Inorg. Chem. **2004**, *43*, 6620–6627

Inorganic Chemistry
Article

New Types of Heterospin Complexes from *trans*-Oxamido-Bridged Copper(II) Binuclear Units and Nitronyl Nitroxide Radicals: Crystal Structure and Magnetic Characterization

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Received June 10, 2004

Three new heterospin complexes derived from *trans*-oxamido-bridged copper(II) binuclear units [Cu_2(oxen), oxen = *N*,*N*-bis(2-aminoethyl)oxamide] and pyridine-substituted nitronyl nitroxides (*o*-, *m*-, and *p*-PYNN) were synthesized and characterized structurally and magnetically. Complexes **1** and **2** are four-spin complexes. Interestingly, it is found that in complex **3**, the Cu(II) ions and *m*-PYNN units are arranged to form 1D double-stranded helical chains, which to the best of our knowledge is the first example of a metal nitronyl nitroxide complex with such a 1D helical structure. The temperature dependencies of the magnetic susceptibilities of **1** and **2** were fitted to the four-spin model with the Hamiltonian $\hat{H} = -2J\hat{S}_{Cu1}\hat{S}_{Cu2} - 2j(\hat{S}_{Cu1}\hat{S}_{rad1} - \hat{S}_{Cu2}\hat{S}_{rad2})$, leading to $J = -150.5$ cm^{-1} and $j = 47.2$ cm^{-1} for complex **1** and $J = -191.7$ cm^{-1} and $j = -18.9$ cm^{-1} for complex **2**. The temperature dependence of the magnetic susceptibility of complex **3** was approximately simulated with a simple model composed of a dimer of Cu(II) ions and two *m*-PYNN molecules. The best fitting leads to the values of $J = -183.0$ cm^{-1} and $zJ' = -0.55$ cm^{-1} for the magnetic exchange of two Cu(II) ions through the oxamide bridge and that between the dimer of Cu(II) ions and two *m*-PYNN molecules, respectively. The antiferromagnetic exchange of oxamido-bridged Cu(II) ions in complexes **1**–**3** is strong. The strength of such antiferromagnetic interactions is also similar for the three complexes.

Introduction

The synthesis and magnetic characterization of heterospin complexes derived from paramagnetic metal ions and organic open-shell molecules have attracted much attention in recent years.[1−4] There are two major research goals in this field: a rational design of molecular assemblies that exhibit a spontaneous magnetization and a better understanding of the magneto−structural correlation that, in return, facilitates the rational design.[5,6]

Nitronyl nitroxides, initially synthesized in the 1970s as new spin probes, have been intensively investigated as stable spin units for molecular magnets since the discovery of the first purely organic ferromagnet [2-(*p*-nitrophenyl)nitronyl nitroxide] in 1991.[7] One important step of these studies is the formation of complexes between nitronyl nitroxides and paramagnetic metal ions. A great number of complexes with various structures have been prepared and characterized in terms of crystal structures and magnetic behaviors.[8,9] Gat-

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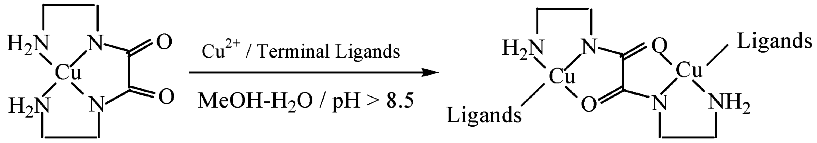
10.1021/ic049247d CCC: $27.50

Scheme 1. Formation of *trans*-Oxamido-Bridged Dinuclear Copper(II) Complexes

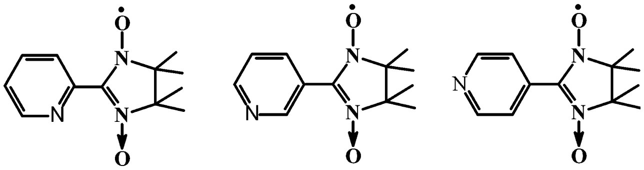


teschi et al. reported very recently that the reaction of Co(hfac)$_2$ (hfac = hexafluoroacetylacetonate) with nitronyl nitroxide leads to a 1D coordination polymer showing interesting magnetic relaxation behavior.[10] However, most of these complexes were based on the coordination of nitronyl nitroxides with M(hfac)$_n$ because nitronyl nitroxides are weak coordination ligands.[11−13] Nitronyl nitroxide derivatives with coligands, such as pyridine and 2,2′-bispyridine, on the other hand, can form metal complexes with a variety of structural topologies without the involvement of the hfac ligand.[14,15]

Coordination of nitronyl nitroxides with metal entities containing more than one metal ion is interesting with regard to the generation of new heterospin complexes which may find potential applications in the area of molecular magnets. The interactions between spin carriers in these types of heterospin complexes will be affected upon the coordination with nitronyl nitroxides, directly or indirectly, via auxiliary ligands, thus providing new examples for the magneto−structural relationship studies.

N,*N*-Bis(coordinating group)-substituted oxamides, such as oxen [*N*,*N*-bis(2-aminoethyl)oxamide], are well-known versatile ligands which can adopt cis or trans conformations upon coordination to metal ions (Scheme 1). Until now, *trans*-oxamido-bridged dinuclear copper(II) complexes with different terminal ligands (such as bpy, N_3^-, and NCO^-) have been investigated.[16] The dependence of antiferromagnetic interactions of two Cu(II) ions on the structural features of these complexes has also been discussed.

Scheme 2. *o*-, *m*-, and *p*-Pyridyl-Substituted Nitronyl Nitroxides (PYNN)



Thus, it would be interesting to obtain oxamido-bridged dimetallic complexes with pyridyl-substituted nitronyl nitroxides, PYNN (Scheme 2), as terminal ligands. In this paper, we will describe the synthesis, crystal structures, and magnetic characterization of the new complexes formed between Cu$_2$(oxen) and pyridine-substituted nitronyl nitroxide (*o*-PYNN, *m*-PYNN, and *p*-PYNN in Scheme 2). For a clear presentation, the three complexes are abbreviated as follows: Cu$_2$(oxen) with *o*-PYNN as complex **1**, Cu$_2$(oxen) with *p*-PYNN as complex **2**, and Cu$_2$(oxen) with *m*-PYNN as complex **3**. Complexes **1** and **2** are four-spin complexes, while complex **3** shows a helical 1D chain structure.

Experimental Section

General. Melting points were measured with an XT$_4$-100X apparatus and were uncorrected. The IR spectra were measured on a Perkin-Elmer SYSTEM FT-IR 2000 spectrophotometer in the form of KBr pellets. Elemental analyses for C, H, and N were carried out on a Carlo-Erba-1106 instrument.

Magnetic Measurement. Variable-temperature magnetic susceptibilities (in the temperature range of 4−300 K) were measured on a Quantum Design MPMS-7 SQUID magnetometer in a field of 1 T. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

X-ray Data Collection and Structural Determination. Single crystals of the complexes were selected and mounted on a Rigaku *R*-axis RAPID IP diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved with direct methods using the SHELX97 program.[17] The

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Table 1. Crystal and Structural Refinement Data for Complexes **1**−**3**

	1	**2**	**3**
formula	$C_{34}H_{52}Cl_2Cu_2N_{10}O_{18}$	$C_{30}H_{36}Cl_2Cu_2N_{10}O_{14}$	$C_{30}H_{40}Cl_2Cu_2N_{10}O_{16}$
formula weight	1086.84	958.66	994.70
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$
a (Å)	13.040(3)	14.896(3)	12.880(3)
b (Å)	23.159(5)	10.915(2)	21.188(4)
c (Å)	7.572(2)	12.452(2)	15.795(3)
β (deg)	98.28(3)	102.06(3)	106.62(3)
V (Å^3)	2262.9(9)	1979.9(6)	4130.5(14)
Z	4	4	4
density (mg/mm^3)	1.462	1.608	1.584
μ (mm^{-1})	1.118	1.284	1.237
temperature (K)	293(2)	293(2)	293(2)
scan range	$1.56° < \theta < 29.46°$	$1.40° < \theta < 27.21°$	$1.81° < \theta < 27.48°$
F (000)	1036	1020	2032
measured reflns	$-16 \le h \le 16$	$-19 \le h \le 19$	$-16 \le h \le 16$
	$-30 \le k \le 30$	$-14 \le k \le 13$	$-27 \le k \le 27$
	$-9 \le l \le 9$	$-15 \le l \le 15$	$-20 \le l \le 20$
no. of reflns collected	9185	7420	15958
no. of independent reflns	4910	4319	9366
R_{int}	0.0264	0.0429	0.0621
goodness of fit	1.060	1.011	0.995
R1^a (all data)	0.0553 (0.0878)	0.0435 (0.0946)	0.0712 (0.1688)
wR2^b (all data)	0.1338 (0.1463)	0.1050 (0.1108)	0.1673 (0.1874)
largest diff. peak, hole (e Å^{-3})	0.750, −0.732	0.333, −0.445	1.426, −1.121

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(F_o^2)^2]^{1/2}$.

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

Cu(1)−N(3)	1.919(3)	Cu(1)−N(1)	2.025(3)
Cu(1)−O(2)	2.146(3)	Cu(1)−O(1)^a	2.277(3)
Cu(1)−N(2)	2.321(4)		
N(3)−Cu(1)−N(1)	175.62(15)	N(3)−Cu(1)−O(2)	100.72(12)
N(1)−Cu(1)−O(2)	82.83(12)	N(3)−Cu(1)−O(1)^a	86.29(12)
N(1)−Cu(1)−O(1)^a	97.06(12)	O(2)−Cu(1)−O(1)^a	77.11(11)
N(3)−Cu(1)−N(2)	81.32(14)	N(1)−Cu(1)−N(2)	95.15(14)
O(2)−Cu(1)−N(2)	108.53(13)	O(1)^a−Cu(1)−N(2)	167.13(12)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x - 1, -y + 2, -z + 2$.

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

Cu(1)−N(1)	1.908(3)	Cu(1)−N(3)	1.986(3)
Cu(1)−O(1)^a	1.994(3)	Cu(1)−N(2)	2.008(3)
N(1)−Cu(1)−N(3)	173.15(14)	N(1)−Cu(1)-O(1)^a	84.24(12)
N(3)−Cu(1)−O(1)^a	92.20(12)	N(1)−Cu(1)−N(2)	82.54(13)
N(3)−Cu(1)−N(2)	101.01(13)	O(1)^a−Cu(1)−N(2)	166.76(11)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1, -y, -z$.

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

Cu(1)−N(8)	1.915(5)	Cu(1)−N(4)	1.987(5)
Cu(1)−O(5)	2.008(4)	Cu(1)−N(7)	2.026(6)
Cu(2)−N(10)	1.922(5)	Cu(2)−O(6)	1.985(4)
Cu(2)−N(1)	2.007(5)	Cu(2)−N(9)	2.020(5)
Cu(2)−O(4)^a	2.436(5)	Cu(1)−O(2)^a	2.493(5)
N(8)−Cu(1)−N(4)	170.6(2)	N(8)−Cu(1)−O(5)	83.7(2)
N(4)−Cu(1)−O(5)	92.0(2)	N(8)−Cu(1)−N(7)	82.6(2)
N(4)−Cu(1)−N(7)	101.8(2)	O(5)−Cu(1)−N(7)	166.25(19)
N(10)−Cu(2)−O(6)	83.7(2)	N(10)−Cu(2)−N(1)	169.0(2)
O(6)−Cu(2)−N(1)	90.89(19)	N(10)−Cu(2)−N(9)	83.0(2)
O(6)−Cu(2)−N(9)	166.18(19)	N(1)−Cu(2)−N(9)	102.8(2)
N(10)−Cu(2)−O(4)^a	101.16(19)	O(6)−Cu(2)−O(4)^a	95.62(17)
N(1)−Cu(2)−O(4)^a	88.88(18)	N(9)−Cu(2)−O(4)^a	83.2(2)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $x + 1/2, -y - 1/2, z - 1/2$.

corresponding crystallographic and refinement data are listed in Table 1. Selected bond lengths and angles of complexes **1**−**3** are included in Tables 2−4. Disorders and/or thermal motions were observed for some ClO_4^- ions or solvent molecules.

Synthesis. *o*-PYNN, *p*-PYNN, *m*-PYNN, and Cu(oxen) were synthesized according to the reported procedures.[16b,c,18]

Complex 1. To a green aqueous methanol solution (20 mL in a 1:1 ratio) containing $Cu(ClO_4)_2·6H_2O$ (74.0 mg, 2 mmol) and Cu(oxen) (50.0 mg, 2 mmol) was added *o*-PYNN (94.0 mg, 4 mmol), dissolved in 10 mL of methanol, while the mixture was being stirred. The mixture was further stirred for 30 min and then filtered out. Well-shaped dark-blue crystals were obtained from the filtrate after evaporation at room temperature for 1 week (0.11 g, 56%). Mp: 213−215 °C. IR (KBr, cm^{-1}) ν:[19] 3190, 3125 (NH_2), 1610 (C═O), 1356, 1370 (N−O). Anal. Calcd for $C_{34}H_{52}Cl_2Cu_2N_{10}O_{18}$: C, 37.57; H, 4.82; N, 12.89. Found: C, 37.76; H, 4.52; N, 13.12.

Complexes **2** and **3** were synthesized in a way similar to that of complex **1**.

Complex 2. Yield: 67%. Mp: 214−216 °C. IR (KBr, cm^{-1}) ν: 3191, 3127 (NH_2), 1613 (C═O), 1371 (N−O). Anal. Calcd for $C_{30}H_{36}Cl_2Cu_2N_{10}O_{14}$: C, 37.59; H, 3.79; N, 14.61. Found: C, 37.72; H, 3.76; N, 14.40.

Complex 3. Yield: 62%. Mp: 224−226 °C. IR (KBr, cm^{-1}) ν: 3190, 3126 (NH_2), 1614 (C═O), 1362, 1370 (N−O). Anal. Calcd for $C_{30}H_{40}Cl_2Cu_2N_{10}O_{16}$: C, 36.22; H, 4.05; N, 14.08. Found: C, 36.04; H, 4.48; N, 14.38.

Results and Discussion

Crystal Structures. Complex 1 [Cu_2(oxen)(*o*-PYNN)$_2$](ClO_4)$_2$·4MeOH. Complex **1** consists of a binuclear cen-

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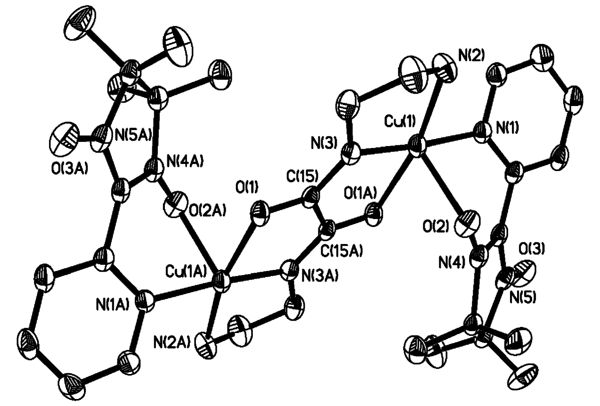

Figure 1. ORTEP drawing of the cation $[Cu_2(oxen)(o\text{-}PYNN)_2]^{2+}$ in complex **1**; thermal ellipsoids are drawn at the 30% probability level.

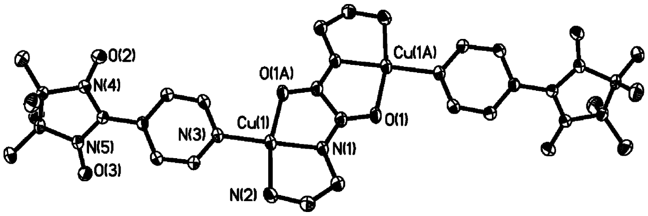

Figure 2. ORTEP drawing of the cation $[Cu_2(oxen)(p\text{-}PYNN)_2]^{2+}$ in complex **2**; thermal ellipsoids are drawn at the 30% probability level.

trosymmetric complex cation $[Cu_2(oxen)(o\text{-}PYNN)_2]^{2+}$, four solvent molecules (MeOH), and two perchlorate anions. The selected bond lengths and angles are given in Table 2. An ORTEP drawing of the binuclear cation is shown in Figure 1. Looking at the *o*-PYNN section, we observe that the imidazoline ring of the nitronyl nitroxide forms a dihedral angle of 35.6° with the pyridine plane.

The nitrogen atom of the pyridine ring and one oxygen atom of the nitronyl nitroxide are coordinated to the *trans*-oxamido-bridged copper(II) binuclear unit, yielding a new complex with four-spin carriers. The coordination geometry around each Cu(II) ion is the distorted square pyramidal CuN_3O_2. The basal plane comprises the carbonyl O(1A), the amide N(2) and the amine N(3) (nitrogen atoms of the oxamide ligand), and N(1) of the pyridine ring. The axial coordination site is occupied by the oxygen atom of the nitronyl nitroxide, and the bond length of Cu(1)−O(2) [Cu(1A)−O(2A)] is 2.146(3) Å, which is shorter than that of the equatorial Cu(1)−O(1A) [Cu(1A)−O(1)] bond [2.277(3) Å]. The mean plane of the imidazoline ring shows a dihedral angle of 40.0° with the basal plane around Cu(1) or Cu(1A). The separation of the nearest Cu(II) ions through the oxamide bridge is 5.473 Å.

Complex 2 $[Cu_2(oxen)(p\text{-}PYNN)_2](ClO_4)_2$. Complex **2** consists of a binuclear centrosymmetric complex cation $[Cu_2(oxen)(p\text{-}PYNN)_2]^{2+}$ and two perchlorate anions. The selected bond lengths and angles are given in Table 3. An ORTEP drawing of the cation is shown in Figure 2. Only the nitrogen atoms of the pyridine rings are coordinated to the *trans*-oxamido-bridged copper(II) binuclear unit to form a four-spin complex. The coordination geometry around each Cu(II) ion is the distorted square plane, composed of one carbonyl oxygen and three nitrogen atoms from the amide, amine, and pyridine groups. The bond lengths of the Cu(II)−N bonds in complex **2** are in the range of 1.908(3)−2.008(3) Å. The N−Cu−N angles range from 93.60(16) to 171.00(16)°, and the N−Cu−O angles range from 83.73(15) to 177.64(17)°. These structural data indicate that the CuN_3O unit is in a distorted square plane geometry. The distance between neighboring Cu(II) ions through the oxamide bridge is 5.193 Å.

Complex 3 $[Cu_2(oxen)(m\text{-}PYNN)_2](ClO_4)_2\cdot 2H_2O$. The building unit of complex **3** is shown in Figure 3, and selected bond lengths and angles are summarized in Table 4. Besides the oxygen and nitrogen atoms of the oxamido-bridged unit, each Cu(II) ion is coordinated to two molecules of *m*-PYNN through the nitrogen atoms of the pyridine rings and one oxygen atom of another nitronyl nitroxide. The coordination geometry around each Cu(II) ion is the distorted square pyramidal CuN_3O_2. The basal plane for the Cu(1) ion consists of the carbonyl O(5) atom, amide N(7) and amine N(8) (nitrogen atoms of the oxamide ligand), and N(4) of the pyridine ring. The axial coordination site of Cu(1) is occupied by the oxygen atom of nitronyl nitroxide, and the bond length of the apical bond Cu(1)−O(2)#1 [#1: $x + {}^{1}/_{2}$, $-y - {}^{1}/_{2}$, $z - {}^{1}/_{2}$] is 2.493(5) Å, which is longer than that of complex **1** or those of the previously reported complexes.[20] The Cu(2) ion shows similar coordination geometry. The basal plane around Cu(1) forms a dihedral angle of 178.4° with that of Cu(2). The two pyridine rings are parallel, with an interplane distance of 3.674 Å. The separation between the neighboring Cu(II) ions through the oxamide bridge is 5.235 Å.

Two molecules of *m*-PYNN are connected through the coordination with two Cu(II) ions to generate a "cyclophane". Interestingly, the cyclophane and $Cu_2(oxen)$ units are alternatively arranged to afford a unique 1D double-stranded helical chain, as illustrated in Figure 4. This striking feature of complex **3** is due to the coordination of each Cu(II) ion with two molecules of *m*-PYNN. As shown in Figure 4a, molecules of *m*-PYNN along the single-stranded chain are coordinated to Cu(II) ions in different directions, sequentially, causing a twist of the chain and finally resulting in the formation of the helical structure. This helical chain runs along a crystallographic 2_1 axis in the *c* direction, with a long pitch of 12.064 Å. In addition, the adjacent helical chains in compound **3**, one exhibiting left-handedness and the other right-handedness, are entangled by the coordinated Cu(II) ions, which are alternatively offered by two helical chains to generate a double-stranded helical chain. Because left-handed and right-handed helical chains coexist in the crystal structure, the whole crystal is mesomeric and does not exhibit chirality. To our knowledge, complex **3** constitutes the first example of a double helical spin chain with the participation of paramagnetic ions and organic radicals.

Magnetic Characterization and Discussion. In complexes **1**−**3**, there exists the magnetic exchange between two Cu(II) ions through the *trans*-oxamide bridge. According to the previous results,[21] such Cu(II)−Cu(II) ions are strongly antiferromagnetically coupled with $|J| > 150\ \text{cm}^{-1}$. The magnetic exchange between Cu(II) ions and nitronyl nitrox-

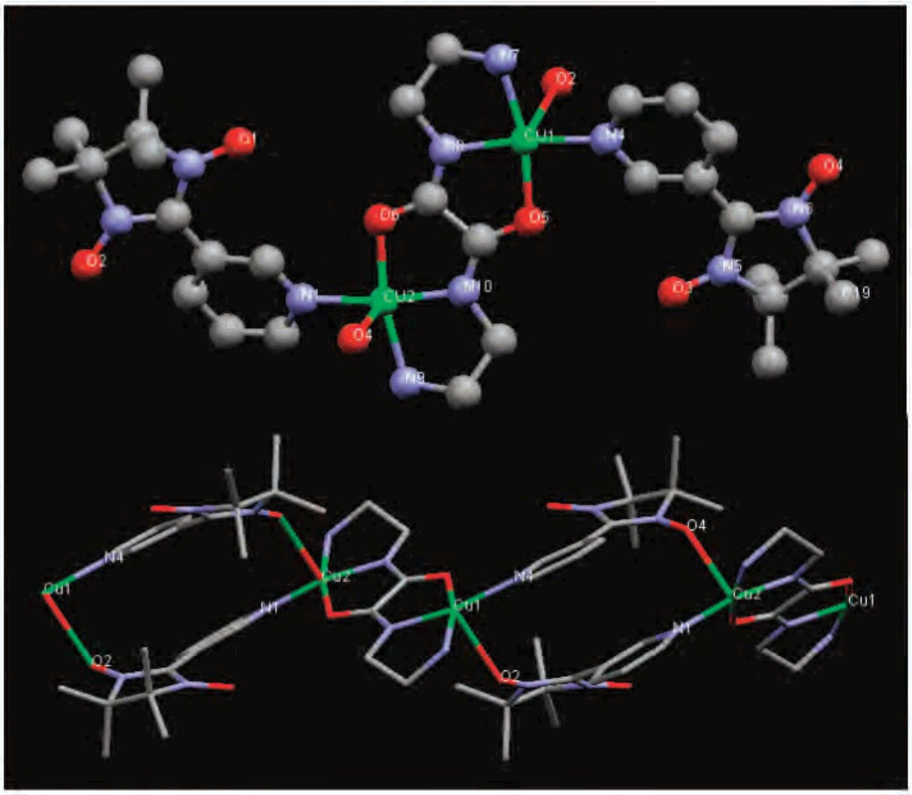

Figure 3. Asymmetric unit and its alternating 1D chain structure of the cations in complex **3**, $[Cu_2(oxen)(m\text{-}PYNN)_2]^{2+}$.

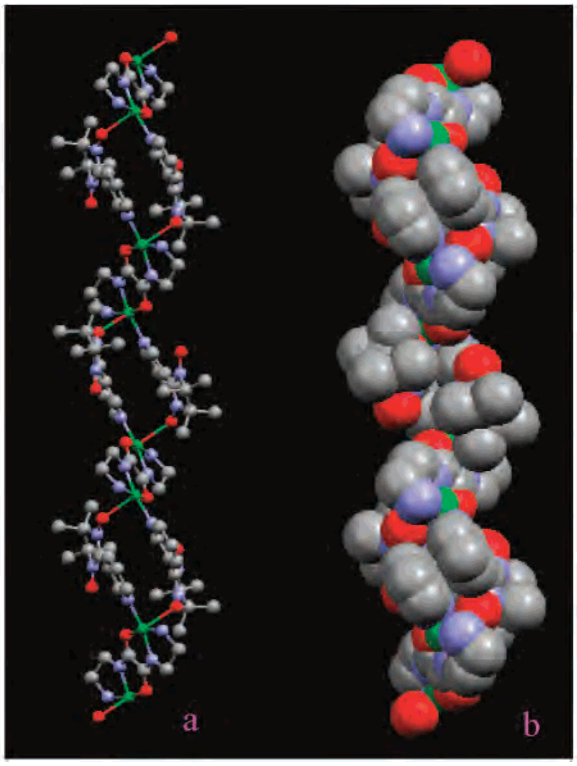

Figure 4. (a) Ball-and-stick plot of the double helical structure and (b) space-filling plot of the cations of complex **3**.

ides in complexes **1**−**3** is operated via the chelated coordination bond involving both the nitrogen atom of the pyridine ring and the oxygen atom of the nitronyl nitroxide, the coordination bond of Cu(II)−N (of the pyridine ring), and the coordination bonds of Cu(II)−O (of the nitronyl nitroxide) and Cu(II)−N (of the pyridine ring). For complexes **1** and **3**, each Cu(II) ion shows a distorted square pyramidal geometry and the oxygen atom of nitronyl nitroxide occupies the apical position. It was reported[22] that the magnetic interaction between the pyridine-substituted nitronyl nitroxide and the Cu(II) ion through the pyridine ring is weakly antiferromagnetic with $|J| < 20$ cm^{-1}. By comparison, the magnetic exchange between the Cu(II) ion and the nitronyl nitroxide via the apical Cu(II)···O (of nitronyl nitroxide) bond is moderately ferromagnetic.

At first, we tried to simulate the magnetic data of complexes **1** and **2** using J. S. Miller's method,[23] but it gave poor fitting results. Instead, the temperature dependencies of the magnetic susceptibilities of **1** and **2** were analyzed in the following way. Complexes **1** and **2** are centrosymmetric, and thus the spin−spin interaction in **1** and **2**, involving two Cu(II) ions and two nitronyl nitroxides, can be illustrated as shown in Scheme 3, where J is the magnetic exchange between two Cu(II) ions and j reflects the magnetic interaction between Cu(II) ions and nitronyl nitroxides. Accordingly, the spin−spin interaction in complexes **1** and **2** can

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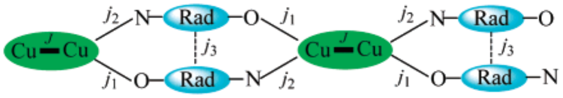
Scheme 3. Illustration of the Spin−Spin Interaction between the Nitronyl Nitroxides and the Cu(II)−Cu(II) Ions of Complexes **1** and **2**

$$\mathrm{Rad}\overset{j}{—}\mathrm{Cu(II)}\overset{J}{—}\mathrm{Cu(II)}\overset{j}{—}\mathrm{Rad}$$

Scheme 4. Spin−Exchange Interaction Pathways in the Alternating Chain System of Complex **3**



be described by the following Hamiltonian $\hat{H} = -2J\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{Cu2}} - 2j(\hat{S}_{\mathrm{Cu1}}\hat{S}_{\mathrm{rad1}} - \hat{S}_{\mathrm{Cu2}}\hat{S}_{\mathrm{rad2}})$. To simplify the question, when $g_{\mathrm{Cu}} = g_{\mathrm{rad}} = g$ is assumed, based on the above isotropic Hamiltonian, the temperature dependence of the magnetic susceptibility is deduced in eq 1, where N is Avogadro's number, g is the average Landé constant of spins, k is the Boltzmann constant, and β is the Bohr magneto.[24]

$$\chi = \frac{Ng^2\beta^2}{kT}\frac{A}{B} \tag{1}$$

$$A = 10\exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/kT) + 2\exp(-E_4/kT)$$

$$B = 5\exp(-E_1/kT) + 3[\exp(-E_2/kT) + \exp(-E_3/kT) + \exp(-E_4/kT)] + \exp(-E_5/kT) + \exp(-E_6/kT)$$

$$E_1 = -j - J/2 \qquad E_2 = j - J/2$$

$$E_3 = J/2 + (J^2 + j^2)^{1/2} \qquad E_4 = J/2 - (J^2 + j^2)^{1/2}$$

$$E_5 = j + J/2 + (4j^2 - 2jJ + J^2)^{1/2}$$

$$E_6 = j - J/2 + (4j^2 - 2jJ + J^2)^{1/2}$$

The spin−spin interaction for the 1D helical chain of complex **3** is shown in Scheme 4. As there are no short interatomic contacts between the neighboring chains, the interchain spin−spin interaction can be neglected. However, there are four types of spin−spin interactions, and thus strict theoretical treatment of the spin−spin interaction for this 1D helical chain would be rather complicated. A more elaborate model, taking into account all of these factors, may be constructed but is then over-parametrized. As a result, the determination of these parameters by the fitting of the experimental data would be meaningless. To prevent the agony, the temperature dependence of the magnetic susceptibility of complex **3** can be analyzed with a simple model as discussed below. On the basis of the X-ray crystal-structure analysis, it is noteworthy that the nitroxide moiety (ONCNO) forms a dihedral angle of 30.4° with the planes of the pyridine ring in the *m*-PYNN, leading to a small spin-density distribution in the pyridine ring due to difficult spin polarization of the π* of the ONCNO group into the pyridine ring of *m*-PYNN. Thus, the values of j_2 and j_3 (see Scheme 4) should be small. On the other hand, the oxygen atoms of the nitronyl nitroxides lie on the apical position of Cu(II), forming Cu(2)−O(4)#1 and Cu(1)−O(2)#1 [#1: $x + {}^1/_2, -y - {}^1/_2, z - {}^1/_2$], with bond lengths of 2.436(5) and 2.493(5) Å, respectively. These are longer than that of complex **1** or those of previously reported complexes.[20] Therefore, the value of j_1 (see Scheme 4) should also be small. As compared to the Cu(II)−Cu(II) magnetic interaction for complex **3**, the magnetic exchange between Cu(II) ions and nitronyl nitroxides either through the pyridine ring or via the Cu(II)···O (of nitronyl nitroxide) bond is weak, and magnetic coupling between the two *m*-PYNN molecules via $\pi-\pi$ interaction is also rather weak. Accordingly, the 1D helical chain can be considered to be composed of a dimer of Cu(II) units and two *m*-PYNN radicals in terms of magnetic behavior.[20c] Approximately, the magnetic interaction between the dimer of Cu(II) ions and the two molecules of *m*-PYNN is simply treated with the molecular field approach.[25] In other words, the temperature dependence of the magnetic susceptibility of complex **3** can be simulated with eqs 2 and 3, where J is the magnetic interaction within the dimer of Cu(II) ions, as indicated in Scheme 4, zJ' reflects the weak magnetic exchange between the dimer of Cu(II) ions and the two molecules of *m*-PYNN, and N_α is the temperature-independent paramagnetism (TIP), while other symbols have the same meanings as for eq 1.

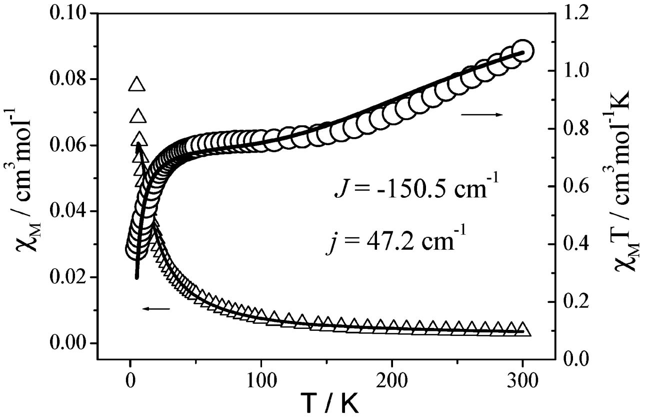


Figure 5. Plots of χ_{M} and $\chi_{\mathrm{M}}T$ versus T for complex **1**. The solid line represents the best fit.

$$\chi' = \frac{2Ng^2\beta^2}{kT[3 + \exp(-2J/kT)]} + \frac{C}{T} + N_\alpha \tag{2}$$

$$\chi_{\mathrm{M}} = \frac{\chi'}{1 - (2zJ'/Ng^2\beta^2)\chi'} \tag{3}$$

Complex 1. The magnetic susceptibility (χ_{M}) was measured in the temperature range of 4−300 K. The variation of χ_{M} and $\chi_{\mathrm{M}}T$ versus T is presented in Figure 5, where χ_{M} is the molar magnetic susceptibility and T is the absolute temperature. The room-temperature value of $\chi_{\mathrm{M}}T$ (1.07 cm^3 K mol^{-1}) is lower than that expected for four uncorrelated spins with $S = {}^1/_2$ ($\chi_{\mathrm{M}}T$ = 1.50 cm^3 K mol^{-1}), and $\chi_{\mathrm{M}}T$ decreases slowly upon lowering of the temperature. This result indicates that there exists a strong antiferromagnetic

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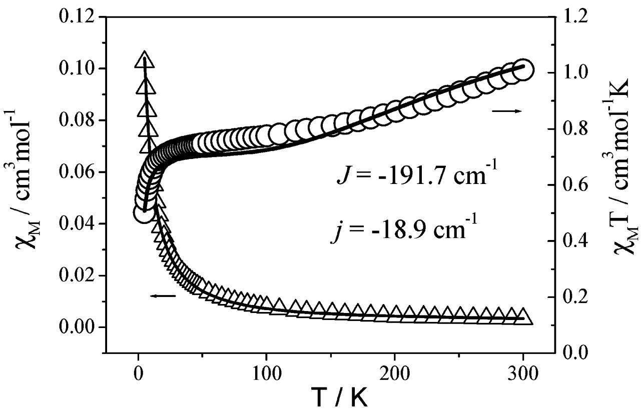

Figure 6. Plots of χ_M and χ_MT versus T for complex **2**. The solid line represents the best fit.

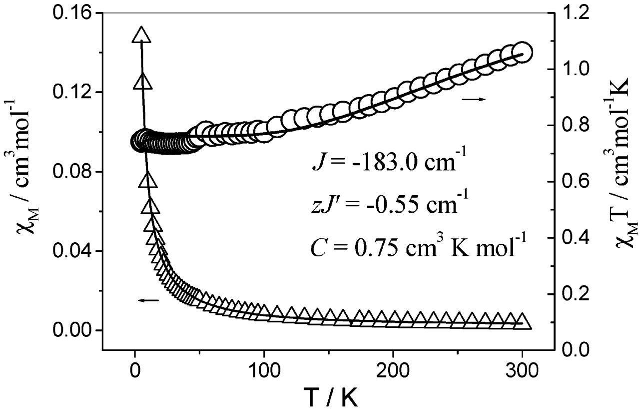

Figure 7. Plots of χ_M and χ_MT versus T for complex **3**. The solid line represents the best fit.

coupling interaction in complex **1**. The variation of χ_M with temperature follows the Curie−Weiss law. The corresponding Curie constant (C) and Weiss constant (θ) are found to be 0.83 cm^3 K mol^{-1} and −2.44 K, respectively.

The temperature dependence of the magnetic susceptibility of complex **1** was fitted to eq 1. The best fitting gives $J = -150.5$ cm^{-1}, $j = 47.2$ cm^{-1}, $g = 2.0$, and the agreement factor $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2 = 2.70 \times 10^{-4}$. As expected, the magnetic interaction between two Cu(II) ions through the *trans*-oxamide bridge is strongly antiferromagnetic. Ferromagnetic exchange is implied for the interaction between Cu(II) and *o*-PYNN in complex **1**. According to the X-ray crystal-structure analysis, the oxygen atom of the nitronyl nitroxide is coordinated to the Cu(II) ion at the apical position of a square pyramidal geometry. In this case, the unpaired electrons of the nitroxide radical delocalized on the π-orbital (five-atom fragment ONCNO) orthogonal to the $d_{x^2-y^2}$ magnetic orbital of the Cu(II) ion. This coordination mode results in the ferromagnetic interaction between Cu(II) and the radical.[26]

Complex 2. The variation of χ_M and χ_MT versus T for complex **2** is represented in Figure 6. The value of χ_MT at room temperature is 1.01 cm^3 K mol^{-1}, which is lower than that expected for four uncorrelated spins with $S = {}^1/_2$ ($\chi_MT = 1.50$ cm^3 K mol^{-1}), and χ_MT decreases upon lowering of the temperature. In the experimental temperature range of 4−300 K, the variation of χ_M with temperature changes follows the Curie−Weiss with $C = 0.83$ cm^3 K mol^{-1} and $\theta = -6.41$ K, indicating that the spins are mainly antiferromagnetic when coupled in complex **2**.

Again, the temperature dependence of the magnetic susceptibility of complex **2** was fitted to eq 1, and the best fitting leads to $J = -191.7$ cm^{-1}, $j = -18.9$ cm^{-1}, $g = 2.0$, and the agreement factor $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2 = 9.53 \times 10^{-5}$.

The magnetic interaction between Cu(II) and nitronyl nitroxide through the pyridine ring is weakly antiferromagnetic. This is in agreement with the following facts: (i) the nitrogen atom of the pyridine ring lies on the basal plane of the Cu(II) ion, and (ii) according to the spin polarization mechanism, the nitrogen atom of the pyridine ring owes small spin density.

Complex 3. Figure 7 shows the variation of χ_M and χ_MT with T for complex **3**. The value of χ_MT at room temperature is 1.03 cm^3 K mol^{-1}, which is lower than that expected for four noncoupled $S = {}^1/_2$ spins: two of the copper(II) ions and two *m*-PYNN radicals in complex **3**. When the temperature is lowered, the value of χ_MT decreases, indicating that the spins are predominately antiferromagnetically coupled. In addition, the plot of $\chi_M{}^{-1}$ versus a temperature range of 4−300 K essentially follows the Curie−Weiss law, with the values of the Curie constant $C = 0.76$ cm^3 mol^{-1} and the Weiss constant $\theta = -7.83$ K.

The fitting of the dependence of χ_M and χ_MT with temperature to eqs 2 and 3 gives the following parameters: $J = -183.0$ cm^{-1}, $zJ' = -0.55$ cm^{-1}, $C = 0.75$ cm^3 K mol^{-1}, $N_\alpha = 120 \times 10^{-6}$ cm^3 mol^{-1}, and the agreement factor $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2 = 5.56 \times 10^{-4}$. The results indicate that the magnetic interaction within the dimer of the Cu(II) ions is strongly antiferromagnetic, while that between the dimer of Cu(II) ions and two *m*-PYNN molecules is rather weak, as expected.

Summary

Three new heterospin complexes derived from *trans*-oxamido-bridged copper(II) binuclear units [Cu$_2$(oxen), oxen = *N*,*N*-bis(2-aminoethyl)oxamide] and pyridine-substituted nitronyl nitroxides (*o*-, *m*-, and *p*-PYNN) were synthesized and characterized both structurally and magnetically. Complexes **1** and **2** are four-spin complexes. In complex **1**, the nitrogen atoms of the pyridine rings and one oxygen atom of nitronyl nitroxide form coordination bonds. Two molecules of *p*-PYNN are linked to the Cu$_2$(oxen) unit through Cu−N coordination bonds in complex **2**. In complex **3**, each Cu(II) ion is coordinated to two molecules of *m*-PYNN through the Cu−N and the apical Cu−O bonds. Interestingly, the Cu(II) ions and *m*-PYNN of complex **3** are arranged to form 1D double-stranded helical chains, which to the best of our knowledge is the first example of a metal complex of nitronyl nitroxide with such a 1D helical structure. The temperature dependencies of the magnetic susceptibilities of complexes **1** and **2** were fitted to the four-spin model. The

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antiferromagnetic interaction between Cu(II)−Cu(II) is very strong for complexes **1** and **2**. The magnetic coupling between Cu(II) and nitronyl nitroxide is ferromagnetic for complex **1** and antiferromagnetic for complex **2**. For complex **3**, showing a 1D double-stranded helical chain, it is very difficult to evaluate quantitatively the magnitude of the spin−exchange interactions. However, the magnetic data of complex **3** were simulated with a simple model in which the 1D chain is considered to be composed of a strong coupling copper(II) dimer and two *m*-PYNN molecules. The result, again, shows a strong antiferromagnetic interaction between Cu(II) ions. For the three complexes, the magnetic exchange between two Cu(II) ions through a *trans*-oxamide bridge is strongly antiferromagnetic, and the strength of such an antiferromagnetic interaction is similar (150−200 cm^{-1}).

Acknowledgment. The present research was financially supported by NSFC (90101025, 20372066, 20331010, and 20391001), Chinese Academy of Sciences, and State Key Basic Research Program. D. Zhang thanks the National Science Fund for Distinguished Young Scholars.

Supporting Information Available: CIF files of the crystal structures of complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049247D