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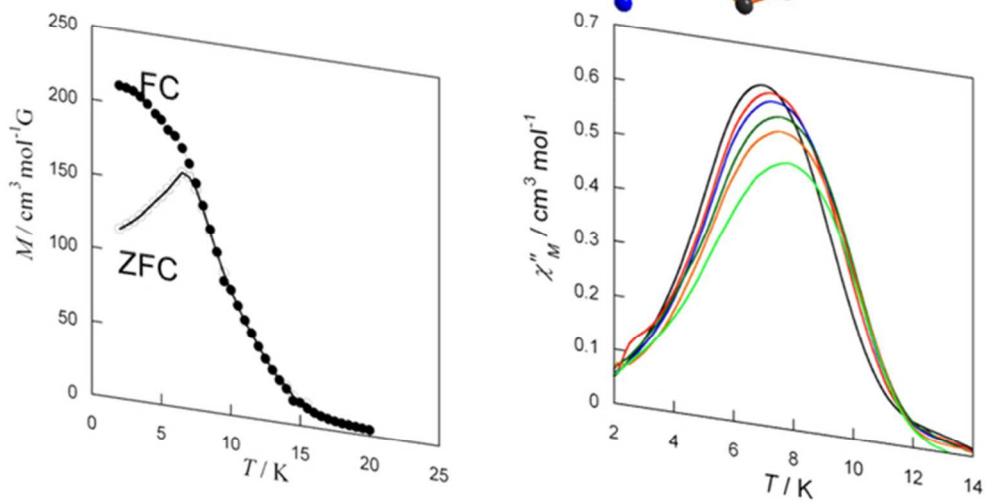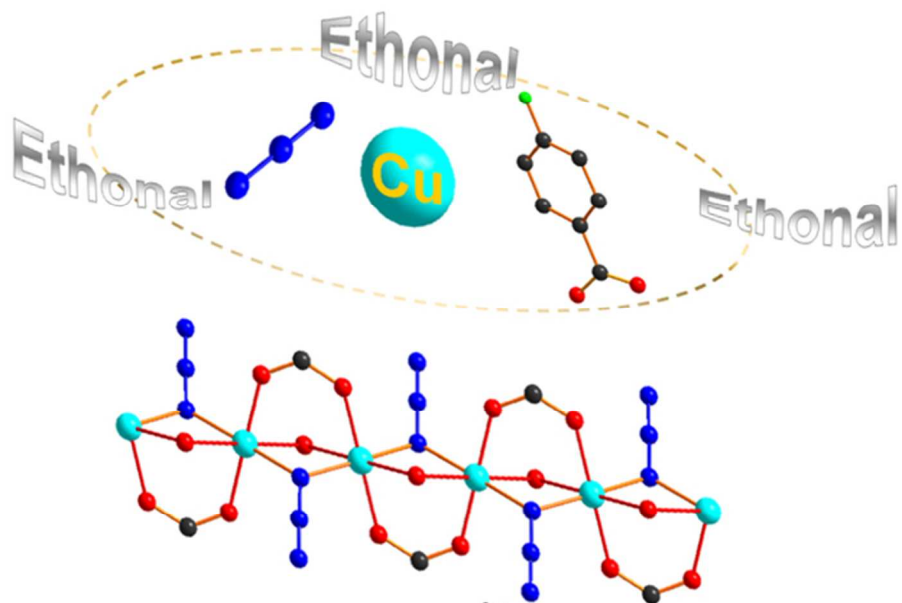
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A Triple-Bridged Azido-Cu(II) Chain Compound fine-tuned by Mixed Carboxylate/Ethonal linkers Displays Slow-relaxation and Ferromagnetic Order: Synthesis, Crystal structure, Magnetic Property with DFT Calculation

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ABSTRACT: A new azido-Cu(II) compound, [Cu(4-fba)(N$_3$)(C$_2$H$_5$OH)] (4-fba = 4-fluorobenzoic acid) (**1**), has been synthesized and characterized. X-ray crystal structure analysis determines that only one crystallographically independent Cu(II) ion in the asymmetric unit of **1** exhibits a stretched octahedral geometry where two azido N atoms and two carboxylic O atoms locate at the equatorial square, while two ethanol O atoms occupy the apical positions, forming a 1D Cu(II) chain with alternating triple-bridge of EO-azido, *syn,syn*-carboxylate, and μ2-ethanol. The title compound consists of ferromagnetically interacting ferromagnetic chains exhibiting a ferromagnetic order (T_c = 7.0 K). The strong ferromagnetic coupling between adjacent Cu(II) ions within each chain is due to the countercomplementarity of the super-exchange pathways whereas the ferromagnetic interchain interactions – responsible for the long-range magnetic ordering – are most likely due to the presence of coordinated ethanol molecules establishing hydrogen bonds with neighboring chains. DFT calculations have been performed on the compound **1** to offer a qualitatively theoretical explanation of the magnetic behavior.

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INTRODUCTION

The synthesis of novel examples of one-dimensional (1D) chain compounds attracts interest from both, a crystal engineering point of view[1] – because of the wide range of structural motifs and topologies that can be found – and also because of the intriguing, and sometimes predictable, magnetic properties they can exhibit. Both factors have equally contributed to the especial attention that scientists working in the field of molecular magnetism[2] have focused in this class of materials during the last three decades.[3] Among the wide plethora of magnetic properties that a given 1D compound can exhibit, those related to the slow-relaxation of the magnetization are especially appealing. In this sense, both the so-called single-chain-magnets (SCMs)[4] and those compounds exhibiting a spontaneous magnetization below a critical temperature (T_c),[5] are significant from the perspectives of basic and applied research, and have rich potential applications such as quantum computation and information storage.[6]

A popular approach for constructing these types of materials is employing short ligands capable to transmit efficiently the magnetic coupling.[7] In this sense, the azido ligand has attracted a lot of attention for its inherent advantage to obtain the magnetic materials.[8] The two typical coordination modes of azido: μ-1,3 (end-to-end, EE) and μ-1,1 (end-on, EO) modes usually correspond to antiferromagnetic and ferromagnetic exchanges,[9] respectively. (Scheme 1)

Scheme 1.

As reported, a large number of azido-bridged metal compounds with alternating 1D chain structure and diversely magnetic properties have been demonstrated in the past decades,[10] such as azido-Cu(II) systems that are considered as the ideal candidates for understanding the fundamental science of magnetic interactions and magneto-structural correlations in molecular systems,[11] exhibit various structures and interesting magnetic properties with the assistance of secondary bridging ligand. For azido-Cu(II) compounds, it has been suggested that the strongest ferromagnetic coupling in the EO-azido linker occurs at Cu-N-Cu bond angle close to 108°, and so antiferromagnetic interaction would probably be found for larger Cu-N-Cu bond angle.[12] Consequently, an effective strategy for tuning the structures of azido-Cu(II) compounds with notable magnetic properties is to introduce carboxylates as coligand into the systems in which the

μ-1,1-azido and *syn,syn*-carboxylate ligands usually bridge the Cu(II) ions to form the tetra-coordinated quadrangular geometry in the previous reports.[13] In particular, molecular orbital calculation supports dramatically the countercomplementary effect enforced by the carboxylate ligand, which weakens the effect of the antiferromagnetic azido ligand to the point where dominant ferromagnetic behavior is obtained.[14] As known, a series of azido/carboxylate/Cu(II) compounds with isolated ferromagnetic chain involving the combinations of μ-1,1-azido, *syn,syn*-carboxylate,[15] have been prepared. However, to our knowledge rare examples of them have shown long-range magnetic ordering.[16]

The case which captures our attention is numerous solvents such as dimethylsulfoxide and alcoholic solvents, as well as aqueous solution, could coordinate to Cu(II) ions as the triple bridging ligand in the azido/carboxylate/Cu(II) systems,[16a,17] regulating the intrachain or interchain structures and thus the magnetic properties: (i) The solvent molecules bridge the Cu(II) ions not only to change the coordination geometry and orbital exchange of Cu(II) ions, but also to fine-tune the structural parameters including the Cu-Cu distances and Cu-N-Cu angles. (ii) The solvent molecules would provide higher possibility to form the weakly interchain interactions like hydrogen-bonding and π-π stacking which are proved as an effective pathway for magnetic transmission, contributing to cause the long-range magnetic order.[18]

Herein, we report the synthesis, structure, and magnetic properties of a new 1D chain-like azido-Cu(II) compound, [Cu(4-fba)(N$_3$)(C$_2$H$_5$OH)] (4-fba = 4-fluorobenzoic acid) (**1**), in which the Cu(II) ions are connected by triple-bridge of μ-1,1-azido, *syn,syn*-carboxylate and μ2-ethanol. The integration of intrachain and interchain magnetic exchanges from the alternating ferromagnetic chain leads to the slow relaxation and long-range order which are rarely observed in most of the known azido/carboxylate-Cu(II) systems with well-isolated 1D chain. Moreover, the strong ferromagnetic coupling between adjacent Cu(II) ions are confirmed by using density functional theory (DFT) calculation as well.

EXPERIMENTAL SECTION

   Physical measurements: Elemental analysis (C, H, N) was performed on a Perkin-Elmer 2400 CHN elemental analyzer. The FT-IR spectra were recorded in the range 400-4000 cm^{-1} using KBr pellets on an EQUINOX55 FT/IR spectrophotometer. The phase purity of the bulk or

polycrystalline samples was verified by powder X-ray diffraction (PXRD) measurements performed on a Rigaku RU200 diffractometer at 60 kV, 300 mA and CuKα radiation (λ = 1.5406 Å), with a scan speed of 5° min^{-1} and a step size of 0.02° in 2θ. Variable-temperature (2.0–300 K) direct current (dc) magnetic susceptibility measurements under an applied field of 50 G ($T < 20$ K) and 5 kG ($T \geq 20$ K), and variable-field (0–5 T) magnetization measurements at 2.0 K were carried out with a Quantum Design SQUID magnetometer. Variable-temperature (2.0–10 K) alternating current (ac) magnetic susceptibility measurements under a zero applied static field were carried out with a Quantum Design Physical Property Measurement System (PPMS). The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder. Dc and ac magnetic measurements were carried out by powdering and restraining the sample in order to prevent any displacement.

Synthesis: All reagents and solvents employed were commercially available and used as received without further purification.

CAUTION! Azido compound of metal ion is potentially explosive. Only a small amount of the materials should be prepared, and they should be handled with care.

[Cu(4-fba)(N$_3$)(C$_2$H$_5$OH)] (1): An ethanol solution (10 mL) of NaN$_3$ (0.013 g, 0.2 mmol) and 4-Hfba (0.056 g, 0.4 mmol) in a tube was layered by aqueous ethanol (50%, 5 mL), and a aqueous solution (10 mL) of Cu(NO$_3$)$_2$ · 3H$_2$O (0.048 g, 0.2 mmol) was carefully added. Slow diffusion at room temperature obtained green crystals of **1** within three weeks. (yield: 80%, based on Cu). Anal. Calcd. For CuC$_9$H$_{10}$FN$_3$O$_3$ (290.74): C, 37.15; H, 3.44; N, 14.45%. Found: C, 37.12; H, 3.39; N, 14.40%. Main IR (KBr, cm^{-1}): 2987 (w), 2088 (s), 1606 (s), 1544 (s), 1415 (s), 1238 (m), 852 (w), 777 (m), 634 (m).

Crystallographic data collection and refinement: Single-crystal diffraction data for **1** was collected on a Rigaku SCX mini CCD diffractometer using graphite-mono-chromatized MoKα radiation (λ = 0.71073 Å) at room temperature. The data integration and reduction were processed with SAINT software. Absorption correction based on multi-scan was performed using the SADABS program.[19a] The structure was solved by the direct method using SHELXTL and refined by a full-matrix least-squares method on F^2 with the SHELXL-97 program.[19b] All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and data collection, refinement parameters are listed in Table 1, selected bond lengths and angles are listed in Table

S1.

Table 1.

Computational methodology

The following computational methodology was used to calculate the coupling constant in the title compound.[20] The spin Hamiltonian suggested originally by Heisenberg can be written as $\hat{H} = -\sum_{(i>j)} J S_i S_j$ (where S_i and S_j are the spin operators of the paramagnetic centers, $S_i = S_j = 1/2$ for Cu(II) ion; and the J constant is the coupling constant between the paramagnetic spin carriers), which can be employed to express the exchange coupling between two transition metal ions, the full Hamiltonian matrix for the entire system can be established.

The DFT calculations are implemented with the ORCA 3.0 package.[21] The hybrid B3LYP functional proposed by Becke[22] and Lee et al.[23] is applied in all calculations. The polarized triple-ζ quality basis set def2-TZVP proposed by Ahlrichs and co-workers was used for all atoms.[24] The calculation model for the compound were built from the experimental results.

RESULTS AND DISCUSSION

Crystal structures: Single crystal X-ray analysis reveals that compound **1** is composed of isolated 1D azido-copper chains. Cu(II) ions located at the inverse center takes a hexa-coordinated environment through an N_2O_4 chromophore in which two nitrogen atoms from two azido anions and two oxygen atoms from two carboxylates [Cu-N1 = 1.988 Å, Cu-O1 = 1.950 Å, Cu-N1A = 1.988 Å and Cu-O2 = 1.943 Å] lie on the equatorial region, while two oxygen atoms from two ethanol molecules occupy apical positions [Cu-O3 = 2.528 Å, Cu-O3B = 2.419 Å] (Figure 1a). All the Cu(II) ions form an elongated octahedral geometry resulting from the typical Jahn-Teller effect. The single EO-azido can be considered as a bridge between neighboring copper atoms in the μ2-1,1 coordination mode, in which all bridging nitrogen atoms are coordinated in equatorial positions. Azido groups are quasi linear with N(3)-N(2)-N(1) angles being 179.1(8)° and exhibit unsymmetric N–N bond lengths, with the bonds involving the donor atoms N(1)–N(2) = 1.208(7) Å being relatively longer than N(2)–N(3) = 1.131(7) Å. *Syn,syn*-carboxylato bridges of deprotonated 4-fluorobenzoic acids are pseudosymmetrical bounded to copper centers with a

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slight different of Cu-O distances [Cu-O1 = 1.950 Å, Cu-O2 = 1.943 Å]. Moreover, the oxygen atoms in ethanol molecules adopt $\mu2$ mode to bridge the coherent Cu(II) ions. Then, adjacent metal ions are simultaneously linked by an μ-1,1 (EO)-azido bridge and a *syn,syn*-carboxylate bridge, as well as an $\mu2$-ethanol bridge, yielding a formally 1D chain along the *a* axes (Figure 1b). The coordination of ethanol shorten the distance between intrachain copper ions [Cu1-Cu1A = 3.160 Å]. As shown in Table S1, the bond lengths between one Cu(II) ion and two ethanol bridging-oxygen atoms are slightly different [Cu-O = 2.528 Å or 2.419 Å], while the Cu-N-Cu angle (105.2°) is in the normal range of EO-azido bridging mode. The interchain hydrogen-bonding between the oxygen atom in coordinated ethanol molecule and the terminal nitrogen atom in the azido ligand [O3-H1$\cdots$N3 = 2.918 Å] might induce magnetic transmission, which integrates all of the Cu(II) chains, constructing the supramolecular framework of **1** (Figure 1c). The nearest distance of interchain Cu(II) ions is of 7.640 Å.

Figure 1.

Magnetic properties: Magnetic measurements were carried out on a polycrystalline sample **1**, which is pure phase as confirmed by PXRD (see Figure S1).

The $\chi_M T$ *vs.* *T* plot of **1**, χ_M being the molar magnetic susceptibility per Cu(II) atom and *T* the temperature, under applied magnetic fields *H* of 5000 G (*T* > 30 K) and 100 G (*T* ≤ 30), is shown in Figure 1. At room temperature, $\chi_M T$ is equal to 0.51 cm^3 mol^{-1} K, a value which is somewhat larger than that expected for a magnetically isolated copper(II) ion [$\chi_M T = (N\beta^2 g_{Cu}{}^2/3k)S_{Cu}(S_{Cu} + 1)$ = 0.41 cm^3 mol^{-1} K with g_{Cu} = 2.1 and S_{Cu} = ½]. Upon cooling, $\chi_M T$ continuously increases to reach a maximum with a $\chi_M T$ value of 6.11 cm^3 mol^{-1} K at 7.54 K (Figure 2a). Below this temperature, $\chi_M T$ decreases rapidly to reach a $\chi_M T$ value of 2.02 cm^3 mol^{-1} K at 1.90 K. This behavior is consistent with a ferromagnetic coupling between the Cu(II) ions along the chain. Such parallel alignment of the neighboring local spins when the bridging ligands are different is well documented and is due to orbital countercomplementarity.[25] The *M* *vs.* *H* plot at 2.0 K, *M* being the molar magnetization per Cu(II) atom and *H* the applied field is shown in Figure 2b. The maximum *M* value at *H* = 5.0 T is very close to 1 $N\beta$ (0.98 $N\beta$), a value which confirms that all the S_{Cu} = 1/2 centers are aligned along the same direction. Interestingly, the χ_M *vs.* *T* plot of **1** (inset of

Figure 2a), reveals that below 15 K, χ_M shows a sharp increase and also an incipient saturation below *ca.* 7.5 K. These features suggest the onset of a long-range ferromagnetic ordering which must be the result of interchain ferromagnetic interactions. This saturation also accounts for the rapid decrease of $\chi_M T$ below 7.54 K (Figure 2a).

Figure 2.

The presence of this ferromagnetic ordering is revealed by the coalescence of the field-cooled magnetization (FCM) and the zero-field-cooled magnetization (ZFCM) curves at 7.0 K (Figure 3). In order to further confirm the presence of the magnetic ordering, ac susceptibility measurements were performed. Figure 4 shows how the out-of-phase magnetic susceptibility becomes nonzero below 12 K and exhibits frequency-independent maxima in the narrow range 7.0-6.0 K. Ferromagnetic ordering is more often observed in high-dimensional (two- and three-dimensional) compounds, however, examples of ferromagnetic chains exhibiting interchain ferromagnetic interactions and long-range magnetic ordering have already been reported.[5,16] The presence of this ferromagnetic ordering indicates the presence of long-range ferromagnetic interchain magnetic interactions at low temperature. An intriguing remaining question lies at the frequency dependence of χ''_M (Figure 4), which is reminiscent of that observed in the so-called single-chain magnets (SCMs).[4] However, this dependence is very weak and the values for the relaxation time (τ_0) and the activation energy (E_a) are physically meaningless. This very weak dependence is commonly observed in spin-glasses,[26] and can be due to the occurrence of competitive Ferromagnetic (F) and Antiferromagnetic (AF) interactions yielding a spin-frustrated system with a vitrification process.[27]

Figure 3.

Figure 4.

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The temperature dependence of the magnetic susceptibility data of **1** was analyzed with the expression proposed by Baker et al.[28] for a ferromagnetic S = ½ chain (eq. 1) which was obtained from a high-temperature series expansion.

$$\chi_M = \frac{N\beta^2 g2}{4kT}\left(\frac{A}{B}\right)^{\frac{2}{3}} \tag{1}$$

$A = 1.0 + 5.7980x + 16.9027x^2 + 29.3769x^3 + 29.8329x^4 + 14.0369x^5$

$B = 1.0 + 2.7980x + 7.0087x^2 + 8.6538x^3 + 4.5743x^4$

$x = J/2kT$

The fitting of the experimental data in the 300-20 K range (solid line in Figure 2a) gave: $g = 2.20$, $J = +36.2$ cm^{-1} and $R = 2.4 \times 10^{-7}$, where J is the intrachain magnetic coupling, g_{Cu} is the Zeeman factor of the Cu(II) ions and R is the agreement factor defined as $R = \sum[(\chi_M T)_{exp}-(\chi_M T)_{calcd}]^2/\sum[(\chi_M T)_{exp}]^2)$. Further attempts to fit the magnetic data below $T = 20$ K were unsuccessful due to the spin-frustrating interactions at low temperatures but also because of the limitations of a law derived from a high-temperature series expansion. In addition, we also tried to include a term that took into account the interchain magnetic interactions (θ). However, interchain magnetic interactions are only relevant at low temperatures. Thus, the fitting of the experimental data in the 300-20 K range, gave always negligible values for θ.

Theoretical study: In order to further demonstrate the ferromagnetic nature of the exchange interaction in the compound **1**, we performed a theoretical study of the isotropic coupling constants J between Cu(II) ions based on DFT calculation at B3LYP level with the aid of ORCA. Considering the structure of **1** and supposing that the dominant magnetic exchange is mediated between adjacent Cu(II) ions through azido, carboxylate and ethanol. The calculation was carried out with the model (for comparing) applied to the magnetic fitting by filling-in all the coordination sites of the Cu(II) ions (Figure 5).

The result of the theoretical calculation and the experimental fitting in terms of the coupling constants are listed in Table 2. The calculated coupling constant is $J = 61.0$ cm^{-1}, which verifies that the strong ferromagnetic coupling is prevailing in compound **1**. Although the calculated value shows a certain deviation from the fitting value, the sign and the relative magnitude of the

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coupling constant agrees well with the experimental value. It is difficult to estimate the accuracy of the theoretical calculation, but the work is only qualitative. This may be resulting from the fact that the real compound is not scattered entities as it has been modeled, but is very complicated in the whole structures.

Figure 5.

Table 2.

Magneto-structural correlation: The magnetic exchanges between Cu(II) ions depend on three kinds of paths in **1** (Figure 6): *syn,syn*-carboxylate and μ-1,1-azido ligand (Cu-N = 1.99 Å, Cu-N-Cu = 105.2°), as well as ethanol molecule coordinates to the Cu(II) ions, forming the hexa-coordinated geometry (Cu-O = 2.42-2.53 Å). Additionally, the intrachain and interchain Cu-Cu bond lengths are determined to be 3.160 Å and 7.640 Å, respectively. Undoubtedly, the coordination of ethanol oxygen atom could close the distance of intrachain Cu(II) ions comparing with that of dual-bridging 1D Cu(II) chain reported previously. As observed, the counter complementarity effect resulting from three different ligands may explain the occurrence of intrachain ferromagnetic exchange. The interchain hydrogen-bonding derived form the ethanol oxygen atom and the terminal nitrogen atom of the azido group affords the additional path to transmit the interaction between the well-isolated ferromagnetic chains. This feature can explain the long-range magnetic ordering observed, which is rarely observed in 1D chain-like Cu(II) compounds containing EO-azido and carboxylate ligands.

Figure 6.

CONCLUSIONS

In the present work, an azido-Cu(II) compound with 4-fluorobenzoic acid as coligand is obtained by using a slow diffusion method. Structural analyses show that compound **1** is a 1D Cu(II) chain with a μ-1,1 (EO)-azido, a *syn-syn*-carboxylate and μ2-ethanol connecting the copper(II) ions. Compared with previously reported 1D Cu(II) chain compounds, which were bridged only by

(EO)-azido and carboxylate ligands, **1** exhibits different intrachain and interchain structures due to the coordination of ethanol molecules which also have influence on the magnetic properties. Magnetic investigations show that compound **1** behaves as a ferromagnet composed of ferromagnetically interacting ferromagnetic chains. The intrachain behavior reflects how the countercomplementary effect imposed by the carboxylate bridge, overcomes the antiferromagnetic effect of the azido bridge giving a resulting overall ferromagnetic interaction. In addition, the long-range ferromagnetic interchain interactions afford the observation of a ferromagnetic order at 7 K. DFT calculations confirm qualitatively the strong ferromagnetic coupling between Cu(II) ions.

SUPPROTING INFORMATION AVAILABLE: Figure S1 and Table S1, crystal structure of compound **1** in CIF format. CCDC number for **1**, 980967. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

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Figure Captions

Scheme 1. Coordination Modes of Bridging Azido

Figure 1. (a) Coordination environment of the Cu ion in **1**. (Hydrogen atoms are omitted for clarity) (b) The 1D chain with mixed ethanol oxygen, carboxylate and azido bridges for **1**. (Hydrogen atoms and benzene rings are omitted for clarity) (c) Hydrogen bonding formed by azido and ethanol molecules between adjacent chains in **1**.

Figure 2. (a) Temperature dependence of $\chi_M T$ under applied dc fields of 50 G ($T < 30$ K) and 5 kG ($T \geq 30$ K). The solid lines correspond to the best-fit curves (see text). The inset shows the thermal dependence of χ_M for **1**. (b) Field dependence of M of **1** at 2.0 K. The solid line is an eye-guide.

Figure 3. Field-Cooled Magnetization (FCM, ●) and the Zero-Field-Cooled Magnetization (ZFCM, ○) of **1**. The solid lines are only eye-guides.
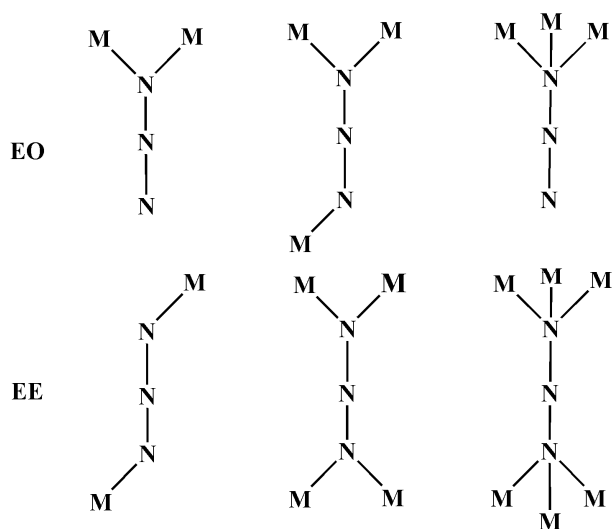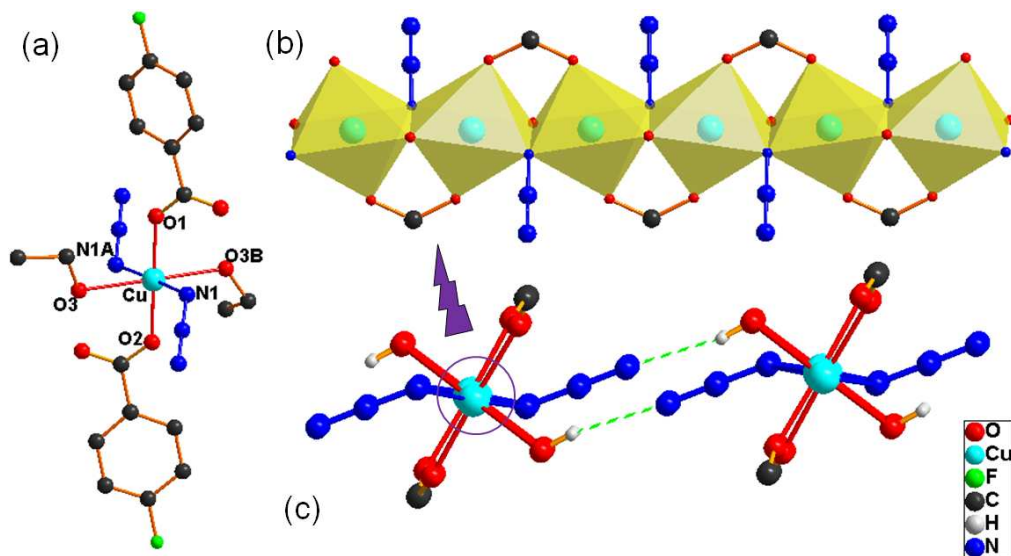
Figure 4. Temperature dependence of the *ac* out-of-phase magnetic susceptibility of **1** at frequencies in the range 10-997 Hz.

Figure 5. Magnetic core of **1** used for computational study.

Figure 6. Magnetic exchange of Cu(II) ions in compound **1**.

Table 1. Crystal Data and Structure Refinement Details for Compound **1**

Table 2. Comparison of the Experimental (from Fitting) and DFT Studies

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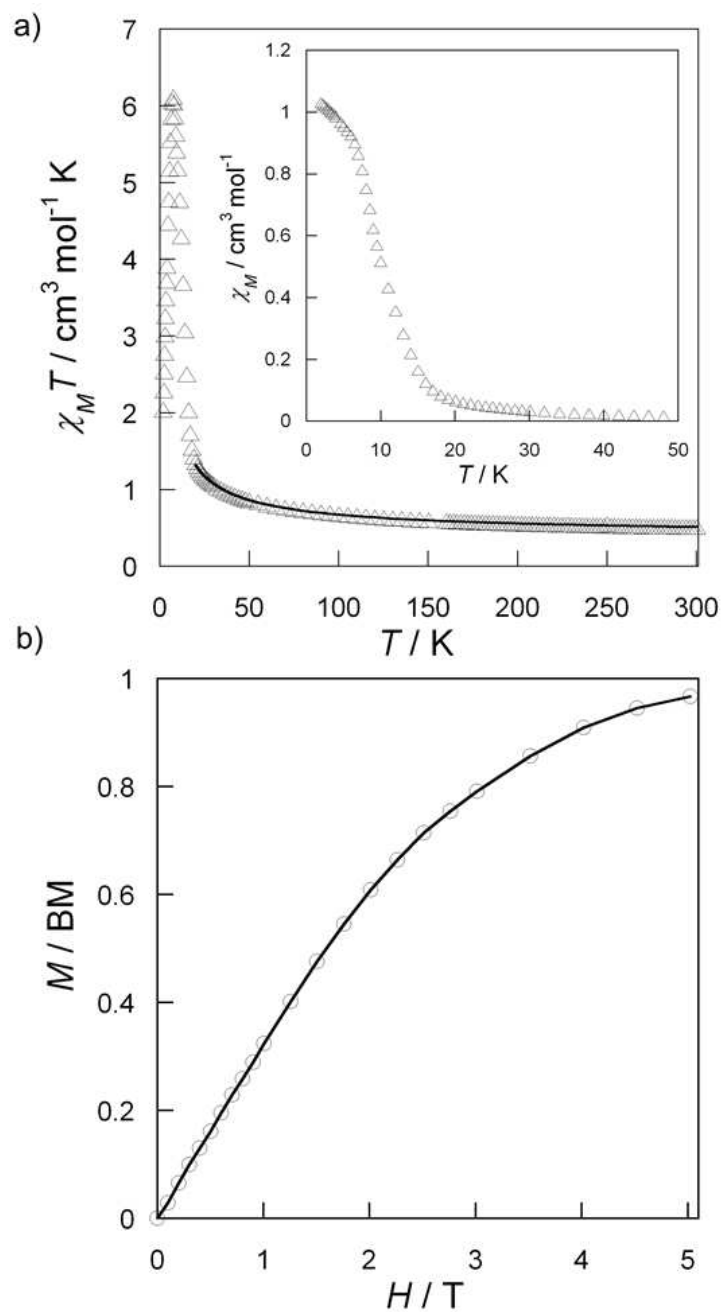
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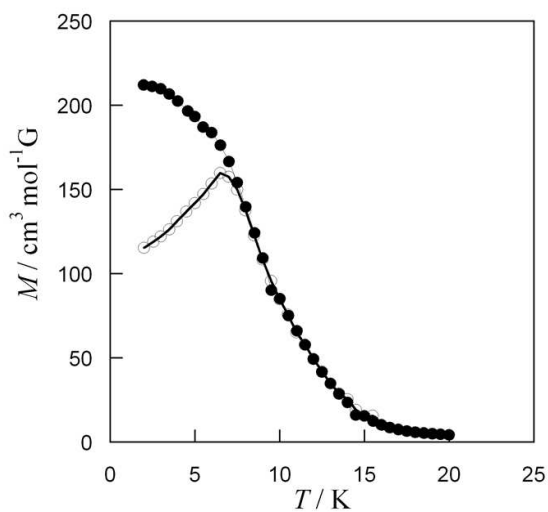
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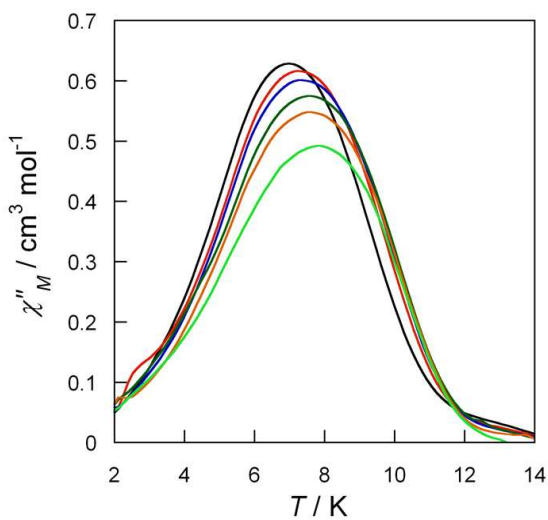

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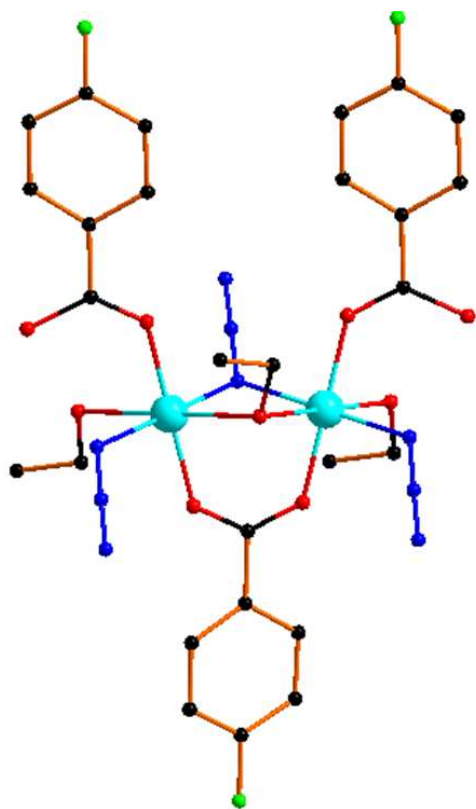
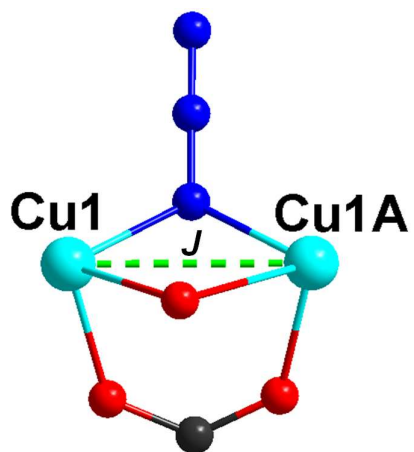**Figure 5.** Magnetic core of **1** used for computational study.

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Table 1. Crystal Data and Structure Refinement Details for Compound **1**

	1
Empirical formula	$C_9H_{10}CuFN_3O_3$
Formula weight	290.74
Crystal system	monoclinic
Space group	$P\,2(1)\,/n$
a (Å)	7.6404(15)
b (Å)	6.3146(12)
c (Å)	24.268(5)
α (°)	90
β (°)	93.497(4)
γ (°)	90
V (Å^3)	1168.7(4)
Z	4
$D_{(calcd)}$, g cm^{-3}	1.652
μ (mm^{-1})	1.882
$F(000)$	588
Θ range, deg	1.68-26.19
Unique reflections	2331
Observed reflections	6021
R_{int}	0.0750
Goodness of fit (F^2)	1.001
Parameters refined	155
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0567$, $wR_2 = 0.1235$
R indices (all data)	$R_1 = 0.1176$, $wR_2 = 0.1542$
Residuals, e Å^{-3}	0.438, -0.692

Table 2. Comparison of the Experimental (from Fitting) and DFT Studies

Compound	J/cm^{-1}	Expt.	DFT(TZVP)
1	J	36.2	61.0