevailing at low temperature. The magnetic susceptibility of **1** follows the Curie-Weiss law $\chi^{-1} = (T-\Theta)/C$ when $T \geq 50$ K, with C = 1.60 cm^3 K mol^{-1} and Θ = 21.86 K. The positive Θ value indicates that ferromagnetic interactions dominate.

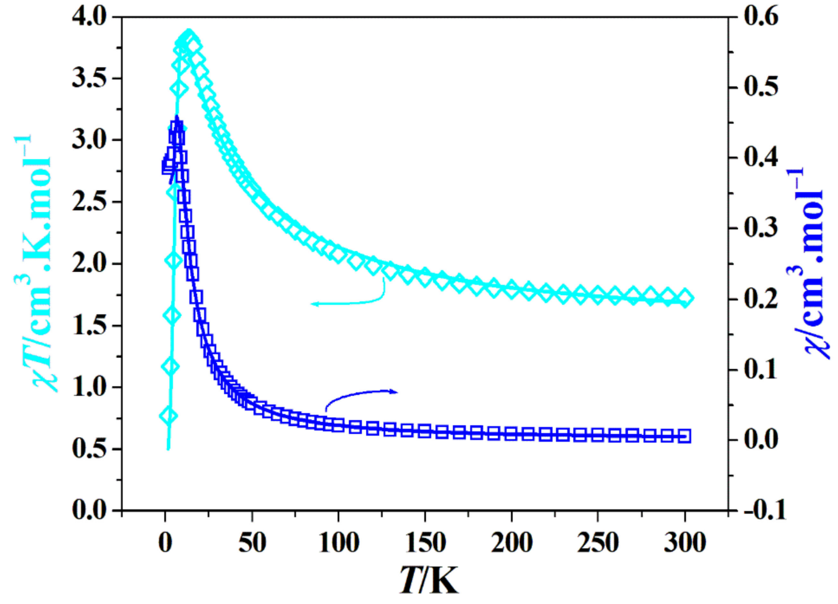


Figure 2. Plots of χT and χ versus T of **1** measured under a 1 kOe dc field. The solid lines represent the best theoretical fitting.

We attempted to simulate the magnetic data of **1** with rigorous models existing for the $S = 1/2$ trimeric chain [41] or the alternating chain J-J-J' in the classical limit [42]. However, no reasonable fitting results could be obtained. So, an approximate model method was utilized [43–47], where **1** is treated as a uniform chain with linear trinuclear $\{Cu_3\}$ as a subunit, for which $\hat{H} = -2J\ (\hat{S}_{Cu1}\hat{S}_{Cu2} + \hat{S}_{Cu1}\hat{S}_{Cu3})$ (for $\{Cu_3\}$) [48] and $\hat{H}$ =

$-2J_c\sum\hat{S}_{T,i}\hat{S}_{T,i+1}$ ($\hat{S}_T$ for {Cu_3} as a classical system [49]). The exchange parameter J reflects the exchange between two Cu(II) ions within the trinuclear {Cu_3} unit, J_c stands for the interunit magnetic interaction. Moreover, the interchain interaction was estimated by the mean field model, in which zJ' is used to calculate the inter-chain magnetic interaction. The following Equations (1)–(5) are derived from the above Hamiltonians and models.

$$\chi_t = \frac{Ng^2\beta^2}{4kT} \times \frac{1 + e^{2J/kT} + 10e^{3J/kT}}{1 + e^{2J/kT} + 2e^{3J/kT}} \tag{1}$$

$$\chi_t = \frac{Ng^2\beta^2}{3kT} S_t(S_t + 1) \tag{2}$$

From Equations (1) and (2), we can get

$$S_t(S_t + 1) = \frac{3}{4} \times \frac{1 + e^{2J/kT} + 10e^{3J/kT}}{1 + e^{2J/kT} + 2e^{3J/kT}} \tag{3}$$

Then, S_t (S_t + 1) is substituted into the following equation:

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT} \times \frac{1 + u}{1 - u} S_t(S_t + 1) = \frac{Ng^2\beta^2}{4kT} \times \frac{1 + u}{1 - u} \times \frac{1 + e^{2J/kT} + 10e^{3J/kT}}{1 + e^{2J/kT} + 2e^{3J/kT}} \tag{4}$$

where $u = \coth\left(\frac{J_c S_t(S_t + 1)}{kT}\right) - \frac{kT}{J_c S_t(S_t + 1)}$.

Finally, zJ' is introduced to the formula of molar susceptibility through the mean field model:

$$\chi_M = \frac{\chi_{chain}}{1 - (2zj'Ng^2\beta^2)\chi_{chain}} \tag{5}$$

The best fitting of the magnetic data gives J = 44.29 cm^{-1}, J_c = 3.57 cm^{-1}, zJ' = −3.22 cm^{-1} and g = 2.27 with $R = 7.2 \times 10^{-4}$ (Figure 2). The results indicate the magnetic exchange interaction through the EO-azido and *syn-syn* carboxylate mixed bridges is ferromagnetic. As known, it is expected to promote antiferromagnetic coupling for the *syn-syn* carboxylato bridge, and when the Cu-N_{azido}-Cu angle is larger than 108°, the EO-azido bridge favors antiferromagnetic interaction [19–26]. The ferromagnetic coupling within the trinuclear unit ($Cu_3(L)_2(N_3)_2(H_2O)_3$) of **1** are mediated by a *syn-syn* carboxylate bridge and an EO-azido bridge with the Cu-N_{azido}-Cu angle of 112.67(11)° (>108°), which can be ascribed to the contercomplementarity effect proposed by Thompson group [33] and Escuer group [34], respectively. According to molecular orbital calculations [34], the dx^2–y^2 orbitals, which allow two combinations of symmetric φ_S and antisymmetric φ_A, are the magnetically active orbitals of Cu^{2+} cations; owing to the contercomplementarity role of the ligand HOMOs, the energy gap (Δ) between the two molecular orbitals φ_S and φ_A is lower with respect to the interaction with two bridging ligands that normally mediate antiferromagnetic coupling. When the value of Δ is very low, a net ferromagnetic interaction from two 'antiferromagnetic' bridging ligands can be produced [34].

Notably, the J value in **1** (44.29 cm^{-1}) is similar in magnitude to those of the trinuclear complex $Cu_3(L)_4(N_3)_2(H_2O)_3$ also containing EO-azido/*syn-syn* carboxylate mixed bridges (34.85 cm^{-1}) [39] and the 1D chain-like coordination polymer $(Cu_{1.5}(L)(N_3)_2(\mu^2\text{–}H_2O))_n$ with EO-azido/*syn-syn* carboxylate/H_2O mixed bridges (44.5 cm^{-1}) [39], in which the Cu-N_{azido}-Cu angles are also larger than 108°; and the J values in these two complexes were obtained by density functional calculations [50]. The positive J_c value indicates that the magnetic exchange interaction through the double EO-azido bridges is ferromagnetic, which is in good agreement with the structural aspect that the corresponding Cu-N_{azido}-Cu angle (100.19(9)°) is smaller than 108°. Furthermore, the J_c value (3.57 cm^{-1}) is also within a reasonable range [50]; according to the density functional calculations [50], this J value is not only related to the Cu-N_{azido}-Cu angle, but also closely related to the Cu-N bond length and the τ value (defined as the out of-plane deviation of the azido group) [50]. In addition, the negative value of zJ' indicates that there are antiferromagnetic interactions among the 1D copper(II) chains.

Further magnetic investigation revealed that complex **1** possesses metamagnetic behaviour. The temperature dependence of the magnetic susceptibility at various fields is shown in Figure 3a. At a low field, the χ versus T curves all display a maximum, revealing the occurrence of an interchain antiferromagnetic coupling. Upon increasing the field, the maximum moves to lower temperatures and finally disappears when the applied magnetic field reaches 30 kOe, which overcomes the interchain antiferromagnetic interaction and a field-induced metamagnetic transition from an antiferromagnetic state to a ferromagnetic state happens. This metamagnetic behaviour is confirmed by the field dependence of magnetization measured at 2.0 K. Referred to the Brillouin function curve, the plot of M versus H shows a distorted sigmoidal shape (Figure 3b); and the critical field H_c (=3 T) is clearly shown as the deepest trough in the field dependence of d^2M/dH^2 (Figure S1), though the field correlation of dM/dH does not show a corresponding peak at 3 T (Figure S2). In addition, the value of the magnetization at 5 T (3.26 Nβ) is very close to 3.30 Nβ, the expected saturated magnetization value for the ferromagnetic Cu_3 system with $S_T = 3/2$ (supposing $g = 2.2$).

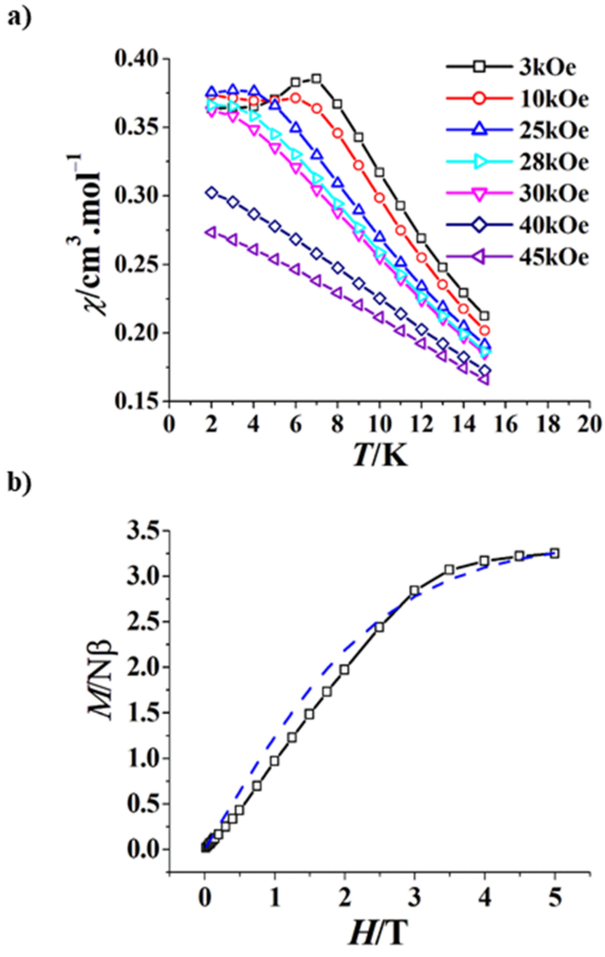


Figure 3. χ versus T plots of **1** at different fields (**a**) and magnetization (M) versus field (H) plot for **1** at 2.0 K, the dot line represents the magnetization calculated from the Brillouin function (**b**).

Interestingly, weak magnet behavior was observed at temperatures below 6.7 K. The divergence of the zero-field cooled (ZFC) and the field cooled (FC) susceptibilities below about 6.7 K indicates the irreversible behavior of long-range magnetic ordering (Figure 4a). A very small remnant magnetization (0.001 Nβ) and a small coercive field (18 Oe) can be detected at 2.0 K (Figures 4b and S3), suggesting that such a molecular magnet is weak and soft. Ac susceptibility measurements showed that χ' (T) are frequency-independent, which have a weak peak at 6.7 K for frequencies of 10–499 Hz, confirming that the long-range magnetic ordering appears at 6.7 K (Figure 5), that is, T_c = 6.7 K for **1**. However, χ'' is negligibly small for all corresponding frequencies, notably, the absence of χ'' in ac susceptibility at zero dc field has also been observed in other chain-like compounds exhibiting both metamagnetic behavior and magnetic ordering, [15,51,52] owing to the interchain antiferromagnetic interaction. When the temperature (7.0 K) is greater than 6.7 K, the *S* shape in the *M-H* curve observed at 2.0 K disappears (Figure S4). As a comparison, although another 1D uneven chain-like compound (Cu$_{1.5}$(L)(N$_3$)$_2$(μ^2–H$_2$O))$_n$ also exhibits ferromagnetic exchange [39], it seems to possess magnetic ordering behavior only at below 2.0 K. As we all know, in the absence of interchain interactions, the 1D magnetic system cannot create long-range magnetic ordering when $T > 0$ K [1,53,54], obviously, the interchain hydrogen bonds in **1** play a critical role in exhibiting long-range magnetic ordering through forming a 3D supramolecular array [18], though the interchain antiferromagnetic interaction may induce the metamagnetic behavior.

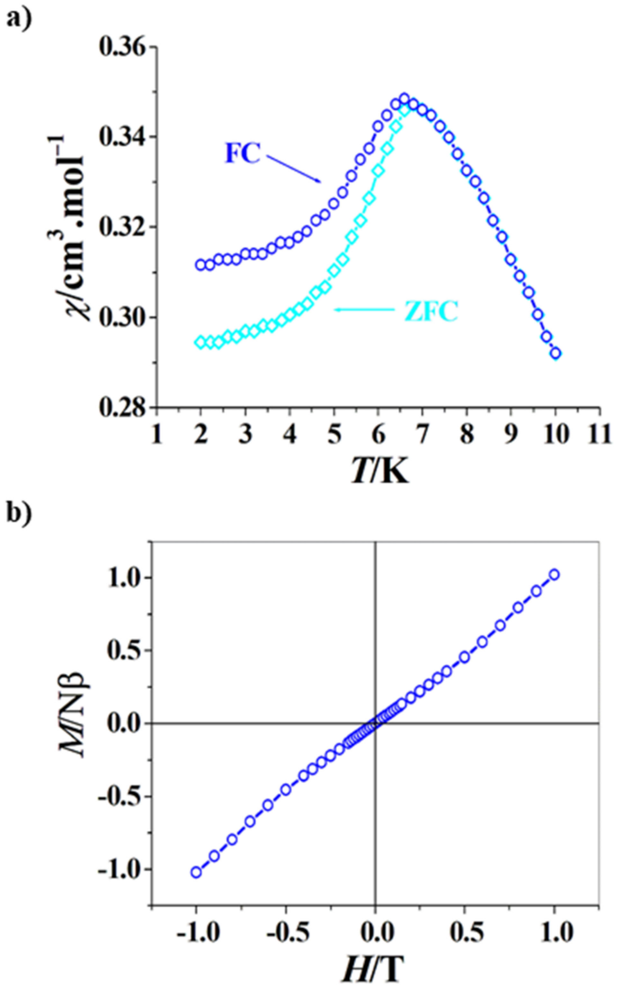


Figure 4. Plots of FC and ZFC susceptibilities versus temperature of **1** at an applied field of 20 Oe (**a**) and hysteresis loop for **1** at 2.0 K (**b**).

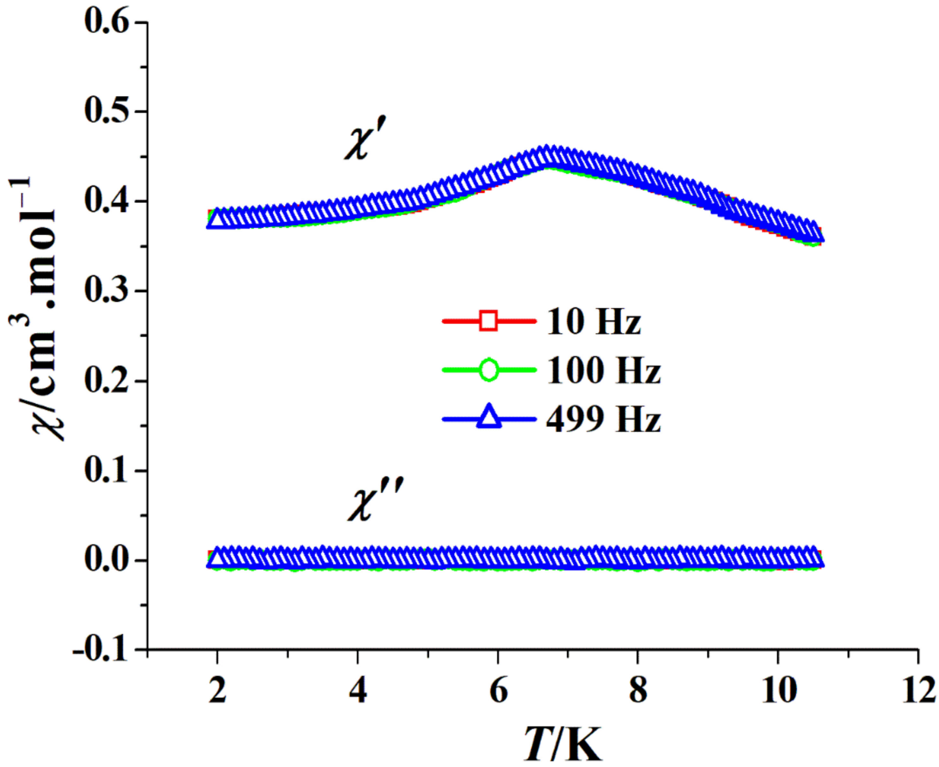


Figure 5. χ' versus T and χ'' versus T plots of **1** at different frequencies.

3. Conclusions

In summary, a 1D uneven chain-like copper(II) coordination polymer showing magnetic ordering has been synthesized and characterized, in which there are not only the double EO-azido bridges but also the azido/carboxylato mixed bridges for the construction of polynuclear subunit. Many interchain hydrogen bonds exist in this complex, which can transfer antiferromagnetic interactions, making this complex display metamagnetic behavior. This work demonstrates that it is feasible to assemble 1D copper(II) coordination polymer molecular magnets by constructing uneven ferromagnetic metal chains; the use of mixed bridging ligands is an important means to achieve this goal.

4. Materials and Methods

4.1. General Remarks

The elemental analyses were performed on a Heraeus Chn-Rapid elemental analyzer. The infrared spectra were recorded on a Pekin-Elmer 2000 spectrophotometer with pressed KBr disk. The magnetic susceptibility measurements were carried out on polycrystalline samples (20.7 mg) on a Quantum Design MPMS-XL5 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms.

4.2. Preparation of **1**

Next, 6-hydroxynicotinic acid (139 mg, 0.5 mmol), NaOH (20 mg, 0.5 mmol) and NaN_3 (65 mg, 1.0 mmol) were dissolved in an aqueous solution (5 mL) and put in one side of the H-tube. To the other side of this H-tube another aqueous solution (5 mL) containing $Cu(ClO_4)_2{\cdot}6H_2O$ (185 mg, 0.5 mmol) was added. Then methanol was carefully added until the solutions in both sides were bridged. Dark-green plate crystals of **1** crystallized after two months, which were collected and washed sequentially by water and methanol. Yield: 50% based on Cu. Anal. Calcd. (%) for $C_{12}H_{16}Cu_3N_{14}O_{10}$: C, 20.39; H, 2.28; N, 27.74%. Found: C, 20.41; H, 2.32; N, 27.72%. IR (KBr): ν = 3356(s), 2100(s), 2071(s), 1646(s), 1607(s), 1567(s), 1538(m), 1411(s), 1293(w), 1273(w), 1207(w), 1126(w), 787(w), 654(w) cm^{-1}.

Caution: $Cu(ClO_4)_2 \cdot 6H_2O$ and NaN_3 are potentially explosive and should be handled with care!

4.3. X-ray Crystallography

A crystal with dimensions 0.44 × 0.26 × 0.18 mm^3 of **1** was used in the intensity data collection on a Rigaku RAXIS RAPID IP imaging plate system with Mo-Kα radiation (λ = 0.71073 Å) at 298(2) K. The structure was solved by direct method and refined by a full matrix least-squares technique based on F^2 using the ShelXL-2015 refinement package. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined as riding atoms and/or located in difference Fourier maps. Selected crystal data and structural refinement parameters for **1** are listed in Table 2.

Table 2. Crystal data and structural refinement parameters for **1**.

	1
formula	$C_6H_8Cu_{1.5}N_7O_5$
F_W	353.50
crystal system	triclinic
space group	*P*-1
a [Å]	7.7542(16)
b [Å]	8.5924(17)
c [Å]	10.103(2)
α [°]	102.91(3)
β [°]	98.26(3)
γ [°]	112.56(3)
V [$Å^3$]	586.0(2)
Z	2
ρ_{calc} [$g \cdot cm^{-3}$]	2.004
μ [mm^{-1}]	2.780
T [K]	298(2)
λ [Å]	0.71073
reflections collected	5236
unique reflections	2616
observed reflections	2155
parameters	193
GoF	1.020
R_1 [$I \geq 2\sigma(I)$]	0.0293
$_WR_2$ [$I \geq 2\sigma(I)$]	0.0692

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/magnetochemistry8010002/s1, Figure S1: Field dependence of d^2M/dH^2 based on magnetization (M) versus field (H) plot for **1** at 2.0 K; Figure S2: Field dependence of dM/dH based on magnetization (M) versus field (H) plot for **1** at 2.0 K; Figure S3: Expansion of hysteresis region of **1** at 2.0 K; Figure S4: Magnetization (M) versus field (H) plot for **1** at 7.0 K. CCDC 651787 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk.

Author Contributions: C.-M.L. designed and was responsible for the project; synthesized and characterized the complex; analyzed magnetic data; wrote and revised the manuscript. Y.S. performed magnetic measurements, analyzed and discussed magnetic properties. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available in Supplementary Materials.

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

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