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Chiral Molecular Ferromagnets Based on Copper(II) Polymers with End-On Azido Bridges

Zhi-Guo Gu, You Song, Jing-Lin Zuo,* and Xiao-Zeng You

Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry,
School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093,
People's Republic of China

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Two homochiral two-dimensional brick-wall complexes with only end-on azido bridges, $[Cu_3((R)\text{-phea})_2(N_3)_6]_n$ (**1**) and $[Cu_3((S)\text{-phea})_2(N_3)_6]_n$ (**2**) (phea = 1-phenylethylamine), have been synthesized and structurally characterized. Magnetic studies show that both complexes are chiral ferromagnets with the magnetic transition temperature at 5.5 K.

The development of new multifunctional materials, such as photomagnets, magneto-optical materials, magnetic conductors, ferroelectromagnets, and chiral magnets, is currently a challenging field of research for both chemists and physicists.[1−4] The design and synthesis of chiral magnets is of particular interest for fundamental investigations on the magnetochiral dichroism (MChD) effect and its potential applications in a variety of new technologies.[5] However, despite many efforts, relatively few optically active magnets have been reported to date because of the difficulties of controlling chirality in the molecular structure as well as in the entire crystal structure.[4]

The versatile binding modes available to the azido ligand offer great flexibility in the self-assembly of interesting clusters and extended networks, giving rise to a broad range of magnetic behaviors including single-molecule or single-chain magnets.[6,7] Although a number of metal−azido coordination polymers of various dimensionality have been reported, there are only a few compounds that exhibit long-range ordering behaviors.[8] Two typical coordination modes of bridging azido, end-on (EO) and end-to-end, favor ferromagnetic and antiferromagnetic exchange interactions, respectively.[9] However, to our knowledge, very few examples of metal−azido polymeric solids with sole EO azido bridges have been reported.[10] To develop new chiral ferromagnets, we focused our attention on chiral metal−azido (especially the EO bridging mode) systems with small organic auxiliary ligands incorporating optical activity. Herein, we report the synthesis, structures, and magnetic properties of unprecedented chiral ferromagnets (ordering at 5.5 K) containing only EO azido bridges, $[Cu_3((R)\text{-phea})_2(N_3)_6]_n$ (**1**) and $[Cu_3((S)\text{-phea})_2(N_3)_6]_n$ (**2**) (phea = 1-phenyl-

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* To whom correspondence should be addressed. E-mail: zuojl@nju.edu.cn.

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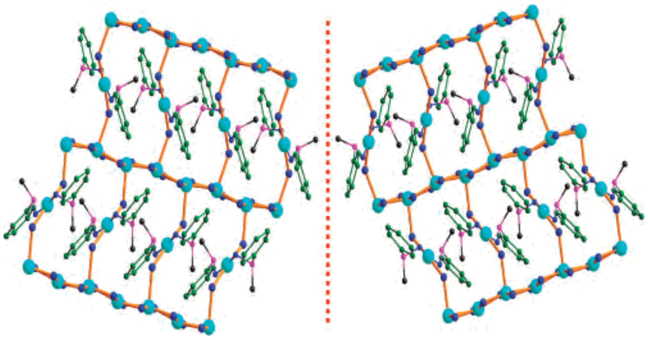

Figure 1. Perspective view of the enantiomorphous layers of **1** (*R* isomer, left) and **2** (*S* isomer, right). Color coding: Cu, light blue; N, blue; C, black, green, purple.

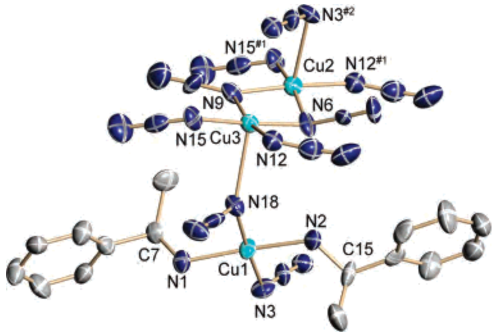

Figure 2. Perspective drawing of complex **1** showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

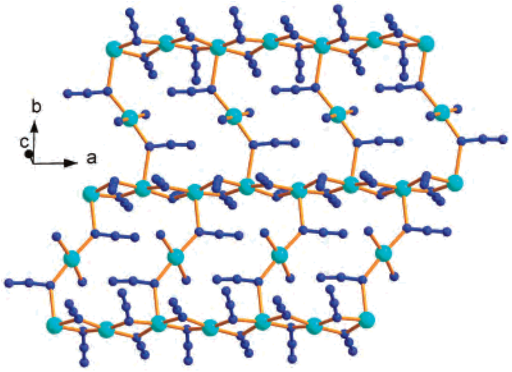

Figure 3. Arrangement of the 2D brick-wall network of **1** (H and C atoms of the amine ligands are omitted for clarity). Color coding: Cu, light blue; N, blue.

ethylamine). They are typical examples of ferromagnets with EO bridges and provide the possibility of a better understanding of the magnetic interactions and magnetostructural correlations for metal−azido systems.

Complexes **1** and **2** were obtained by the self-assembly reaction of $Cu(NO_3)_2 \cdot 3H_2O$, NaN_3, and (*R*)-phea or (*S*)-phea in a CH_3OH/H_2O solution in a molar ratio of 2:20:1.[11] IR spectroscopic analysis of **1** and **2** revealed four intense absorptions at 2031, 2057, 2089, and 2108 cm^{-1} corresponding to the combination modes of vibration of the azido bridges.

The X-ray crystallography revealed that **1** and **2** are enantiomers and crystallized in the chiral space group $P2_12_12_1$; no detailed structural descriptions are presented here for **2**. Complex **1** consists of neutral two-dimensional (2D) brick-wall layers with a repeating azido-bridged eight-membered copper brick $[Cu_8(N_3)_{12}((R)\text{-phea})_4]$ (Figure 1). The length of each brick is equal to the *a* axis of the unit cell [6.025(8) Å]. There are three crystallographically independent Cu ions in **1**: a planar Cu1 center, consisting of two azido N atoms (N8 and N3) and two N atoms from two (*R*)-phea ligands; two square-pyramidal Cu2 and Cu3 centers, both being composed of five azido ligands [$Cu-N_{basal}$, 1.935(7)−2.057(8) Å; $Cu-N_{apical}$, 2.456(7)−2.462(6) Å; Figure 2]. The Cu2 and Cu3 ions link each other alternately through double EO azido bridges, leading to one-dimensional copper−azido chains along the *a* axis, with the $Cu-N_{EO}-Cu$ angles varying from 96.2(3)° to 101.8(3)°. The copper−azido chains further link $[Cu((R)\text{-phea})_2]^{2+}$ units through the single EO azido bridges [$Cu-N_{EO}-Cu$, 132.6(4)−137.1(3)°] to generate an extended 2D brick-wall network (Figure 3). It should be noted that **1** and **2** are the first examples of 2D polymeric metal complexes with only EO azido bridges. The shortest intralayer Cu⋯Cu separations are 3.015 and 3.038 Å for Cu2⋯Cu3 and 4.107 and 4.169 Å for Cu2⋯Cu1. The neutral 2D layer lies in the *ab* plane, and the monodentate (*R*)-phea ligands project between the layers with a large interlayer distance of 13.2 Å (Figure S1 in the Supporting Information). Between the layers, no efficient $\pi-\pi$ stacking interaction or hydrogen bonding was observed in **1** and the interlayer magnetic interactions will be relatively weak from the viewpoint of the magnetism.

The circular dichroism (CD) spectra measured in KBr pellets further confirm the enantiomeric nature of the optically active complexes **1** and **2** (Figure 4). Complex **1** (*R* isomer) exhibits a positive Cotton effect around 365 nm and a negative dichroic signal centered around 405 and 460 nm, while **2** (*S* isomer) shows Cotton effects of the opposite sign at the same wavelengths.

The magnetic susceptibilities of complexes **1** and **2** for polycrystalline samples were measured on a Quantum Design MPMS-XL7 SQUID magnetometer. Both enantiomers exhibit identical magnetic behaviors. The $\chi_M T$ vs T plot of **1** is shown in Figure 5. At 300 K, its $\chi_M T$ value is 1.27 emu K mol^{-1}, which is slightly higher than that expected for three uncoupled Cu^{II} ions. Upon lowering of the temperature, $\chi_M T$ increases gradually, then shows an abrupt rise below 20 K, up to a maximum value of 19.73 emu K mol^{-1} at 6 K, and then decreases to 8.10 emu K mol^{-1} at 1.8 K. No maximum was observed in the χ_M vs T plot (inset of Figure 5). The

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(11) Preparation of complexes **1** and **2**: A methanolic solution (10 mL) containing copper(II) nitrate trihydrate (48 mg, 0.2 mmol) was mixed with an aqueous solution of sodium azide (130 mg, 2 mmol) dissolved in a minimum volume of water. (*R*)-phea (11 mg, 0.1 mmol) in 3 mL of water was added to this reaction mixture with continuous stirring. The resulting dark-green solution was filtered and left to stand at 5 °C. Brown plate-shaped crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of the solvents within 2 weeks. Complex **2** was obtained using a method similar to that of **1**, except that (*S*)-phea was used. Yield: 54%. Elem anal. Calcd for $C_{16}H_{22}Cu_3N_{20}$: C, 28.05; H, 3.24; N, 40.89. Found: C, 27.86; H, 3.37; N, 40.63. IR: $\nu = 2031$, 2057, 2089, and 2108 cm^{-1} (vs) for the azido groups. Crystal data for **1**: $C_{16}H_{22}Cu_3N_{20}$, $M_r = 685.16$, $T = 291(2)$ K, space group $P2_12_12_1$, $a = 6.025(8)$ Å, $b = 16.660(2)$ Å, $c = 26.145(4)$ Å, $V = 2624.2(6)$ Å^3, $Z = 4$, R1 = 0.0651, wR2 = 0.1365 [$I > 2\sigma(I)$], Flack $\chi = 0.09(3)$. Data for **2**: R1 = 0.0634, wR2 = 0.1288 [$I > 2\sigma(I)$], Flack $\chi = 0.07(3)$.

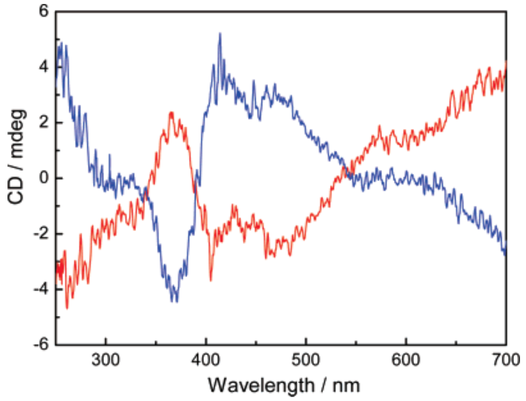

Figure 4. CD spectra of **1** (*R* isomer, red line) and **2** (*S* isomer, blue line) in KBr pellets.

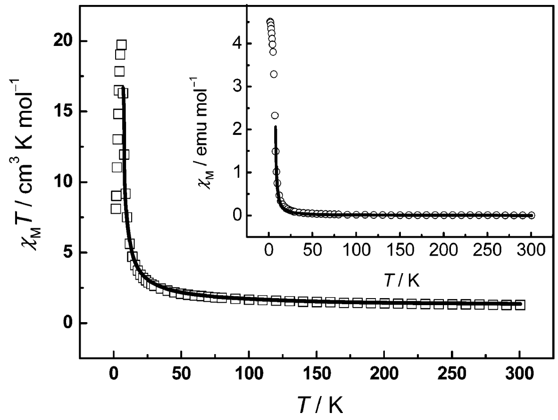

Figure 5. Plots of $\chi_M T$ vs T for **1** at a field of 2 kOe. The inset shows the plots of χ_M vs T for **1** at a field of 2 kOe. The solid lines represent the best fittings of the data.

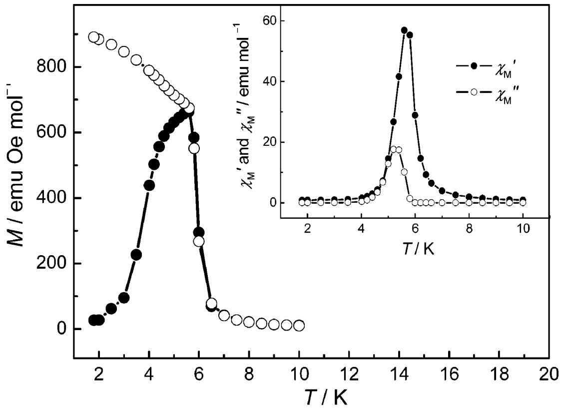

Figure 6. ZFC magnetization (●) and FC magnetization (○) vs T measured at 10 Oe for **1**. The inset shows the temperature dependence of in-phase χ_M' and out-of-phase χ_M'' ac magnetic susceptibility for **1** obtained at zero external magnetic field, $H_{ac} = 3$ Oe at 10 Hz.

temperature dependence of $1/\chi_M$ above 40 K obeys the Curie–Weiss law with a positive Weiss constant θ of 26.05 K (Figure S2 in the Supporting Information). The successive increase of χ_M and the positive θ value suggest the operation of ferromagnetic interaction between adjacent Cu^{II} ions through EO azido bridges. To evaluate the in-plane ferromagnetic interaction, we tried to use an approximate approach similar to that previously used for 2D complexes. Taking into account the structure of **1**, the 2D sheet was roughly treated as a system of interacting chains. The uniform chain is formed by the copper–azido chain and the mononuclear Cu((*R*)-phea)$^{2+}$ ion, where J and zJ' stand for the exchange integrals within the chain and between the chains, respectively. (See the Supporting Information).

With this rough model, the magnetic susceptibilities above 6 K were simulated, given the best fit with parameters $g = 2.06$, $J = 15.27$ cm^{-1}, and $zJ' = 1.34$ cm^{-1} ($R = 8.6 \times 10^{-3}$), which confirms the intralayer ferromagnetic coupling between Cu^{II} ions.

At a low applied field of 10 Oe in the temperature range of 1.8–10 K, the magnetizations after zero-field cooling (ZFC) and subsequent field cooling (FC) reveal nonreversibility and bifurcation, confirming the long-range magnetic ordering below 5.5 K to produce a ferromagnet (Figure 6). The alternating current (ac) susceptibility measurements in an ac field of 3 Oe oscillation also indicate a magnetic phase transition, showing a peak in the in-phase (χ_M') signal and an out-of-phase (χ_M'') signal that is nonzero below 5.5 K, defining T_c for this magnet (inset of Figure 6). No frequency dependence was observed in the ac measurements, thus excluding any glassy behavior in complex **1**.

The field dependence of magnetization measured at 1.8 K shows a rapid saturation of the magnetization at ca. 25 kOe, which is quite typical for long-range ferromagnetic ordering, and reaches 3.03 $N\beta$ mol^{-1} at 70 kOe, which corresponds to the theoretical saturation value for a ferromagnetic Cu$_3$ system with $S = {}^3/_2$ and $g = 2.0$ (Figure S3 in the Supporting Information). Furthermore, as shown in the inset of Figure S3 in the Supporting Information, a characteristic hysteresis loop is observed at 1.8 K with a remnant magnetization (M_r) of 1.00 $N\beta$ mol^{-1} and a coercive field (H_c) of 140 Oe, which strongly supports the ferromagnetic ordering of **1** in the bulk.

In summary, two enantiomorphous chiral complexes were synthesized, and they are ferromagnets with the magnetic transition temperature of 5.5 K. These compounds represent the first chiral magnets with all EO azido bridges and demonstrate the feasibility for constructing an azido-bridged chiral magnet by tuning the monodentate chiral amine ligands.

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Supporting Information Available: More magnetic data (PDF) and X-ray structure data in CIF format. The material is available free of charge via the Internet at http://pubs.acs.org.

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