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Coordination Complexes of 2-(4-Quinolyl)nitronyl Nitroxide with M(hfac)$_2$ [M = Mn(II), Co(II), and Cu(II)]: Syntheses, Crystal Structures, and Magnetic Characterization

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Three new complexes of the formula M_2L_2 derived from 2-(4-quinolyl)nitronyl nitroxide (4-QNNN) and M(hfac)$_2$ [M = Mn(II), Co(II), and Cu(II)], (4-QNNN)$_2$•[Mn(hfac)$_2$]$_2$ (**1**), (4-QNNN)$_2$•[Co(hfac)$_2$]$_2$•2H$_2$O (**2**), and (4-QNNN)$_2$•Cu(hfac)$_2$•Cu′(hfac)$_2$ (**3**), were synthesized and characterized structurally as well as magnetically. Complexes **1** and **2** are four-spin complexes with quadrangle geometry, in which both the nitrogen atoms of quinoline rings and oxygen atoms of nitronyl nitroxides are involved in the formation of coordination bonds. For complex **3**, however, the nitrogen atoms of quinoline rings are coordinated with Cu(II) ion to afford a three-spin complex, which is further linked to another molecule of Cu(hfac)$_2$ (referred to as Cu′(hfac)$_2$) to form a 1D alternating chain. The magnetic behaviors of the three complexes were investigated. For complex **1**, as the nitronyl nitroxides and Mn(II) ions are strongly antiferromagnetically coupled, consequently its temperature dependence of magnetic susceptibility was fitted to the model of spin-dimer with $S = 2$, yielding the intradimer magnetic exchange constant of $J = -0.82$ cm^{-1}. For complex **2**, the temperature dependence of the magnetic susceptibility in the $T > 50$ K region was simulated with the model of two-spin unit with $S_1 = 3/2$ and $S_2 = 1/2$, leading to $J = -321.9$ cm^{-1} for the magnetic interaction due to Co(II)•••O coordination bonding, $D = -16.3$ cm^{-1} (the zero-field splitting parameter), $g = 2.26$, and $zJ = -3.8$ cm^{-1} for the magnetic interactions between Co(II) ions and nitronyl nitroxides through quinoline rings and those between nitronyl nitroxides due to the short O•••O short contacts. The temperature dependence of magnetic susceptibility of **3** was approximately fitted to a model described previously affording $J_1 = -6.52$ cm^{-1} and $J_2 = 3.64$ cm^{-1} for the magnetic interaction between nitronyl nitroxides and Cu(II) ions through the quinoline unit via spin polarization mechanism and the weak O•••Cu coordination bonding, respectively.

Introduction

The coordination of paramagnetic metal ions with organic open-shell molecules to make heterospin systems has become one of the very promising strategies for the design and synthesis molecular magnetic materials. By employment of this approach, a large number of complexes with various structures have been prepared and characterized in terms of crystal structures and magnetic behaviors.[1] Some of these complexes have been found to be bulk magnets with T_c up to 46 K.[2] Gatteschi et al. have reported very recently that the reaction of Co(hfac)$_2$ with nitronyl nitroxide leads to a 1D coordination polymer showing interesting magnetic relaxation behavior.[3] The scope of this approach to molecular magnetic materials has been expanded with regard to both the structures of stable organic radicals and the kinds of metal

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(1) See, for examples: (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) Caneschi, A.;. Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392. (c) Caneschi, A.; Gatteschi, D.; Sessoli, R. In *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; p 215. (d) Gatteschi, D.; Rey, P. In *Magnetic Properties of Organic Materials*; Lahti, P. M.; Marcel Dekker: New York, 1999. (e) Iwamura, H.; Inoue, K.; Hayamizu, T. *Pure Appl. Chem.* **1996**, *68*, 243.

(2) Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Ohashi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1803.

(3) Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio, C.; Sessoli, R.; Venturi, G.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1760.

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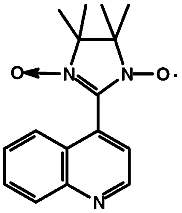
ions. For instance, besides nitronyl nitroxides, *N-tert*-butylnitroxides[4] and verdazyls[5] have been also used as paramagnetic ligands to afford new heterospin complexes. Apart from 3d metal ions, rare earth metal ions have also received attention in forming new heterospin systems with organic radicals.[6]

To obtain new bulk molecular magnets, one pursuing goal of this strategy is to obtain the extended 2D and even 3D complexes by employing organic stable radicals featuring coligands.[7] However, discrete complexes with definite geometry resulting from paramagnetic metal ions and organic radicals are good candidates for the fundamental studies of magneto−structural correlations, in particular the manner how structural factors affect the metal ion−organic radical interactions.[8] Such investigations are necessary not only for understanding the magnetic characteristics of these metal ion−organic heterospin systems but also for guiding the molecular design of new paramagnetic ligands for achieving high-T_c molecular magnets. Interesting cyclic dimer complexes of the formula M_2L_2 with quadrangle geometry were described by Iwamura et al.[9] and Lahti et al.[10] by using *N-tert*-butylnitroxides with phenylimidazole, pyridine, and phenylpyrimidine groups. However, only a few cyclic dimer M_2L_2 complexes were described for the nitronyl nitroxides with coligands such as imidazole and pyridine, one of which is formed between Cu(II) ion and 3-pyridylnitronyl nitroxide showing unusual temperature-dependent magnetic behavior.[8d,e] In this report, we describe the syntheses, crystal structures, and magnetic studies of new M_2L_2 complexes derived from 2-(4-quinolyl)nitronyl nitroxide (4-QNNN, Chart 1) with $M(hfac)_2$ [M = Mn(II), Co(II), and Cu(II); hfac = hexafluoroacetylacetonate]. For clear presentation, the three complexes are abbreviated as follows: $Mn(hfac)_2$ with 4-QNNN as complex **1**, $Co(hfac)_2$ with 4-QNNN as complex **2**, and $Cu(hfac)_2$ with 4-QNNN as complex **3**. Among the three new complexes, complexes **1** and **2** are four-spin cyclic dimers with quadrangle geometry.

Chart 1 Chemical Structure of 4-QNNN



Experimental Section

General Methods. Melting points were measured with an XT_4-100X apparatus and uncorrected. The IR spectra were measured on 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 5−300 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-monochrometed Mo Kα radiation (λ = 0.710 73 Å). The structure was solved with direct methods using the SHELX97 program.[11] The corresponding crystallographic and refinement data were listed in Table 1. Selected bond lengths and angles of complexes **1**−**3** were included in Table 2. Disorders and/or thermal motions were observed for fluorine atoms.

Synthesis. 4-QNNN was synthesized according to the reported procedures.[12]

Complex 1. A solution of 94 mg (0.2 mmol) of $Mn(hfac)_2$ in 30 mL of dry *n*-heptane was heated under reflux for 5 h. After that, the solution was cooled to 60 °C, and a solution of 4-QNNN (0.2 mmol) in 12 mL of CH_2Cl_2 was added. The resulting mixture was stirred for 15 min at this temperature and then cooled to room temperature. After filtration, the resulting solution was allowed to stand at room temperature for 5 days to produce well-shaped dark-blue crystals (95.6 mg, 63.4%). Mp: 225−226 °C. IR (KBr, cm^{-1}): 1651, 1531, 1500, 1364, 1257, 1215, 1148. Anal. Calcd for $C_{52}H_{40}N_6O_{12}F_{24}Mn_2$: C, 41.45; H, 2.68; N, 5.58. Found: C, 41.37; H, 2.73; N, 5.49.

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

Complex **2**: yield 24.1%; mp 227−228 °C; IR (KBr, cm^{-1}) 1644, 1527, 1361, 1258, 1206, 1147. Anal. Calcd for $C_{52}H_{40}N_6O_{12}F_{24}Co_2\cdot 2H_2O$: C, 40.27; H, 2.86; N, 5.42. Found: C, 40.38; H, 2.74; N, 5.48.

Complex **3**: yield 62.2%; mp 157−158 °C; IR (KBr, cm^{-1}) 1643, 1527, 1371, 1259, 1210, 1148. Anal. Calcd for $C_{52}H_{40}N_6O_{12}F_{24}Cu_2$: C, 40.98; H, 2.65; N, 5.51. Found: C, 40.61; H, 2.62; N, 5.30.

Results and Discussion

Synthesis. The synthesis of 4-QNNN was reported elsewhere.[12b] The preparation of complexes **1**−**3** was per-

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(4) See, for examples: (a) Inoue, K.; Hayamizu, T.; Iwamura, H. *Mol. Cryst. Liq. Cryst.* **1995**, *273*, 67. (b) Iwamura, H.; Inoue, K.; Koga, N. *New. J. Chem.* **1998**, 201. (c) Kumagai, H.; Inoue, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 1601.

(5) (a) Hicks, R. G.; Lemaire, M. T.; Thompson, L. K.; Barclay, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 8077. (b) Barclay, T. M.; Hicks, R. G.; Lemaire, M. T.; Thompson, L. K. *Inorg. Chem.* **2003**, *42*, 2261. (c) Barclay, T. M.; Hicks, R. G.; Lemaire, M. T.; Thompson, L. K. *Inorg. Chem.* **2001**, *40*, 5581.

(6) See, for example: Benelli, C.; Caneschi, A.; Gatteschi, D.; Sessoli, R. *Adv. Mater.* **1992**, *4*, 504.

(7) See, for examples: (a) Fegy, K.; Luneau, D.; Ohm, T.; Paulsen, C.; Rey, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1270. (b) Fegy, K.; Luneau, D.; Belorizky, E.; Novac, M.; Tholence, J.-L.; Paulsen, C.; Ohm, T.; Rey, P. *Inorg. Chem.* **1998**, *37*, 4524.

(8) (a) Francese, G.; Romero, F. M.; Neels, A.; Stoeckli-Evans, H.; Decurtins, S. *Inorg. Chem.* **2000**, *39*, 2087. (b) Vostrikova, K. E.; Luneau, D.; Wernsdorfer, W.; Rey, P.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 718. (c) Luneau, D.; Romero, F. M.; Ziessel, R. *Inorg. Chem.* **1998**, *37*, 5078. (d) Caneschi, A.; Gatteschi, D.; Sessoli, R. *Inorg. Chim. Acta* **1991**, *184*, 67. (e) Lanfranc de Panthou, F.; Belorizky, E.; Calemczuk, R.; Luneau, D.; Marcenat, C.; Ressouche, E.; Turek, P.; Rey, P. *J. Am. Chem. Soc.* **1995**, *117*, 11247.

(9) (a) Ishimura, Y.; Inoue, K.; Koga, N.; Iwamura, H. *Chem. Lett.* **1994**, 1693. (b) Kitano, M.; Ishimura, Y.; Inoue, K.; Koga, N.; Iwamura, H. *Inorg. Chem.* **1994**, *33*, 6012. (c) Iwamura, H.; Koga, N. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 437.

(10) (a) Field, L. M.; Lahti, P. M.; Palacio, F.; Paduan-Filho, A. *J. Am. Chem. Soc.* **2003**, *125*, 10110. (b) Field, L. M.; Lahti, P. M.; Palacio, F. *Chem. Commun.* **2002**, 636.

(11) Sheldrick, G. M. *SHELXL97*, *Structure Refinement Program*; University of Göttingen: Göttingen, Germany, 1996.

(12) (a) Ullman, E. F.; Osiecki, J. H.; Brocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049. (b) Zhang, D.; Zhu, H.; Xu, W.; Shuai, Z.; Zhu, D. *Synth. Met.* **2003**, *139*, 479.

Table 1. Crystallographic and Refinement Data for Complexes **1**, **2**, and **3**

	complex **1**	complex **2**	complex **3**
formula	$C_{26}H_{20}N_3O_6F_{12}Mn$	$C_{26}H_{22}N_3O_7F_{12}Co$	$C_{26}H_{20}N_3O_6F_{12}Cu$
fw	753.39	775.40	761.99
cryst system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calc} (mg/m^3)	1.552	1.526	1.606
μ (mm^{-1})	0.521	0.619	0.807
a (Å)	10.159(2)	30.184(6)	8.789(2)
b (Å)	11.370(2)	10.690(2)	13.433(3)
c (Å)	15.162(3)	21.586(4)	14.647(3)
α (deg)	68.83(3)	90	76.48(3)
β (deg)	86.69(3)	104.20(3)	72.61(3)
γ (deg)	80.87(3)	90	75.92(3)
V (Å^3)	1612.4(6)	6752(2)	1576.2(6)
Z	2	8	2
reflections collected/unique	8109/6230	9742/5258	9568/6597
R(int)	0.1152	0.1258	0.0461
R ($I \geq 2\sigma(I)$)^a	0.1057	0.0642	0.0527
wR$_2$^{a}	0.2464	0.1209	0.1301

^{a} $R = \Sigma|F_o| - \{|F_c|\}/\{\Sigma|F_o|\}$, w$R_2 = [\Sigma(w(F_o{}^2 - F_c{}^2)^2)/\Sigma(F_o{}^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**−**3**^{a}

complex **1**		complex **2**		complex **3**	
Mn(1)−O(41)	2.1153(14)	Co−O(2)	2.034(2)	Cu(1)−O(4)	1.967(3)
Mn(1)−O(21)^{i}	2.1320(13)	Co−O(1)	2.049(2)	Cu(1)−O(4)^{iii}	1.967(3)
Mn(1)−O(32)	2.1499(14)	Co−O(4)	2.051(2)	Cu(1)−O(3)	1.978(3)
Mn(1)−O(31)	2.1696(17)	Co−O(3)	2.089(2)	Cu(1)−O(3)^{iii}	1.978(3)
Mn(1)−O(42)	2.2139(18)	Co−O(5)	2.104(2)	Cu(1)−N(1)^{iii}	2.381(4)
Mn(1)−N(11)	2.3245(17)	Co−N(1)^{ii}	2.193(3)	Cu(1)−N(1)	2.381(4)
N(11)−C(11)	1.354(2)	C(12)−N(1)	1.298(4)	Cu(2)−O(5)	1.919(3)
N(11)−C(19)	1.388(2)	C(13)−N(1)	1.367(4)	Cu(2)−O(5)^{iv}	1.919(3)
N(21)−O(21)	1.3092(18)	C(20)−N(3)	1.349(4)	Cu(2)−O(6)	1.948(3)
N(21)−C(21)	1.363(2)	C(20)−N(2)	1.354(3)	Cu(2)−O(6)^{iv}	1.948(3)
N(22)−O(22)	1.2735(19)	C(19)−C(20)	1.471(4)	C(10)−N(3)	1.349(5)
N(22)−C(21)	1.350(2)	N(2)−O(5)	1.288(3)	C(10)−N(2)	1.351(5)
C(13)−C(21)	1.438(3)	N(3)−O(6)	1.213(3)	C(3)−C(10)	1.451(6)
O(41)−Mn(1)−O(32)	161.90(5)	O(2)−Co−O(4)	171.42(9)	N(2)−O(1)	1.279(4)
O(21)^{i}−Mn(1)−O(42)	177.07(6)	O(3)−Co−O(5)	177.42(8)	N(3)−O(2)	1.279(4)
O(31)−Mn(1)−N(11)	173.93(5)	O(1)−Co−N(1)^{ii}	172.90(10)	O(4)−Cu(1)−O(4)^{iii}	180.00(4)
O(41)−Mn(1)−N(11)	96.74(5)	O(1)−Co−O(4)	84.81(9)	O(3)−Cu(1)−O(3)^{iii}	180.0
O(21)^{i}−Mn(1)−N(11)	90.95(5)	O(1)−Co−O(3)	85.54(9)	N(1)^{iii}−Cu(1)−N(1)	180.000(1)
O(32)−Mn(1)−N(11)	96.33(6)	O(2)−Co−O(1)	88.56(9)	O(4)−Cu(1)−N(1)^{iii}	87.88(13)
O(42)−Mn(1)−N(11)	87.39(6)	O(1)−Co−O(5)	92.44(9)	O(4)^{iii}−Cu(1)−N(1)$^{ii\ i}$	92.12(13)
O(41)−Mn(1)−O(31)	83.54(6)	O(2)−Co−N(1)^{ii}	92.81(9)	O(3)−Cu(1)−N(1)^{iii}	93.73(12)
O(21)^{i}−Mn(1)−O(31)	95.07(6)	O(4)−Co−N(1)^{ii}	93.13(9)	O(3)^{iii}−Cu(1)−N(1)$^{ii\ i}$	86.27(12)
O(32)−Mn(1)−O(31)	82.14(6)	O(3)−Co−N(1)^{ii}	87.61(9)	O(4)−Cu(1)−N(1)	92.12(13)
O(31)−Mn(1)−O(42)	86.56(6)	O(5)−Co−N(1)^{ii}	94.46(9)	O(4)^{iii}−Cu(1)−N(1)	87.88(13)
				O(3)−Cu(1)−N(1)	86.27(12)
				O(3)^{iii}−Cu(1)−N(1)	93.73(12)

^{a} Equivalent positions: (i) $-x + 2, -y, -z + 2$; (ii) $-x + 1, y, -z + 3/2$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, -y + 2, -z$.

formed similarly according to the previous procedures.[13] For complexes **1** and **2**, both the nitrogen atoms of quinoline rings and the oxygen atoms of nitronyl nitroxides are involved in the formation of coordination bonds with Mn(II) and Co(II), respectively, to form the four-spin cyclic dimer complexes with quadrangle geometry. Under the same conditions, the reaction of 4-QNNN with Cu(hfac)$_2$ leads to complex **3** in which the nitrogen atoms of quinoline rings are found to form coordination bonds with Cu(II) ion affording a three-spin complex. Besides, there is one molecule of Cu(hfac)$_2$ (referred to as Cu′(hfac)$_2$), to which the three-spin complex is connected to form a 1D alternating chain, in the building unit of complex **3**, and thus it has the same molecular formula of M_2L_2 as complexes **1** and **2**. Variation of the reaction conditions (reactants ratio, temperature, and solvents) did not change the nature of products. By comparison, reaction of the *N-tert*-butylnitroxide containing phenylpyrimidine with Mn(hfac)$_2$ and Cu(hfac)$_2$, respectively, under similar conditions all led to the cyclic dimer complexes as reported recently by Lahti et al.[10]

Crystal Structures. Complex 1. Figure 1 shows the ORTEP drawing of the molecular structure of complex **1**. On the whole, the structure is central symmetric. Two molecules of 4-QNNN as paramagnetic ligands are linked through coordination bonds with two molecules of Mn(hfac)$_2$ to generate a four-spin cyclic dimer complex. For the paramagnetic ligand part, the nitronyl nitroxide unit (imidazoline ring) is not coplanar with the quinoline ring to which the nitronyl nitroxide unit is directly linked, forming a dihedral angle of 62.1°. Around Mn(1) [Mn(1A)], four oxygen atoms O(31), O(32), O(41), and O(42) [O(31A),

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(13) See, for examples: (a) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *J. Am. Chem. Soc.* **1987**, *109*, 2191. (b) Caneschi, A.; Gatteschi, D.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1988**, *27*, 1756.

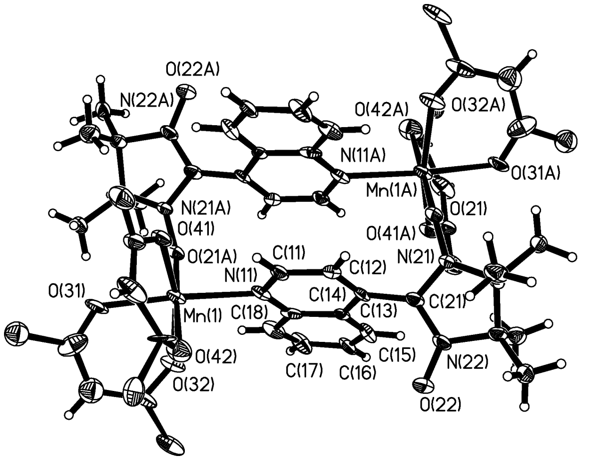

Figure 1. ORTEP diagram for complex **1**. Fluorine atoms are hidden for the ease of viewing, and some atoms were not labeled for clarity of presentation.

O(32A), O(41A), and O(42A)] from the hfac ligand, one oxygen atom O(21A) [O(21)] from the nitronyl nitroxide unit, and the nitrogen atom N(11) from the quinoline ring form a slightly distorted octahedron. On the basis of the bond lengths and angles (see Table 2), O(21A), O(32), O(41), and O(42) define the basal plane while N(11) and O(31) occupy the apical positions. The bond lengths of Mn(1)−N(11) and Mn(1)−O(21A) are 2.3245(17) and 2.1320(13) Å, being comparable to those of the complexes formed between nitronyl nitroxide substituted-pyridine and Mn(II) ion[14] and the complexes of nitronyl nitroxides with Mn(hfac)$_2$,[15] respectively. This basal plane shows a dihedral angle of 112.6° with the imidazoline ring of nitronyl nitroxide unit. The two quinoline planes, atoms C(12) [C(12A)], C(17) [C(17A)], and C(19) [C(19A)] of which deviate slightly from the planes, of complex **1** are crystallographically identical and parallel with an interplane distance of ~3.378 Å. Such short interplane separation implies the $\pi-\pi$ interaction between the two quinoline rings in complex **1**. In the crystal lattice of complex 1 (Figure 2), there are short interatomic contacts of O···O (3.388 Å) of nitronyl nitroxides among the cyclic dimers.

Complex 2. As shown in Figure 3, complex **2** shows almost the same structure as complex **1**. Both the nitrogen atoms of quinoline rings and the oxygen atoms of nitronyl ntroxide units are involved in the formation of coordination bonds. On the basis of the bond lengths and angles (see Table 2), the oxygen atoms O(5) [O(5A)] of nitronyl nitroxides lie on the basal plane while the nitrogen atoms N(1A) [N(1)] of quinoline units occupy the apical positions. Similar to complex **1**, the two quinoline planes are parallel with an average interplane distance of 3.651 Å. The neighboring M$_2$L$_2$ complexes interact through the short interatomic contact of O···O (3.181 Å) of nitronyl nitroxides to yield one-dimensional chain consisting of the cyclic dimers as indicated in Figure 4.

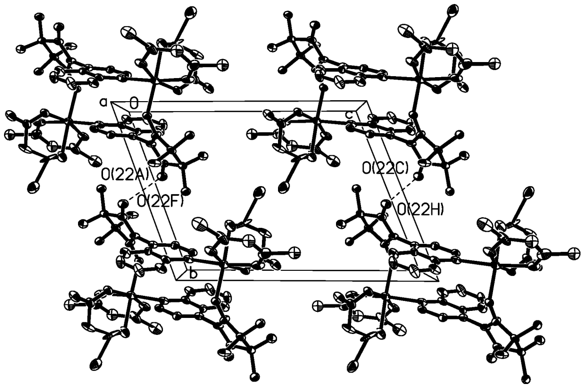

Figure 2. Intermolecular arrangements for complex **1** and indication of the short interatomic contact of O···O of nitronyl nitroxides (3.388 Å) among the cyclic dimers.

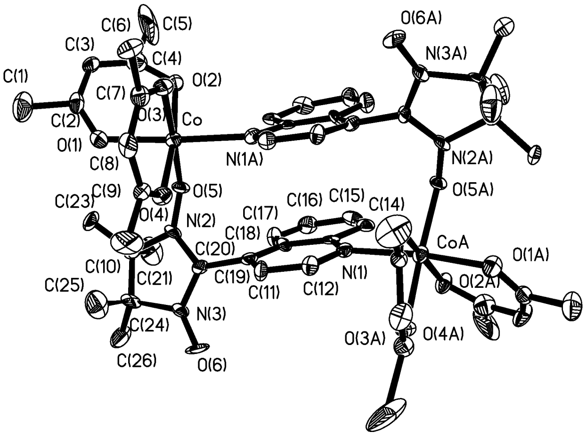

Figure 3. ORTEP diagram for complex **2**. Fluorine and hydrogen atoms are hidden for the ease of viewing, and some atoms were not labeled for clarity of presentation. The water molecules are also removed for the same reason.

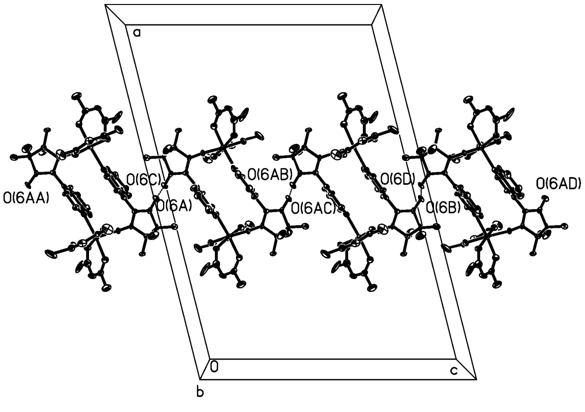

Figure 4. Intermolecular arrangements for complex **2** and indication of the short interatomic contact of O···O of nitronyl nitroxides (3.181 Å) among the cyclic dimers.

Complex 3. Figure 5 shows the ORTEP drawing of the molecular structure of complex **3**. The nitrogen atoms of quinoline rings are coordinated to Cu(II) ion to form a three-spin complex. This complex has an inversion center, at which the Cu(II) ion is located. By considering the bond lengths and angles, the two nitrogen atoms N(1) and N(1A) occupy the apical positions and the four oxygen atoms of hfac unit define the basal plane of the octahedron formed around the periphery of Cu(II) ion. The imidazoline ring shows a

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(14) Fettouhi, M.; Khaled, M.; Waheed, A.; Golhen, S.; Ouahab, L.; Sutter, J.-P.; Kahn, O. *Inorg. Chem.* **1999**, *38*, 3967.

(15) (a) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 3314. (b) Tanaka, M.; Matsuda, K.; Itoh, T.; Iwamura, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 810.

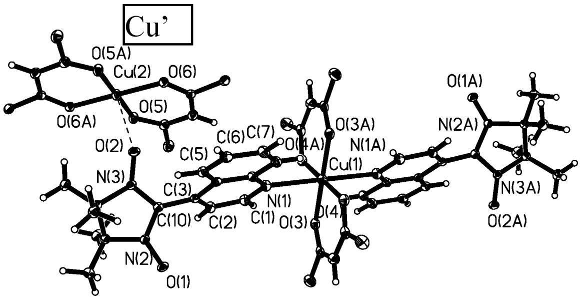

Figure 5. ORTEP diagram for complex **3**. Fluorine atoms are hidden for the ease of viewing, and some atoms were not labeled for clarity of presentation.

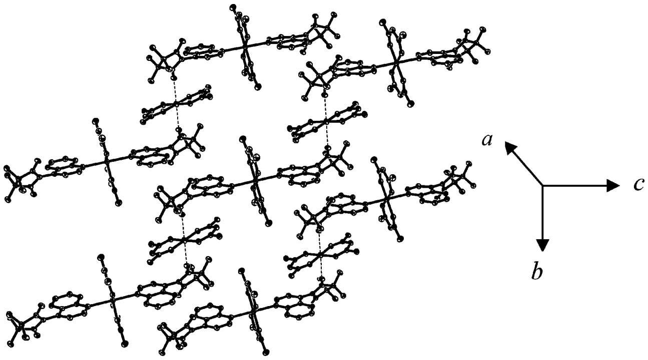

Figure 6. Formation of a 1D chain structure through the Cu′(II)···O coordination bonding and the interchain arrangements for complex **3**.

dihedral angle of 57.1° with the quinoline plane, which is almost perpendicular to the basal plane of the coordination sphere of Cu(II) ion. As mentioned above, there is another molecule of Cu(hfac)$_2$, which is referred to as Cu′(hfac)$_2$ in the building unit of complex **3**. Interestingly, weak coordination bonds are formed between the Cu(II) ions of Cu′(hfac)$_2$ and the oxygen atoms of each nitronyl nitroxide of the three-spin complex, and the oxygen atoms occupy the apical positions. As a result, a 1D alternating chain consisting of the three-spin complex and Cu′(hfac)$_2$ is formed as shown in Figure 6. The bond length of such a weak coordination bond [Cu(2)−O(2)] is 2.548 Å, and the bond angle of N(3)−O(2)−Cu(2) is 140.3° (Figure 5). The imidazoline rings of nitronyl nitroxides are not coplanar with the equatorial plane of Cu′(hfac)$_2$, forming a dihedral angle of 52.4°. These results indicate that the N−O bonds of nitronyl nitroxides are not perpendicular to the equatorial plane of Cu′(hfac)$_2$.

Magnetic Characterization and Discussion. The temperature dependence of the magnetic susceptibility for the three complexes was investigated in the temperature range 5−300 K under a magnetic field of 1 T. Figure 7 shows the variation of the reciprocal of χ_M and $\chi_M T$ with temperature for complex **1**, where χ_M is the molar magnetic susceptibility and T is the absolute temperature. The value of $\chi_M T$ at 300 K is 6.27 emu·K·mol^{-1}, close to the spin-only value (6.00 emu·K·mol^{-1}) expected for two uncorrelated spin system with $S = 2$ and $g = 2.00$. From 300 to 120 K, the value of $\chi_M T$ almost keeps constant. Below 120 K, it decreases gradually by lowering the temperature further. The variation of χ_M with temperature follows the Curie−Weiss equation as there is a linear relationship between $1/\chi_M$ and T. The corresponding Curie constant (C) and Weiss constant (Θ) are found to be 6.42 emu·K·mol^{-1} and −8.46 K, respectively. The value of C is close to two-spin system with $S = 2$ and $g = 2.00$. The result implies that each Mn(II) ion is so strongly antiferromagnetically coupled with the nitronyl nitroxide, one oxygen atom of which lies on the basal plane of coordination sphere of the Mn(II) ion, that one net spin with $S = 2$ is resulted. This assumption is in accordance with previous results.[16] Consequently, the experimental data of $\chi_M T$ versus T for complex **1** was fitted to equations 1 and 2[17] for spin pairing of $S = 2$ spin units, and the interdimer spin−spin interaction due to the short interatomic contact of O···O of nitronyl nitroxides was treated simply with the mean-field theory. Here, g is the Landé constant for $S = 2$ spin units, k is the Boltzmann constant, β is the Bohr magneton constant, and N is Avogadro's number, while J and zJ reflect the intra- and interdimer spin−spin interactions, respectively. The best fitting leads to $J = -0.82$ cm^{-1} and $zJ = -0.05$ cm^{-1} for $g = 2.04$.

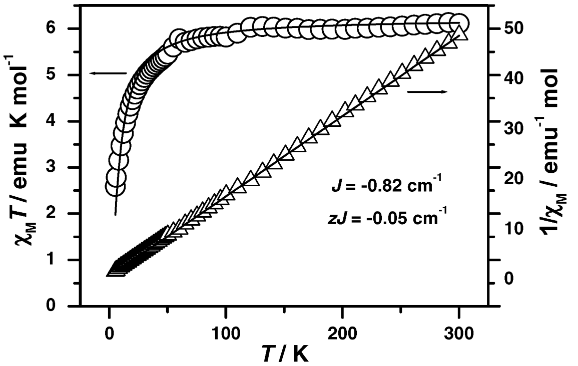

Figure 7. Plot of $1/\chi_M$ and $\chi_M T$ vs temperature for complex **1**. The solid line represents the best theoretical fitting with eqs 1 and 2 (see text).

$$\chi_{\text{dimer}} = \left(\frac{Ng^2\beta^2}{3kT}\right) \times \frac{84 + 6\exp(-10x) + 30\exp(-6x) + 180\exp(8x)}{7 + \exp(-12x) + 3\exp(-10x) + 5\exp(-6x) + 9\exp(8x)} \qquad x = J/kT \quad (1)$$

$$\chi_M = \frac{\chi_{\text{dimer}}}{1 - (2zJ/Ng^2\beta^2)\chi_{\text{dimer}}} \qquad (2)$$

Iwamura et al.[9] and Lahti et al.[10] reported separately the cyclic dimer complexes formed between *N*-*tert*-butylnitroxides containing pyridine, phenylimidazole, and phenylpyrimidine with Mn(hfac)$_2$. In these cases, the Mn(II) ion is strongly antiferromagnetically coupled with *N*-*tert*-butylnitroxide, and thus it can be considered as a net-spin with $S = 2$. The spin−spin interaction for the spin-dimer with $S = 2$ can be well understood by spin parity analysis as illustrated

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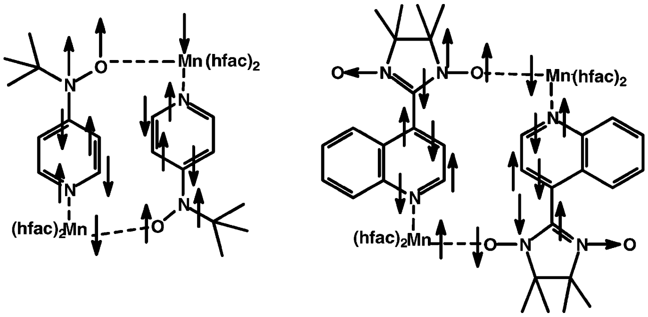
(16) (a) Caneschi, A.; Gatteschi, D.; Sessoli, R. *Inorg. Chem.* **1993**, *32*, 4612. (b) Caneschi, A.; Gatteschi, D.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1991**, *30*, 3936. Gatteschi et al. analyzed the temperature dependence of magnetic susceptibility of a similar complex of nitronyl nitroxide with Mn(hfac)$_2$ in a more complicated manner (see ref 8d), but the results showed that Mn(II) ions and the nitronyl nitroxides were strongly antiferromagnetically coupled.

(17) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, Germany, 1986.

Scheme 1. Spin Parity Analysis for the Spin−Spin Interaction in the Cyclic Dimers of the Complex Derived from *N*-*tert*-Butylnitroxide with Pyridine and Mn(hfac)$_2$ and Complex **1**



in Scheme 1[10] with *N*-*tert*-butylnitroxides containing pyridine as an example. Previous experimental and theoretical results[18] have indicated the carbon atom of nitronyl nitroxide unit, which is directly linked to the aromatic ring such as phenyl, pyridine, and quinoline, has negative spin-density. As a result, the nitrogen atom of quinoline ring of 4-QNNN has the opposite sign of spin density as compared to the nitrogen atom of the pyridine ring of 4-*N*-*tert*-butylnitroxide pyridine. Therefore, according to the spin parity analysis (Scheme 1), the antiferromagnetic interaction for spin-dimer with $S = 2$ for complex 1 is anticipated, since the intradimer spin−spin interaction is ferromagnetic with $J = +6.04$ cm^{-1} for the cyclic dimer complex of 4-*N*-*tert*-butylnitroxide pyridine with Mn(hfac)$_2$.[9b] This is just in agreement with the fitting result on the basis of the experimental magnetic data as discussed above. But the spin−spin ($S = 2$) interaction for complex 1 is rather weak as compared again to that of the cyclic dimer complex derived from 4-*N*-*tert*-butylnitroxide pyridine and Mn(hfac)$_2$. This may be explained by the following points: (1) For nitronyl nitroxides, the spin densities are mostly distributed in the imidazoline ring, and only small portion of the spin densities are resided on the atoms of substituted groups. As a result, the nitrogen atom of the quinoline ring of 4-QNNN possesses rather small spin density compared with the corresponding nitrogen atom of 4-*N*-*tert*-butylnitroxides pyridine. (2) Within the cyclic dimer, atoms of the two parallel quinoline rings with short interatomic contacts have opposite spin densities, and hence according to the McConnell principle,[19] such interatomic contacts would lead to ferromagnetic spin−spin interaction. Thus, such through-space interaction may partially weaken the antiferromagnetic spin−spin coupling via the spin polarization pathway.

Owing to the strong antiferromagnetic interaction between the nitronyl nitroxides and Mn(II) ion in complex **1**, the spin density of the oxygen atoms of nitronyl nitroxides will be largely reduced. Consequently, the spin−spin coupling due to the short interatomic contact of O···O (see Figure 2) would be rather weak. This is in agreement with the rather small value of *zJ* obtained by fitting the magnetic data to eqs 1 and 2 as mentioned above.

Figure 8 shows the temperature dependence of the molar magnetic susceptibility in terms of the reciprocal of χ_M and $\chi_M T$ for complex **2**. The value of $\chi_M T$ at 300 K is 3.11 emu·K·mol^{-1}, much smaller than that expected for the uncorrelated spins of two Co(II) ($S = 3/2$) ions and two nitronyl nitroxide units ($S = 1/2$). But it is close to that for two $S = 1$ spins with $g \approx 2.7$. From 300 to 130 K, the value of $\chi_M T$ keeps almost constant. Below 130 K, it decreases gradually by decreasing the temperature, reaching 0.38 emu·K·mol^{-1} at 5.0 K. Above 50 K, the variation of $1/\chi_M$ with temperature follows the Curie−Weiss equation with $C = 3.985$ emu·K·mol^{-1} and $\Theta = -20.9$ K.

The strict analysis of the magnetic data for Co(II) complexes needs to consider the effects of spin−orbit coupling and zero-field splitting. For complex **2**, there exists at least two types of spin−spin exchange between the nitronyl nitroxides and Co(II) ions, one through the direct bonding of the oxygen atoms of nitronyl nitroxides and Co(II) ions and the other through the quinoline ring via the spin-polarization mechanism. Besides, short interatomic O···O contacts of nitronyl nitroxides are found among the neighboring four-spin complexes of **2**. Moreover, the low-temperature magnetic behavior is more difficult to analyze, since the octahedral Co(II) energy levels become largely depopulated, until eventually a single Kramers doublet is occupied. In this limit antiferromagnetic coupling within **2** would yield a nonmagnetic ground state. Such effect should also contribute to the decrease of $\chi_M T$ at low temperature for **2**. A more elaborate model, taking into account all these factors, may be constructed but is then overparametrized. As a result, the determination of these parameters by fitting of the experimental data would become meaningless. Nevertheless, we try to simulate the temperature dependence of the magnetic susceptibility of 2 in the $T > 50$ K region.

Previous studies of the complexes of nitronyl nitroxides with Co(hfac)$_2$ indicated that Co(II) ion ($S = 3/2$) and nitronyl nitroxide, oxygen atoms of which were directly bonded to Co(II) ion, were strongly antiferromatically coupled.[20] As the coordination mode and corresponding bond lengths and angles are similar to those of the reported complexes, it is reasonable to assume that the antiferromagnetic interaction between Co(II) ions ($S = 3/2$) and nitronyl nitroxides via Co(II)···O coordination bonding in **2** is also very strong. In comparison, it was reported that the magnetic exchange between paramagnetic metal ions and nitronyl nitroxides through pyridine ring was rather weak.[21] Thus, it can be deduced that the magnetic interaction between Co(II) ions and nitronyl nitroxides through quinoline ring in **2** should be also rather weak. This is very likely due to the fact that for pyridine- or quinoline-substituted nitronyl nitroxides most spin densities of nitronyl nitroxides are distributed in imidaziline rings and those in the pyridine or quinoline rings are rather small. As a result, the strong

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[18] (a) Zheludev, A.; Barone, V.; Bonnet, M.; Delley, B.; Grand, A.; Ressouche, E.; Rey, P.; Subra, R.; Schweitzer, J. *J. Am. Chem. Soc.* **1994**, *116*, 2019. (b) Yamaguchi, K.; Okumura, M.; Nakano, M. *Chem. Phys. Lett.* **1992**, *191*, 237.

[19] McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

[20] Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1988**, *27*, 1553.

[21] (a) Dasna, I.; Golhen, S.; Ouahab, L.; Daro, N.; Sutter, J.-P. *New. J. Chem.* **2001**, *25*, 1572. (b) Dasna, I.; Golhen, S.; Ouahab, L.; Fettouhi, M.; Pena, O.; Daro, N.; Sutter, J.-P. *Inorg. Chim. Acta* **2001**, *326*, 37.

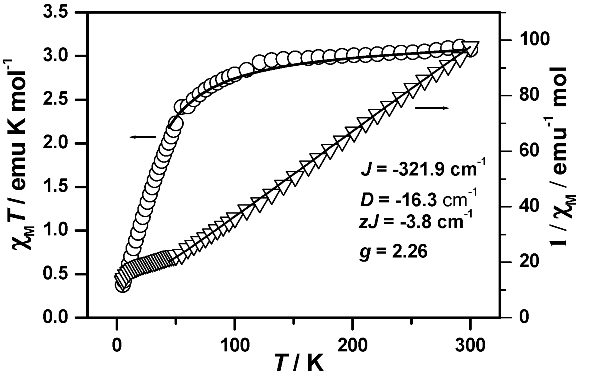

Figure 8. Plot of $1/\chi_M$ and $\chi_M T$ vs temperature for complex **2**. The solid line represents the best theoretical fitting with eqs 3 and 4 (see text).

antiferromagnetic interaction between Co(II) ions ($S = 3/2$) and nitronyl nitroxides via Co(II)$\cdots$O coordination bonding is mainly responsible for the magnetic behavior of **2**. If the strongly antiferromagnetically coupled Co(II) ion and nitronyl nitroxide are treated as one unit, complex **2** can be considered as the dimer of this unit. The temperature dependence of the magnetic susceptibility due to the strong antiferromagnetic interaction of Co(II) ion ($S = 3/2$) and nitronyl nitroxide can be analyzed with eq 3 derived from the Hamiltonian: $\hat{H} = -2J\cdot\hat{S}_{Co}\cdot\hat{S}_R - DS_z^2$ for the two spin unit with $S_1 = 3/2$ and $S_2 = 1/2$, where J refers to the magnetic exchange between Co(II) ($S = 3/2$) and nitronyl nitroxide, and D is the zero-field splitting parameter for Co(II) ion, while other symbols have the same meanings as for eqs 1 and 2. The contribution of the magnetic interactions between Co(II) ions and nitronyl nitroxides through quinoline rings and those between nitronyl nitroxides due to the short O$\cdots$O short contacts are simply treated with the mean-field theory, which is represented by zJ in eq 4. As illustrated in Figure 8, the temperature dependence of the magnetic susceptibility of 2 in the $T > 50$ K region can be well fitted to eqs 3 and 4, leading to $J = -321.9$ cm^{-1}, $D = -16.3$ cm^{-1}, $zJ = -3.8$ cm^{-1}, and $g = 2.26$. The results show the antiferromagnetic interaction between Co(II) ions ($S = 3/2$) and nitronyl nitroxides via Co(II)$\cdots$O coordination bonding in **2** is very strong.

$$\chi_{\text{dimer}} = \frac{2Ng^2\beta^2}{kT} \times \frac{\exp(A_1) + 4\exp(A_3) + \exp(A_5)}{2\exp(A_1) + \exp(A_2) + 2\exp(A_3) + \exp(A_4) + 2\exp(A_5)} \tag{3}$$

$$A_1 = [4J + 5D/4 - (4J^2 - 2DJ + D^2)^{1/2}]/kT$$

$$A_2 = (2J + D/4)/kT$$

$$A_3 = (6J + 9D/4)/kT$$

$$A_4 = (6J + D/4)/kT$$

$$A_5 = [4J + 5D/4 + (4J^2 - 2DJ + D^2)^{1/2}]/kT$$

$$\chi_M = \frac{2\chi_{\text{dimer}}}{1 - \chi_{\text{dimer}}(2zJ/Ng^2\beta^2)} \tag{4}$$

Figure 9 shows the temperature dependence of the molar magnetic susceptibility in terms of the reciprocal of χ_M and $\chi_M T$ for complex **3**. The value of $\chi_M T$ at 300 K is 1.50 emu·K·mol^{-1}, very close to that expected for the uncorrelated spins of two Cu(II) ($S = 1/2$) ions and two nitronyl nitroxide units ($S = 1/2$). From 300 to 200 K, the value of $\chi_M T$ increases slightly. Below 50 K, it decreases gradually with decreasing temperature. Above 15 K, the variation of χ_M with temperature follows the Curie−Weiss equation with $C = 1.596$ emu·K·mol^{-1} and $\Theta = -14.7$ K.

As mentioned above, the three-spin complex fragment with two nitronyl nitroxides and one unit of Cu(hfac)$_2$ and the Cu′(hfac)$_2$ unit are arranged alternately to form a 1D chain. The interchain spin−spin interaction can be neglected. The spin−spin interaction along the 1D chain is illustrated in Scheme 2, where J_1 and J_2 stand for the spin−spin interactions of nitronyl nitroxides and Cu(II) ions through the quinoline unit via spin-polarization mechanism and the weak coordination bonds with the oxygen atoms of nitronyl nitroxides occupying the apical positions, respectively. It has been reported that complexes derived from pyridine-substituted nitronyl nitroxide and Cu(hfac)$_2$ display antiferromagnetic interaction. For the complexes of nitronyl nitroxides and Cu(hfac)$_2$, in which the oxygen atoms of nitronyl nitroxides are directly coordinated to Cu(II) ion in the apical positions, the Cu(II) ion and nitronyl nitroxides are moderately ferromagnetically coupled.[22] By considering the fact that the coordination bond lengths and angles around Cu(hfac)$_2$ and Cu′(hfac)$_2$ in complex 3 are similar to those of the corresponding Cu(II) complexes, the magnetic interaction between nitronyl nitroxides and Cu(II) ions with the quinoline unit as the exchange path is expected to be antiferromagnetic with $J_1 < 0$, while that via the Cu′(II)$\cdots$O (of nitronyl nitroxides) coordination bonds is expected to be ferromagnetic with $J_2 > 0$ on the basis of previous studies. Therefore, strict theoretical treatment of the present 1D alternating magnetic chain would be difficult.[23] Instead, the temperature dependence of the magnetic susceptibility of complex 3 was approximately simulated with eqs 5 and 6,[24] in which χ_t[25]

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(22) (a) Caneschi, A.; Gatteschi, D.; Grand, A.; Laugier, J.; Pardi, L.; Rey, P. *Inorg. Chem.* **1988**, *27*, 1031. (b) Luneau, D.; Rey, P.; Laugier, J.; Fries, P.; Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. Am. Chem. Soc.* **1991**, *113*, 1245.

(23) Nevertheless, we tried to simulate the magnetic data of complex 3 with the Hamiltonian $H = -J_1(\vec{S}_1\cdot\vec{S}_2 + \vec{S}_2\cdot\vec{S}_3 + \vec{S}_5\cdot\vec{S}_6 + \vec{S}_6\cdot\vec{S}_7 + \vec{S}_9\cdot\vec{S}_{10} + \vec{S}_{10}\cdot\vec{S}_{11} - J_2(\vec{S}_3\cdot\vec{S}_4 + \vec{S}_4\cdot\vec{S}_5 + \vec{S}_7\cdot\vec{S}_8 + \vec{S}_8\cdot\vec{S}_9)$, in which only the spins of 3 three-spin complex fragments and 2 Cu′(hfac)$_2$ were considered, because of the computer calculation limit. S_i represents spins ($S = 1/2$) of the nitronyl nitroxides and Cu(II)/Cu′(II) ions, and J_1 and J_2 have the same meanings as in eqs 5 and 6. The best fitting leads to $J_1 = -19.8$ cm^{-1} and $J_2 = 11.8$ cm^{-1}. Although their values of J_1 and J_2 are relatively large, the signs of J_1 and J_2 are in agreement with those obtained by fitting to eqs 5 and 6 (see text). It should be noted that this is a rather approximate simulation.

(24) (a) Drillon, M.; Coronado, E.; Beltran, D.; Georges, R. *Chem. Phys.* **1983**, *79*, 449. (b) Kou, H.-Z.; Zhou, B.-C.; Gao, S.; Liao, D.-Z.; Wang, R.-J. *Inorg. Chem.* **2003**, *42*, 5604.

(25) Veit, R.; Girerd, J.-J.; Kahn, O.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 4175.

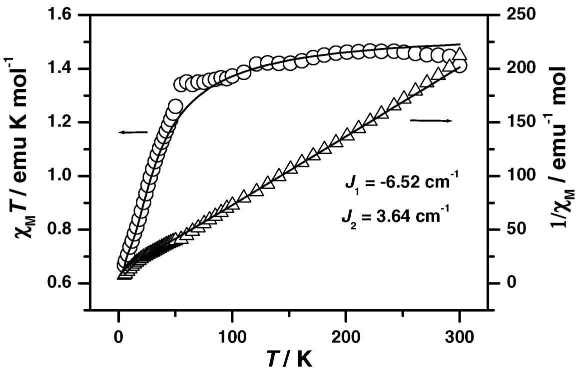
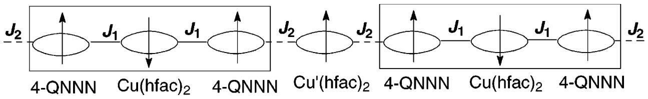


Figure 9. Plot of $1/\chi_M$ and $\chi_M T$ vs temperature for complex **3**. The solid line represents the best theoretical fitting with eqs 5 and 6 (see text).

Scheme 2. Illustration of the Spin−Spin Interaction between the Nitronyl Nitroxides and Cu(II)/Cu′(II) Ions for Complex **3**



and S_t are the magnetic susceptibility and effective spin of the three-spin complex fragment, respectively:

$$\chi_t = \frac{Ng^2\beta^2}{3kT} S_t(S_t + 1) \tag{5}$$

$$\chi_t = \frac{Ng_{rad}g_{Cu}\beta^2}{4kT}\left[\frac{1 + \exp(-2J_1/kT) + 10\exp(J_1/kT)}{1 + \exp(-2J_1/kT) + 2\exp(J_1/kT)}\right]$$

$$\chi_{chain} = \frac{2N\beta^2}{3kT}\left[\bar{g}^2\frac{1+u}{1-u} + \delta^2\frac{1-u}{1+u}\right]$$

$$\bar{g} = [g\sqrt{S_t(S_t+1)} + g_{Cu}\sqrt{S_{Cu}(S_{Cu}+1)}]/2 \tag{6}$$

$$\delta = [g\sqrt{S_t(S_t+1)} - g_{Cu}\sqrt{S_{Cu}(S_{Cu}+1)}]/2$$

$$u = \coth(J_e/kT) - kT/J_e \quad J_e = J_2\sqrt{S_t(S_t+1)S_{Cu}(S_{Cu}+1)}$$

The best fit to the experimental magnetic data gives the following parameters: $J_1 = -6.52$ cm^{-1} and $J_2 = +3.64$ cm^{-1} for $g_{rad} = g_{Cu} = 2.0$. As expected, J_1 is negative, and its value is comparable to those for the complexes of pyridine-substituted nitronyl nitroxide and Cu(hfac)$_2$.[21] J_2 is positive, indicating the magnetic interaction due to the Cu′(II)···O coordination bonding is ferromagnetic. But this ferromagnetic magnetic interaction is weak compared with those of other Cu(II) complexes of nitronyl nitroxides, in which the oxygen atoms of nitronyl nitroxides lie on the apical position. This may be ascribed to the fact that the imidazoline planes of nitronyl nitroxides are not parallel to the equatorial planes of Cu′(hfac)$_2$ in complex **3** as discussed above, and thus the interacting magnetic orbitals of nitronyl nitroxides and Cu′(II) ions are not orthogonal. Such structural a feature may lead to the partial overlapping of the corresponding magnetic orbitals, and consequently, the ferromagnetic interaction due to the Cu′(II)···O coordination bonding will be weakened.

Summary

Reaction of 2-(4-quinolyl)nitronyl nitroxide (4-QNNN) with M(hfac)$_2$ [M = Mn(II), Co(II), and Cu(II)] under the same conditions yielded three new complexes **1**−**3** of the formula M_2L_2. Crystal structural analyses indicate that complexes **1** and **2** are four-spin cyclic dimers, in which both the nitrogen atoms of quinoline rings and oxygen atoms of nitronyl nitroxides are involved in the formation of coordination bonds. For complex **3**, however, the nitrogen atoms of quinoline rings are coordinated with Cu(II) ion to afford a three-spin complex, which is further linked to another molecule of Cu(hfac)$_2$ to form a 1D alternating chain. The magnetic properties of the three complexes were investigated with SQUID magnetometry. The temperature dependence of magnetic susceptibility of **1** was fitted to the model of spin-dimer with $S = 2$. For complex 2, the temperature dependence of the magnetic susceptibility in the $T > 50$ K region was simulated with the model of two-spin unit with $S_1 = 3/2$ and $S_2 = 1/2$, and the contribution due to the magnetic interactions between Co(II) ions and nitronyl nitroxides through quinoline rings and those between nitronyl nitroxides due to the short O···O short contacts were treated with mean-field theory. The temperature dependence of the magnetic susceptibility of complex **3** has been fitted to a model described previously, and the fitting magnetic exchange constants are comparable to those of similar structures. Further investigations include synthesis of cyclic complexes of nitronyl nitroxides with M(hfac)$_2$ displaying different geometries and correlation of the spin−spin exchange strength as a function of structure.

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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.

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