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One-Dimensional Azido-Bridged Chiral Metal Complexes with Ferromagnetic or Antiferromagnetic Interactions: Syntheses, Structures, and Magnetic Studies

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One-dimensional chiral copper(II) and manganese(II) coordination polymers with single asymmetric end-to-end (EE) azide bridges, $[\mathrm{Cu}(R\text{-}\mathrm{L})_2(\mathrm{N}_3)]_n(\mathrm{ClO}_4)_n$ (**1**), $[\mathrm{Cu}(S\text{-}\mathrm{L})_2(\mathrm{N}_3)]_n(\mathrm{ClO}_4)_n$ (**2**), $[\mathrm{Mn}(R\text{-}\mathrm{L})_2(\mathrm{N}_3)]_n(\mathrm{ClO}_4)_n$ (**3**), and $[\mathrm{Mn}(S\text{-}\mathrm{L})_2(\mathrm{N}_3)]_n(\mathrm{ClO}_4)_n$ (**4**) (*R*-L or *S*-L = *R*- or *S*-pyridine-2-carbaldehyde-imine), have been synthesized, using azide ions as bridging groups and chiral Schiff bases as auxiliary ligands, and characterized. The crystal structure determination of complexes **1** and **2** reveals the formation of one-dimensional chiral chains, in which the central Cu(II) ion is six-coordinate in the form of an elongated octahedron. Complex **3** consists of chiral helical polymeric chains, in which the central Mn(II) has a slightly distorted octahedral geometry. They all crystallize in the chiral space group $P2_1$. Complexes **1** and **2** are rare examples that exhibit ferromagnetic interaction between copper(II) ions through the single end-to-end azido bridge. Fitting the susceptibility data for **1** using a 1D uniform chain model led to the parameters $J = 0.70(3)$ cm^{-1}, $g = 2.06(2)$, and $zj' = 0.07(2)$ cm^{-1}. The magnetic studies on **3** and **4** show that there is weak antiferromagnetic coupling between the manganese(II) ions.

Introduction

Chiral coordination polymers have received much attention because of their wide application in enantioselective synthesis, asymmetric catalysis, assembly of chiral supermolecular structure, and advanced material preparation.[1] Since Rikken and Raupach observed the weak magnetochiral dichroism (MChD) effect in a chiral paramagnetic material,[2] the investigation of chiral magnets combining magnetism and optical activity has become an active research topic for their important potential application as multifunctional materials.[3−5] The design and synthesis of chiral molecule-based magnets is currently a challenging target because the chirality must be controlled in both the molecular structure and the entire crystal structure.[4,5] It is well-known that the azide anion is an efficient and versatile mediator for magnetic coupling, and pseudohalide-bridging ligands were more commonly employed in the design of polynuclear transition-metal complexes with remarkable diversity in structure and magnetism.[6−8] The azido ion has been shown to be able to link two or more metal ions in various modes: μ-1,1 (end-on, EO), μ-1,3 (end-to-end, EE), μ-1,1,3, and others. A variety of zero-, one-, and two-dimensional copper(II),

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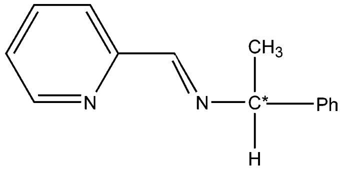
manganese(II), cobalt(II), and nickel(II) complexes have been synthesized[9−14] using 2,2-bipyridine, pyridine and its derivatives, Schiff bases, or other polydentate N-donor organic ligands as auxillary ligands. It has been established that the magnetic coupling mediated by the azido bridge is generally ferromagnetic (F) for the symmetric EO mode and antiferromagnetic (AF) for the symmetric EE mode,[14b−c,15−17] but the asymmetric end-on complexes display magnetic properties from weak ferromagnetic to slightly antiferromagnetic and the asymmetric end-to-end complexes exhibit magnetic properties from slightly ferromagnetic to strongly antiferromagnetic.[18,19] The simultaneous presence of both bridging azide modes leads to more magnetic behavior.[10e,20] Theoretical calculations show the possibility of ferromagnetic interaction through an EE azido pathway, and recently several examples of ferromagnetic interaction through the EE azido bridge have been reported.[17a,19−22]

Scheme 1 *R*- or *S*-pyridine-2-carbaldehyde-imine



In our previous work, we prepared a one-dimensional chiral copper complex with chiral 2,2′-bipyridine and an end-on azide bridge.[23] In this paper, as part of an effort to develop new examples of chiral azido-bridged coordination polymers, using a chiral Schiff base, *R*- or *S*-pyridine-2-carbaldehyde-imine (*R*-L and *S*-L, Scheme 1) as an auxiliary ligand, and azide ions as bridges, we successfully synthesized two new one-dimensional chiral copper(II) polymeric complexes, $[\mathrm{Cu}(R\text{-L})_2(\mathrm{N}_3)]_n(\mathrm{ClO}_4)_n$ (**1**) and $[\mathrm{Cu}(S\text{-L})_2(\mathrm{N}_3)]_n(\mathrm{ClO}_4)_n$ (**2**), and two chiral manganese(II) complexes with helix polymeric chains, $[\mathrm{Mn}(R\text{-L})_2(\mathrm{N}_3)]_n(\mathrm{ClO}_4)_n$ (**3**) and $[\mathrm{Mn}(S\text{-L})_2(\mathrm{N}_3)]_n(\mathrm{ClO}_4)_n$ (**4**) (*R*-L or *S*-L = *R*- or *S*-pyridine-2-carbaldehyde-imine). They are characterized by X-ray crystal structure

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Table 1. Crystallographic Data for the Complexes **1**−**3**

	1	**2**	**3**
formula	$C_{28}H_{26}ClN_7O_4Cu$	$C_{28}H_{26}ClN_7O_4Cu$	$C_{28}H_{28}ClN_7O_4Mn$
fw	625.56	625.56	616.96
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$P2_1$
a (Å)	12.581(3)	12.599(5)	12.822(3)
b (Å)	8.4606(18)	8.461(3)	8.3655(19)
c (Å)	13.465(3)	13.480(5)	13.658(3)
α (deg)	90	90	90
β (deg)	95.936(4)	96.006(12)	94.668(5)
γ (deg)	90	90	90
Z	2	2	2
V (Å^3)	1425.5(5)	1429.0(9)	1460.0(6)
D_{calcd} (g cm^{-3})	1.457	1.454	1.403
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	0.907	0.905	0.590
F(000)	646	646	638
θ range (deg)	2.11−26.00	1.52−26.00	2.10−26.00
index range (h, k, l)	$-11 \le h \le 15$	$-15 \le h \le 14$	$-15 \le h \le 15$
	$-10 \le k \le 10$	$-10 \le k \le 10$	$-9 \le k \le 10$
	$-16 \le l \le 16$	$-16 \le l \le 16$	$-13 \le l \le 16$
reflns collected	7640	9484	7879
independent reflns	5256 [$R_{(int)} = 0.0285$]	5224 [$R_{(int)} = 0.0272$]	4972 [$R_{(int)} = 0.0251$]
data/restraints/params	5256/1/372	5224/1/372	4972/1/372
GOF on F^2	1.020	1.040	1.016
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0559$	$R_1 = 0.0435$	$R_1 = 0.0463$
	$R_2 = 0.1077$	$R_2 = 0.1009$	$R_2 = 0.0983$
R indices (all data)	$R_1 = 0.0705$	$R_1 = 0.0484$	$R_1 = 0.0587$
	$R_2 = 0.1103$	$R_2 = 0.1024$	$R_2 = 0.1016$
absolute structure params	0.015(15)	0.020(15)	0.03(2)
largest diff. peak and hole (e Å^{-3})	0.804 and −0.495	0.211 and −0.426	0.194 and −0.354

determination, CD spectra, and variable-temperature magnetic susceptibility measurements. Interestingly, both chiral complexes **1** and **2** exhibit ferromagnetic coupling between neighboring Cu^{II} ions through the single asymmetric end-to-end azido bridge, which presents a successful example of generating new multifunctional materials (ferromagnetic and optically active) from chiral ligands.

Experimental Section

Materials. Manganese(II) perchlorate hexahydrate, copper(II) perchlorate hexahydrate, sodium azide, (*R*)-PhCHMeNH$_2$, and (*S*)-PhCHMeNH$_2$ were purchased from commercial sources and used as received. The (*R*)- and (*S*)-pyridine-2-carbaldehyde-imine ligands were synthesized as described in the literature.[24] Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer.

Caution! Although we have experienced no problem with the compounds reported in this work, perchlorate salts and sodium azide are often explosive and should be handled with great caution.

Physical Measurements. The IR spectra were taken on a Vector22 Bruker Spectrophotometer (400−4000 cm^{-1}) with KBr pellets. The visible spectra were recorded on a Shimadzu UV-3100 spectrometer. The circular dichroism spectra were recorded on a JASCO J-810 Spectropolarimeter with KBr pellets. The magnetic susceptibility was measured using a Quantum Design MPMS-XL7 SQUID magnetometer at temperatures ranging from 1.8 to 300 K.

Single-Crystal Structure Determination. The crystal structures of complexes **1**, **2**, and **3** were determined on a Siemens (Bruker) SMART CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data were collected using the following strategy: 606 frames of 0.3° in ω with $\phi = 0°$, 435 frames of 0.3° in ω with $\phi = 90°$, and 235 frames of 0.3° in ω with $\phi = 180°$. An additional 50 frames of 0.3° in ω with $\phi = 0°$ were collected to allow for decay correction. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by Bruker. Structures were solved by direct methods using the program SHELXL-97. The positions of metal atoms and their first coordination spheres were located from direct-method *E* maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, were refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso}. A summary of the crystal data collection and refinement parameters is given in Table 1.

Preparation of $[Cu(\boldsymbol{R}\text{-L})_2(N_3)]_n(ClO_4)_n$ (1). A methanolic solution (5 mL) of NaN$_3$ (32.5 mg, 0.5 mmol) was added to a methanolic solution (25 mL) containing (*R*)-pyridine-2-carbaldehyde-imine (105.2 mg, 0.5 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (93 mg, 0.25 mmol). A little yellow-green precipitate formed after 30 min and was filtered off. The green needle-shaped crystals were obtained after 3 days by slow evaporation of the above filtrate at room temperature. Yield: ca. 53%. Anal. Calcd for $C_{28}H_{28}ClN_7O_4Cu$: C, 53.76; H, 4.51; N, 15.67. Found: C, 53.27; H, 4.46; N, 15.61. IR (KBr, cm^{-1}): ν 2063, 2028 (ν_{asym} N_3^-).

Preparation of $[Cu(\boldsymbol{S}\text{-L})_2(N_3)]_n(ClO_4)_n$ (2). Compound **2** was prepared as green needle-shaped crystals in a manner similar to that of **1**, except that (*S*)-pyridine-2-carbaldehyde-imine was used. Yield: ca. 46%. Anal. Calcd for $C_{28}H_{28}ClN_7O_4Cu$: C, 53.76; H, 4.51; N, 15.67. Found: C, 53.65; H, 4.48; N, 15.98. IR (KBr, cm^{-1}): ν 2063, 2028 (ν_{asym} N_3^-).

Preparation of $[Mn(\boldsymbol{R}\text{-L})_2(N_3)]_n(ClO_4)_n$ (3). A methanolic solution (10 mL) of (*R*)-pyridine-2-carbaldehyde-imine (105.2 mg, 0.5 mmol) was added to a methanolic solution (25 mL) containing

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Cu(1)−N(1)	2.018(4)	N(5)−N(6)	1.172(5)
Cu(1)−N(2)	2.340(4)	N(6)−N(7)	1.170(6)
Cu(1)−N(3)	2.023(4)	N(1)−C(5)	1.357(6)
Cu(1)−N(4)	2.057(4)	N(2)−C(6)	1.244(6)
Cu(1)−N(5)	1.975(4)	C(5)−C(6)	1.507(7)
N(1)−Cu(1)−N(2)	77.54(16)	N(5)−Cu(1)−N(1)	93.60(16)
N(1)−Cu(1)−N(3)	174.13(16)	N(5)−Cu(1)−N(2)	94.52(15)
N(3)−Cu(1)−N(4)	80.07(14)	N(5)−Cu(1)−N(3)	90.33(15)
N(2)−Cu(1)−N(4)	98.92(14)	N(5)−Cu(1)−N(4)	165.25(14)
N(5)−N(6)−N(7)	175.5(5)	N(6)−N(5)−Cu(1)	127.7(4)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**

Cu(1)−N(1)	2.019(3)	N(5)−N(6)	1.175(5)
Cu(1)−N(2)	2.060(3)	N(6)−N(7)	1.155(5)
Cu(1)−N(3)	2.008(3)	N(4)−C(19)	1.266(5)
Cu(1)−N(4)	2.339(4)	N(3)−C(18)	1.353(5)
Cu(1)−N(5)	1.971(3)	C(18)−C(19)	1.477(6)
N(1)−Cu(1)−N(2)	80.14(12)	N(5)−Cu(1)−N(1)	90.23(13)
N(1)−Cu(1)−N(3)	175.52 (14)	N(5)−Cu(1)−N(2)	165.76(13)
N(3)−Cu(1) −N(4)	77.51(13)	N(5)−Cu(1)−N(3)	93.19(13)
N(2)−Cu(1)−N(4)	98.86(12)	N(5)−Cu(1)−N(4)	93.75(14)
N(5)−N(6)−N(7)	176.0(4)	N(6)−N(5)−Cu(1)	128.0(3)

NaN_3 (32.5 mg, 0.5 mmol) and $Mn(ClO_4)_2\cdot 6H_2O$ (91 mg, 0.25 mmol). After the mixture stood for 10 min, it was filtered. After 3 days, yellow needle-shaped crystals were obtained by slow evaporation of the above filtrate at room temperature. Yield: ca. 53%. Anal. Calcd for $C_{28}H_{28}ClN_7O_4Mn$: C, 54.51; H, 4.57; N, 15.89. Found: C, 54.45; H, 4.67; N, 16.11. IR (KBr, cm^{-1}): ν 2118, 2073 (ν_{asym} N_3^-).

Preparation of $[Mn(S\text{-}L)_2(N_3)]_n(ClO_4)_n$ (4). Compound **4** was prepared as yellow needle-shaped crystals using a method similar to that used for **3**, except that (*S*)-pyridine-2-carbaldehyde-imine was used. Yield: ca. 52%. Anal. Calcd for $C_{28}H_{28}ClN_7O_4Mn$: C, 54.51; H, 4.57; N, 15.89. Found: C, 54.40; H, 4.56; N, 16.12. IR (KBr, cm^{-1}): ν 2118, 2073 (ν_{asym} N_3^-).

Results and Discussion

Synthesis. Compounds **1**−**4** were synthesized in methanol by slow evaporation at room temperature. They are all air stable.

Crystal Structure. Complexes **1**, **2**, and **3** are characterized by X-ray crystallography. Selected bond lengths and angles for complexes **1** and **2** are listed in Tables 2 and 3. Complexes **1** and **2** are a pair of enantiomers, and they have similar crystal structures; no detailed descriptions are presented here for **2**.

The ORTEP drawing of the cation of complex **1** is shown in Figure 1. In the $[Cu(R\text{-}L)_2(N_3)]^+$ unit, the central Cu(II) ion is six-coordinate in the form of a elongated octahedron, CuN_6 (Figure 1a and 1b). Three nitrogen atoms of the two pyridine-2-carbaldehyde-imine ligands and the nitrogen atom of the bridging end-to-end azide group occupy the equatorial plane positions. The average bond length of Cu−N (plane) is 2.018(6) Å. The central Cu(II) slightly deviates from the equatorial plane. The axial positions are occupied by the nitrogen atom of the pyridine-2-carbaldehyde-imine ligand (Cu(1)−N(2) = 2.340(4) Å) and the nitrogen atom of the bridging azide group ($Cu(1)-N(7)^{\#1}$ = 2.683(4) Å; #1 $1 - x$, $1/2 + y$, $2 - z$). The octahedrons are elongated by ca. 0.5 Å. The azide is quasi-linear (N(5)−N(6)−N(7) = 175.5(5)°). The bond angles of N(6)−N(5)−Cu(1) and N(6)−N(7)−$Cu(1)^{\#1}$ are 128.0(3) and 143.4(4)°, respectively. Each azido ligand links two copper atoms by equatorial−axial positions.

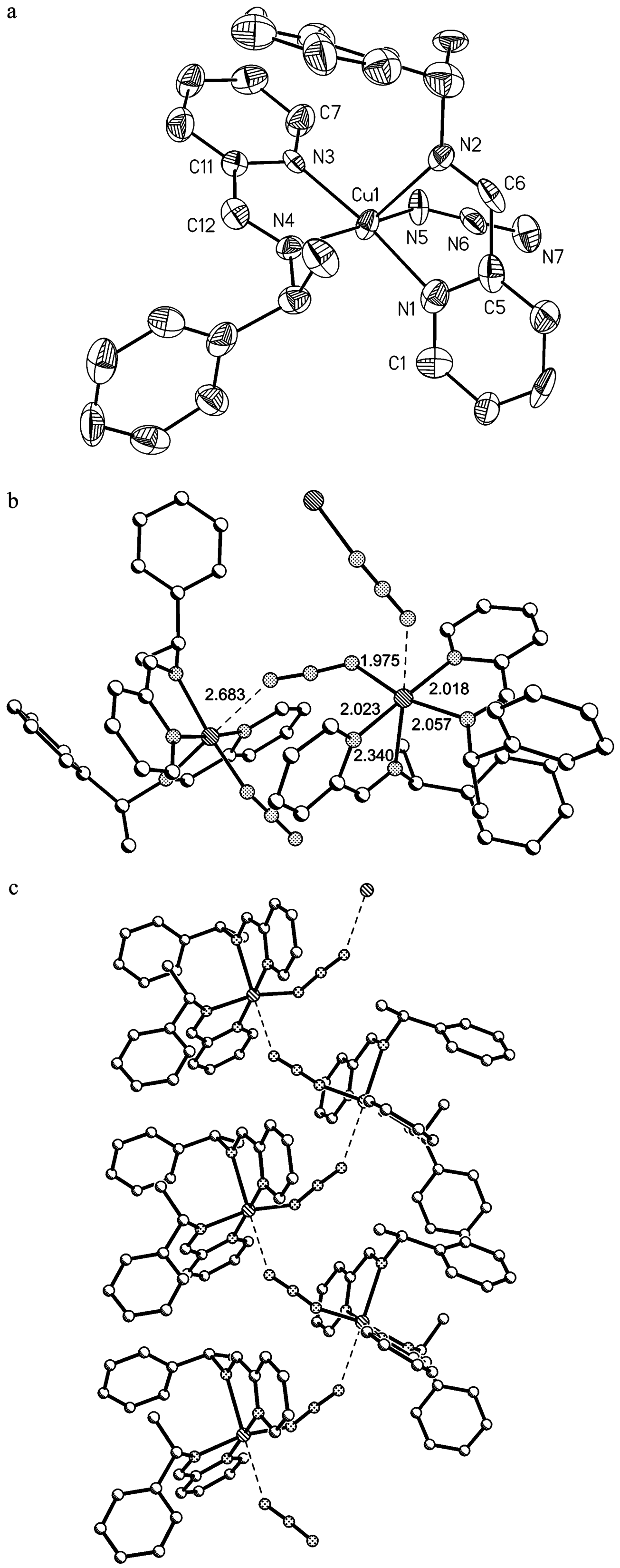

Figure 1. Structure of segments of the 1D chain of complex **1**. Thermal ellipsoids are shown at the 50% probability level (a). A perspective view of the 1D chain with the atom labeling scheme (b and c). Hydrogen atoms and anions are omitted for clarity.

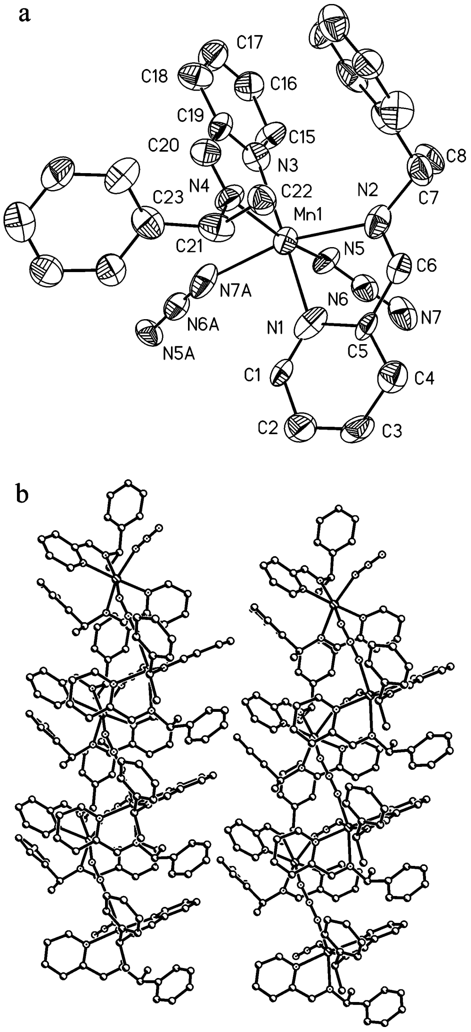

Figure 2. Structure of segments of the 1D chain of complex **3.** Thermal ellipsoids are shown at the 50% probability level (a). A perspective view of the 1D chain with the atom labeling scheme (b). Hydrogen atoms and anions are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **3**[a]

Mn(1)−N(1)	2.237(3)	N(5)−N(6)	1.191(5)
Mn(1)−N(2)	2.355(4)	N(6)−N(7)	1.180(5)
Mn(1)−N(3)	2.215(3)	N(1)−C(5)	1.348(5)
Mn(1)−N(4)	2.261(3)	N(2)−C(6)	1.270(5)
Mn(1)−N(5)	2.098(3)	C(5)−C(6)	1.482(6)
Mn(1)−N(7)$^{\#1}$	2.206(5)		
N(1)−Mn(1)−N(2)	73.35(14)	N(5)−Mn(1)−N(2)	89.95(13)
N(2)−Mn(1)−N(3)	105.15(13)	N(5)−Mn(1)−N(3)	92.50(12)
N(3)−Mn(1)−N(7)$^{\#1}$	91.18(14)	N(5)−Mn(1)−N(7)$^{\#1}$	94.67(13)
N(7)$^{\#1}$−Mn(1)−N(1)	89.68(15)	N(5)−N(6)−N(7)	176.7(4)
N(4)−Mn(1)−N(5)	165.30(12)	N(6)−N(5)−Mn(1)	136.7(3)
N(5)−Mn(1)−N(1)	96.91(11)	N(6)−N(7)−Mn(1)$^{\#2}$	151.5(3)

[a] #1 $-x + 2$, $y + 1/2$, $-z + 1$; #2 $-x + 2$, $y - 1/2$, $-z + 1$.

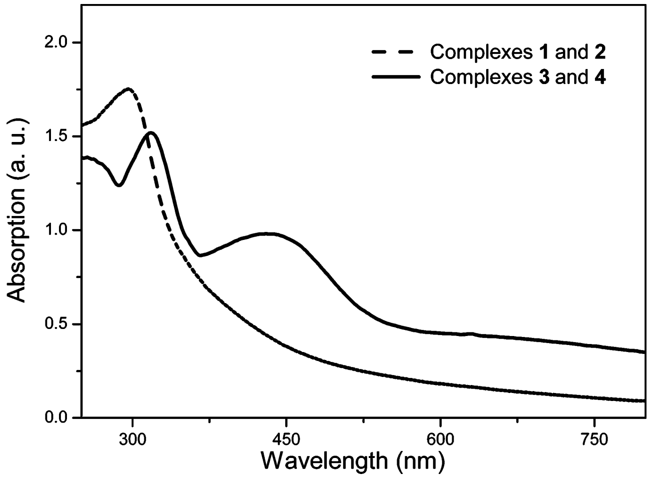

Figure 3. Solid-state UV−vis absorption spectrum of complexes **1**−**4** in KBr pellets.

The cationic units are linked together through it with bond lengths of 1.975(4) and 2.683(4) Å for Cu(1)−N(5) and Cu(2)−N(7)$^{\#1}$, respectively, resulting in a one-dimensional helical chain with single asymmetric azide-bridged bonds (Figure 1c). The helical chains are propagating along the *b* axis. The shortest intrachain Cu···Cu distance is 6.074 Å.

The labeled ORTEP plot for the cation of complex **3** is shown in Figure 2. Selected bond lengths and angles are listed in Table 4. The crystal structure of **3** is a one-dimensional coordination polymer, in which the central manganese(II) ion has a slightly distorted octahedral geometry, coordinated by four nitrogen atoms of the two pyridine-2-carbaldehyde-imine ligands and two nitrogen atoms of the azide bridges (Figure 2a). The bond lengths of Mn−N(azide) (Mn(1)−N(5) = 2.098(3) Å, Mn(1)−N(7)$^{\#1}$ = 2.206(5) Å; #1 $-x + 2$, $y + 1/2$, $-z + 1$) are shorter than those of the two pyridine-2-carbaldehyde-imine ligands. Each azide acts as a cis-bridging end-to-end ligand (cis-μ-(1,3), EE), and the adjacent monomeric units are related by a 2-fold screw axis, resulting in a one-dimensional helical chain propagating along the *b* axis (Figure 2b). The bond angles of N(5)−Mn(1)−N(7)$^{\#1}$, N(5)−Mn(1)−N(3), N(5)−Mn(1)−N(2), N(5)−Mn(1)−N(1), and N(5)−Mn(1)−N(4) are 94.67(13), 92.50(12), 89.95(13), 96.91(11), and 165.30(12)°, respectively. The end-to-end bridging azides are quasi-linear (N(5)−N(6)−N(7) = 176.7(4)°) and the bond lengths of N(5)−N(6) and N(6)−N(7) are 1.191(5) and 1.180(5) Å, respectively. The shortest intrachain Mn···Mn distance is 5.928 Å. The crystal structure of complex **4** is identical to that of complex **3**, and they are enantiomers.

Spectroscopic Studies. In general, the bridging and terminal azide groups are usually differentiated by the positions of the corresponding stretching absorption bands. The bridging azide ligands lead to a shift to higher wavenumbers. The IR spectra of polymeric metal complexes show two sharp bands at 2063 and 2028 cm^{-1} for **1** and **2** and at 2118 and 2073 cm^{-1} for **3** and **4**, which are consistent with the occurrence of single end-to-end bridging azides.

The UV−vis absorption spectra, recorded in a KBr matrix, show three absorption peaks at 320, 450, and 600 nm for **1** and **2** and one strong absorption peak at 300 nm for complexes **3** and **4** (Figure 3). The circular dichroism measurements were used to confirm the enantiomeric nature of these compounds (Figures 4 and 5). Compound **1** (R isomer) exhibits positive Cotton effects at $\lambda_{\max} = 450$ and 600 nm and a negative dichroic signal centered at $\lambda = 750$ nm, while compound **2** (S isomer) shows Cotton effects of the opposite sign at the same wavelengths. Compound **3** (R isomer) exhibits positive Cotton effects at $\lambda_{\max} = 325$ nm and a negative dichroic signal centered at $\lambda = 250$ nm, while

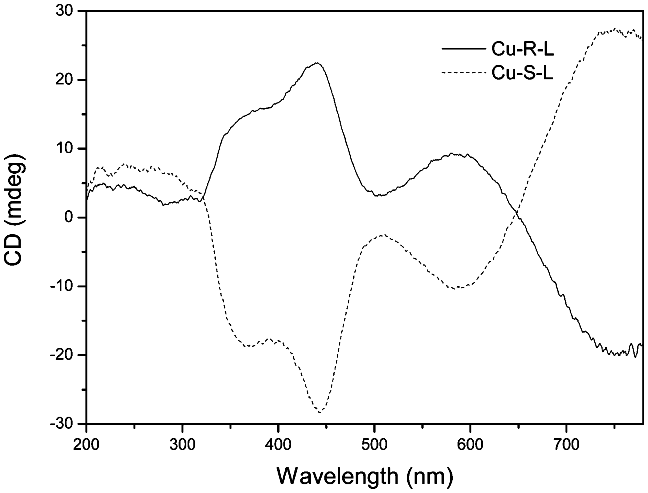

Figure 4. Circular dichroism spectra of 1D chiral copper(II) complexes **1** (R isomer, solid) and **2** (S isomer, dashed) in KBr pellets.

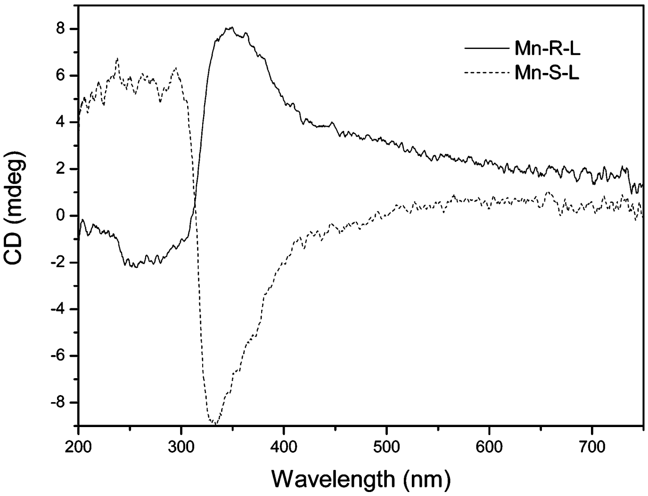

Figure 5. Circular dichroism spectra of 1D chiral manganese(II) complexes **3** (R isomer, solid) and **4** (S isomer, dashed) in KBr pellets.

compound **4** (S isomer) shows Cotton effects of the opposite sign at the same wavelengths. The corresponding absorption spectra are dominated by a charge-transfer band located around 400 nm, and the absorption spectra observed in the visible region can easily be assigned to the d−d transition. Furthermore, the SHG efficiency was measured to confirm the optical activity of these compounds. According to the principle proposed by Kurtz and Perry,[25] we estimated the second-order nonlinear optical effect of chiral complexes, and they show an SHG efficiency with a value of 0.4 times, for **1** and **2**, and 0.6 times, for **3** and **4**, that of urea.

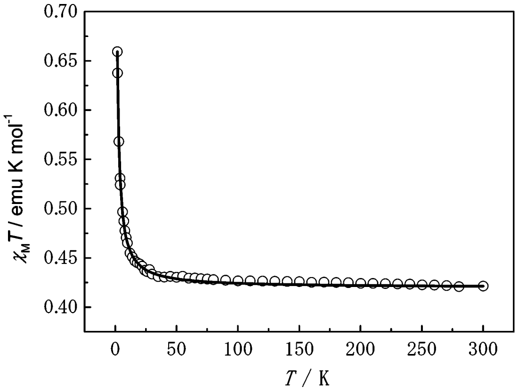

Figure 6. Temperature dependence of the magnetic susceptibility in the form of $\chi_M T$ vs T for complex **1** at 2 kOe; the solid line represents the best-fit curve from 300 to 1.8 K.

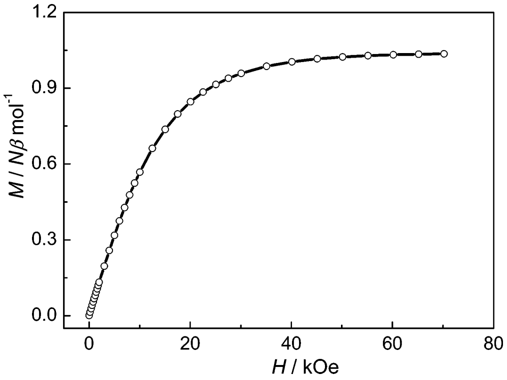

Figure 7. Field dependence of the magnetization for complex **1** at 1.8 K. The solid line is a guide for the eye.

Magnetic Properties. Magnetic susceptibility measurements for complexes **1** and **2** were obtained on the Quantum Design MPMS-XL7 SQUID magnetometer at temperatures ranging from 1.8 to 300 K. Because complexes **1** and **2** are a pair of enantiomers, they show the same magnetic behavior. As shown in Figure 6, the $\chi_M T$ value for complex **1** gradually increases from 0.42 emu K mol^{-1} at room temperature to 0.47 emu K mol^{-1} at 10 K; then, it rapidly increases to 0.66 emu K mol^{-1} at 1.8 K, indicating the presence of ferromagnetic coupling between the neighboring azide-bridged Cu^{II} ions. The field dependence of magnetization (0−70 kOe) measured at 1.8 K displays the saturation of the magnetization (Figure 7), reaching 1.04 $N\beta$ at 70 kOe for a ferromagnetic copper(II) system. According to the structure, complex **1** can be described as a 1D uniform chain,[26] and the susceptibilities expression is

$$\chi = \frac{Ng^2\beta^2}{4kT}\left[\frac{N}{D}\right]^{2/3} \tag{1}$$

where

$$N = 1.0 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5$$

$$D = 1.0 + 2.7979916y + 7.0086780y^2 + 8.6538644y^3 + 4.5743114y^4$$

$$y = J/2kT$$

A molecular approximation is taken into account for the interchain interaction (zj') as eq 3, the best-fit parameters for $\chi_M T$ versus T were $g = 2.06(2)$, $J = 0.70(3)$ cm^{-1}, and $zj' = 0.07(2)$ cm^{-1} with the final agreement factor $R = 4.1 \times 10^{-8}$. The positive J value confirms the presence of a ferromagnetic exchange coupling transmitted by a single end-to-end azido bridge. The intrachain-exchange interaction in

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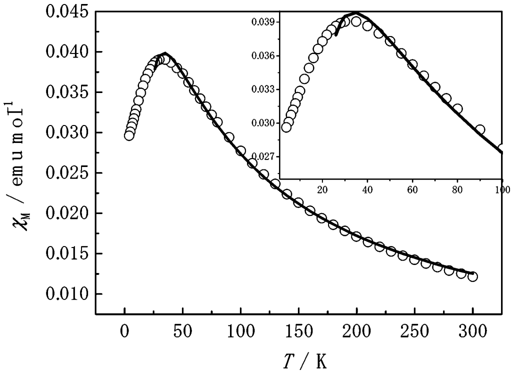

Figure 8. Temperature dependence of the magnetic susceptibility χ_M vs T for complex **3** at 2 kOe; the solid line represents the best-fit curve from 300 to 25 K.

complex **1** is slightly weaker than that reported previously because of the longer coordination bonds, N7−Cu, by the axis.[22] As we know, there are rare examples showing ferromagnetic coupling for copper complexes with single end-to-end azido bridges.[19,22]

In complexes **1** and **2**, the azide group is quasi-linear. Their structures show two magnetic exchange pathways of σ and π in complexes **1** and **2** as reported in ref 22a, and the $d_{x^2-y^2}$ magnetic orbitals, between the neighboring Cu^{II} ions, are strictly orthogonal. Furthermore, the single end-to-end azido bridge in both complexes is asymmetric with short Cu(1)−N(5) bond (1.975(4) Å) at the equatorial position and a long Cu(1)−N(7)$^{\#1}$ bond (2.683(4) Å) at the axial position. The mediation of weak ferromagnetic exchange interactions between Cu^{II} ions is also consistent with the results from DFT calculations on the nature of the magnetic coupling in those asymmetric end-on and end-to-end azido bridges.[27]

Complexes **3** and **4** also are a pair of enantiomers, and they show the same magnetic behavior. For complex **3**, as the typical measurements, the value of $\chi_m T$ at room temperature is 3.636 emu K mol^{-1}, which is smaller than the expected spin-only value of 4.375 emu K mol^{-1} per Mn(II) unit ($g_{Mn} = 2$, $S_{Mn} = 5/2$), indicating the possible antiferromagnetic coupling between Mn^{II} ions. As the sample is cooled, the $\chi_m T$ value decreases with the temperature and reaches 0.05 emu K mol^{-1} at 1.8 K, indicating that the antiferromagnetic interaction between the Mn(II) ions dominates the properties of complex **1**. In the plot of $\chi_m - T$, a broad maximum at 31 K was observed (Figure 8), suggesting the spins' short-range antiferromagnetic ordering within the chain in complex **3**.[28]

From a magnetic viewpoint, the different bridging modes of the azide ligand associated with the structural parameters (bridged bond lengths, bond angles, etc.) mediate different magnetic couplings.[15−20,27,29] For the Mn−azide system, the antiferromagnetic behavior is consistent with the end-to-end azido-bridged structure of complexes. Assuming a Heisenberg chain of S =5/2, the uniform chain model can be used here.[30] When the intermolecular interaction is taken into account, the van Vleck formula is written as

$$\chi = \frac{Ng^2\beta^2 S(S+1)}{3kT}\,\frac{1+u}{1-u} \tag{2}$$

$$\chi_{\text{chain}} = \frac{\chi}{1-(2zj'/Ng^2\beta^2)\chi} \tag{3}$$

where

$$u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$$

The data could be fitted from 300 to 25 K and the best fit by least-squares gives the parameters $g = 2.04(1)$, $J_1 = -4.7(2)$ cm^{-1}, $zj' = -0.9$ cm^{-1}, and $R = 1.4 \times 10^{-7}$ ($R = \sum[(\chi_M T)_{\text{calcd}} - (\chi_M T)_{\text{obs}}]^2/\sum(\chi_M T)_{\text{obs}}{}^2$). The fitting results indicate that this kind of azide bridge mediates very weak antiferromagnetic exchange between the metal ions in complex **3**. A possible explanation of the very weak antiferromagnetic exchange may be related with the arrangement of single EE azido bridges. In complex **3**, according to the structural data, the EE azido bridges are in a cis arrangement, the only superexchange pathway is derived from the d_{z^2} orbital of d^5 manganese(II), and the effective orbital overlap is very low. This result is close to the same as that for nickel(II) chains with a single azido bridge.[31]

In summary, our studies show that there are ferromagnetic interactions through single asymmetric EE azide bridges in the helical chains of the chiral copper(II) complexes, while antiferromagnetic behavior is observed in one-dimensional manganese(II) complexes with single EE azides. This work represents a successful method aimed at generating new multifunctional materials (ferromagnetic and optical active). Further work on polymeric metal complexes with chiral ligands and azide ions and achieving new functional molecular compounds, such as chiral magnets and nonlinear optical materials, is still underway in our laboratory.

Acknowledgment. This work was supported by the Major State Basic Research Development Program (G2000077500), the National Natural Science Foundation of China, and the Natural Science Foundation of Jiangxi Province.

Supporting Information Available: X-ray crystallographic files in CIF format for **1**−**3** and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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