Experimental Evidence for the Triplet-Like Spin State Appearing in Ground-State Singlet Biradicals as a Key Feature for Generalized Ferrimagnetic Spin Alignment

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The authors have previously proposed a theoretical model for exotic spin alignment in organic molecular assemblages: The alternating chain of organic biradicals in a singlet ($S_b = 0$) ground state and monoradicals with $S = {}^1/_2$ has a ferrimagnetic ground state for the whole chain, which has been termed generalized ferrimagnetism. An important feature of the generalized ferrimagnetic spin alignment has been found in the deviation of the expectation value $\langle \mathbf{S}_b{}^2 \rangle$ of the biradical spin from zero. Even a triplet-like spin state $\langle \mathbf{S}_b{}^2 \rangle = 2$ ($S_b = 1$) has been predicted in the theoretical calculations. In this study, we have found experimental evidence for the pseudo-triplet state appearing in the ground-state singlet biradical of a real open-shell compound. At first, we have demonstrated from theoretical calculations that the singlet biradical has $\langle \mathbf{S}_b{}^2 \rangle = 2$ ($S_b = 1$) in a molecular pair with an $S = 1$ metal ion as well as with the $S = {}^1/_2$ monoradical. The pseudo-triplet state of the biradical affords a singlet state of the whole system of the biradical-metal ion pair, which is readily detectable in experiments for verifying the theoretical prediction. As a model compound for the biradical-metal ion pair, a transition metal complex, [(bnn)(Ni(hfac)$_2$)$_{1.5}$(H$_2$O)] (**1**), has been synthesized from a nitronyl nitroxide-based ground-state singlet biradical bnn and Ni(hfac)$_2$. From X-ray crystallographic analyses, the compound contains a molecular pair of bnn and Ni(hfac)$_2$, which serves as a model system under the above theoretical studies. It has been found from the analysis of the temperature dependence of magnetic susceptibility that the bnn−Ni(hfac)$_2$ pair has the singlet ($S = 0$) ground state. The singlet ground state of the pair results from an antiparallel coupling of the pseudo-triplet of the biradical and the $S = 1$ spin on the Ni ion. The pseudo-triplet state in the ground-state singlet biradical has thus been verified experimentally, which is crucially important to realize the generalized ferrimagnetic spin alignment.

Introduction

The past decades have witnessed a rapid development of molecule-based magnetism.[1] The construction of molecule-based magnets and other molecular functionality magnetics has been the focus of the current subjects in materials science and spin chemistry.[1] Ferrimagnetism is one of the categories in magnetism, the physical picture of which has been initiated by Néel:[2] An antiparallel coupling of different spin quantum numbers, e.g., $S = 1$ and $S = {}^1/_2$, gives an ordered state with bulk and net magnetization due to incomplete cancellation of magnetic moments. Our previous theoretical papers[3,4] have dealt with the possibility of ferrimagnetic-like spin alignment in an alternating chain consisting of a biradical in a singlet ($S = 0$) ground state and a monoradical with $S = {}^1/_2$. The spin Hamiltonian describing the system is written as[3−6]

$$H_{\text{chain}} = \sum_{i=1}^{N} [-2J_1 \mathbf{S}_{i,\text{b1}} \cdot \mathbf{S}_{i,\text{b2}} - 2J_2(\mathbf{S}_{i,\text{b2}} \cdot \mathbf{S}_{i,\text{m}} + \mathbf{S}_{i,\text{m}} \cdot \mathbf{S}_{i+1,\text{b2}}) - 2aJ_2(\mathbf{S}_{i,\text{b1}} \cdot \mathbf{S}_{i,\text{m}} + \mathbf{S}_{i,\text{m}} \cdot \mathbf{S}_{i+1,\text{b1}})] \quad (1)$$

where $\mathbf{S}_{i,\text{b1}}$, $\mathbf{S}_{i,\text{b2}}$, and $\mathbf{S}_{i,\text{m}}$ denote the spin-${}^1/_2$ operators and N stands for the number of unit cells. The Hamiltonian (eq 1) is schematically shown in Figure 1a. The two $S = {}^1/_2$ spins, $\mathbf{S}_{i,\text{b1}}$ and $\mathbf{S}_{i,\text{b2}}$, are coupled by the intramolecular antiferromagnetic exchange interaction $J_1 < 0$ within the biradical in the *i*th unit cell. These two spins are coupled with another $S = {}^1/_2$ spin, $\mathbf{S}_{i-1,\text{m}}$ and $\mathbf{S}_{i,\text{m}}$, on the neighboring monoradicals by the intermolecular interactions J_2 and aJ_2 ($0 \le a \le 1$). When the intermolecular exchange interactions J_2 and aJ_2 are antiferromagnetic, the alternating chain has three kinds of ground spin states; two with seemingly ferrimagnetic spin alignments and one with a spinless (diamagnetic) state.[3] The spin alignment of the two ferrimagnetic ground states is schematically drawn in Figure 2 which is based on the spin−spin correlation functions calculated for the spin Hamiltonian (eq 1).[3] The arrows in the figure are classical or Ising-like visualization of the correlation functions for the seemingly ferrimagnetic states. The spinless state is, however, known to have an extremely short spin−spin correlation length, preventing us from showing any schematic views of arrows for spin magnetic moments.[3] On the other hand, the ferromagnetic exchange interactions ($J_2 > 0$ and $aJ_2 > 0$) between the biradical and the monoradical molecules result in two kinds of ground spin states.[4] One is a high-spin state, in which all the spins are parallel to each other, and the other is a low-spin state depending on the topology of the intermolecular exchange interactions.[4] In the both cases of the ferromagnetic

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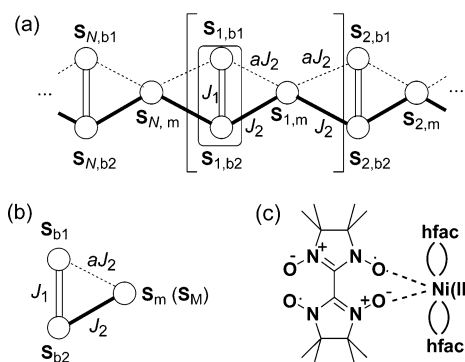⊥ E-mail: takui@sci.osaka-cu.ac.jp.

Figure 1. (a) Schematic view of the Heisenberg spin Hamiltonian of the alternating chain with N of repeating units. The rounded rectangle represents the biradical molecule with two unpaired electron spins ($S_{i,b1}$ = $^1/_2$ and $S_{i,b2}$ = $^1/_2$) interacting with the adjacent monoradicals with $S_{i,m}$ = $^1/_2$. The periodic boundary condition ($S_{N+1,I}$ = $S_{1,I}$; I = b1, b2 and m) is imposed. The intramolecular exchange interaction in the biradical is defined as J_1. The solid and dashed lines denote the intermolecular interactions J_2 and aJ_2, respectively. (b) Heisenberg model of the three-spin system. (c) Triangular three-spin moiety of bnn−Ni(hfac)$_2$ in the complex [(bnn)(Ni(hfac)$_2$)$_{1.5}$(H$_2$O)] (**1**).
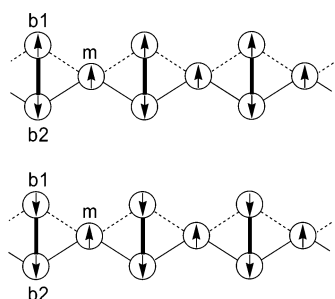

Figure 2. Schematic drawings of the spin alignments in the two kinds of ferrimagnetic ground states.[3]

and antiferromagnetic intermolecular exchange interactions, the energy preference of the ground spin states depends on the relative magnitude of the interactions J_1, J_2 and aJ_2. These exotic spin alignments have been termed "generalized ferrimagnetism".[3,4]

An important feature of the spin alignment of the generalized ferrimagnetism is found in the deviation of the expectation value of the biradical spin from zero[3,4]

$$\langle \mathbf{S}_b{}^2 \rangle \equiv \langle (\mathbf{S}_{1,b1} + \mathbf{S}_{1,b2})^2 \rangle \neq 0 \qquad (2)$$

in the ground state for arbitrary values of J_2 and aJ_2. The "pure" singlet ($S_b = 0$) appears only when the biradical is isolated with the negligible intermolecular exchange interactions $J_2 \sim 0$ and $aJ_2 \sim 0$. It has been found from numerical calculations of the spin Hamiltonian eq 1 that the spin value $\langle \mathbf{S}_b{}^2 \rangle$ of the ground-state singlet biradical embedded in the exchange-coupled assemblage contributes to the bulk magnetization.[3,4] The nontrivial, nonvanishing spin value, eq 2, results from a spin frustration effect inherent in the triangular geometry of the three-spin system of the unit cell (Figure 1, parts a and b) and the noncommutativity between the spin operator of the biradical site $\mathbf{S}_b{}^2$ and the Hamiltonian eq 1[3,4]

$$[\mathbf{S}_b{}^2, H_{\text{chain}}] \neq 0 \qquad (3)$$

The nonvanishing spin magnetic moment eq 2 in the ground-state singlet biradical is acceptable in the framework of the phenomenological spin Hamiltonian eq 1 when the balance of the competing exchange interactions is considered. The non-

trivial, nonvanishing magnetic moment $\langle \mathbf{S}_b{}^2 \rangle \neq 0$, however, has not been found in real singlet biradical compounds yet, which is essential to the occurrence of the generalized ferrimagnetic spin alignment. In this study, we have examined the experimental evidence for the deviation $\langle \mathbf{S}_b{}^2 \rangle \neq 0$ occurring in a real open-shell compound, which is a three-spin model system mimicking the unit cell of the chain in eq 1, as illustrated in Figure 1b. The compound consists of an organic nitronyl nitroxide biradical (bis[2,2′-(1-oxyl-3-oxido-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl)]; abbreviated as bnn) and a Ni(II) ion with $S = 1$, [(bnn)(Ni(hfac)$_2$)$_{1.5}$(H$_2$O)] (**1**). The biradical bnn is known to have the intramolecular exchange coupling of $J/k_B = -224$ K.[7,8] The biradical serves as an open-shell chelating ligand, giving a triangular frustrating motif of the three-spin system, as depicted in Figure 1c. The metal ion is a substitute for the monoradical in the theoretical model. When the spin quantum number S_m is one-half as in the previous theoretical model,[3,4] the ground state for the antiferromagnetic system ($J_2 < 0$ and $aJ_2 < 0$) has a total spin of $S_T = ^1/_2$, regardless of the relative ratios of J_2/J_1 and a, and the experimental verification of the nonvanishing $\langle \mathbf{S}_b{}^2 \rangle$ is not feasible. When S_m is one, on the other hand, the theoretical prediction of $\langle \mathbf{S}_b{}^2 \rangle$ is easily verified by monitoring the total spin of the three-spin system as described below. We report theoretical calculations of the three-spin system of bnn and the $S_m = 1$ ion and the synthesis and the crystal structure of the model compound **1**. The ground spin state of the complex **1** has been discussed on the basis of the theoretical calculation and the magnetic susceptibility, verifying experimentally the nonvanishing $\langle \mathbf{S}_b{}^2 \rangle$ on the ground-state singlet biradical.

Experimental Section

The biradical bnn was synthesized by literature procedures.[9,10] A dark brown solution was obtained by combining bnn (70.0 mg, 0.224 mmol) in dichloromethane (50 mL) and Ni(hfac)$_2$ (100.9 mg, 0.214 mmol) in diethyl ether (10 mL). To the solution was added 16 mL of *n*-heptane and the combined solution was stored at 2 °C for 24 h, and brown crystals of the complex **1** were collected (35.4 mg, 15.9% yield). The composition was found to be [(bnn)(Ni(hfac)$_2$)$_{1.5}$(H$_2$O)] from elemental analysis. Anal. Calcd for C$_{29}$H$_{29}$F$_{18}$N$_4$Ni$_{1.5}$O$_{11}$: C, 33.51; H, 2.81; N, 5.39. Found: C, 33.63; H, 2.73; N, 5.41.

The X-ray diffraction measurements were made on a Rigaku Mercury CCD diffractometer at 193 K with graphite monochromated Mo Kα radiation up to $2\theta_{\text{max}} = 55°$. The crystal structure was solved by direct methods (SIR92)[11] and succeeding Fourier syntheses followed by the full-matrix least-squares refinement with the anisotropic approximation for non-hydrogen atoms. Positions of the hydrogen atoms participating in hydrogen bonds were found in a differential map and refined isotropically. Positions of other hydrogen atoms were calculated and included in the final refinement. All the calculations were made by use of the program package *CrystalStructure* by Rigaku/Molecular Structure Corporation.[12]

The magnetic susceptibility of **1** was measured for randomly oriented polycrystalline samples on a Quantum Design SQUID magnetometer MPMS-XL with an applied magnetic field of 0.1 T in the temperature range 1.9−298 K.

Results and Discussion

1. Spin State of the Pair of a Biradical and an $S = 1$ Ion. The spin state of the triangular three-spin system consisting of a ground-state singlet biradical and a transition metal ion with an $S_M = 1$ spin is examined on the basis of the Heisenberg

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spin Hamiltonian

$$H_{tri} = -2J_1\mathbf{S}_{b1}\cdot\mathbf{S}_{b2} - 2J_2\mathbf{S}_{b2}\cdot\mathbf{S}_M - 2aJ_2\mathbf{S}_M\cdot\mathbf{S}_{b1} \quad (4)$$

where $\mathbf{S}_{b1}$, $\mathbf{S}_{b2}$ and $\mathbf{S}_M$ denote spin-$^1/_2$ and spin-1 operators. The two $S = {}^1/_2$ spins $\mathbf{S}_{b1}$ and $\mathbf{S}_{b2}$ are coupled by the intramolecular antiferromagnetic exchange interaction J_1 in the biradical molecule and they are coupled with a neighboring $S = 1$ spin $\mathbf{S}_M$ on a metal ion M by the antiferromagnetic interactions J_2 and aJ_2 ($0 \leq a \leq 1$), as illustrated in Figure 1b. The Hamiltonian matrix with a dimension of $(2 \times 2 \times 3)^2$ was analytically diagonalized to give energy eigenvalues $E(i)$ and eigenvectors $|i\rangle$. The energy eigenvalue $E(i)$ and the total spin S_T

$$\langle i|(\mathbf{S}_{b1} + \mathbf{S}_{b2} + \mathbf{S}_M)^2|i\rangle = S_T(S_T + 1) \quad (5)$$

of the eigenstates are listed in Table 1. For the antiferromagnetic exchange interactions $J_1 < 0$, $J_2 < 0$, and $aJ_2 < 0$, the ground state of the triangular three-spin system has either $S_T = 0$ ($i = 1$) or $S_T = 1$ ($i = 2$). The energy preference of the two states depends on the relative amplitude of the exchange interactions J_1, J_2, and aJ_2. The boundary for the two regions in the parameter space of $\{J_2/J_1, a\}$ is expressed as

$$J_2/J_1 = (1+a)/4a \quad (6)$$

The spin configuration for the ground state in the two regions is examined from the eigenvectors of the Hamiltonian eq 4 in the ket space, which is spanned by a set of direct products of the three spins in the triangular system $\{|m_{b1},m_{b2},m_M\rangle_{1/2,1/2,1}\}$ ($m_{b1} = {}^1/_2, -{}^1/_2$; $m_{b2} = {}^1/_2, -{}^1/_2$; $m_M = 1, 0, -1$). In one of the two regions, $J_2/J_1 > (1+a)/4a$, the ground-state eigenvector with $S_T = 0$ ($i = 1$) is given as

$$|S_T = 0\rangle = \frac{1}{\sqrt{3}}\left\{\left|+\frac{1}{2}, +\frac{1}{2}, -1\right\rangle_{1/2,1/2,1} + \right.$$
$$\left|-\frac{1}{2}, -\frac{1}{2}, +1\right\rangle_{1/2,1/2,1} - \frac{1}{\sqrt{2}}\left(\left|+\frac{1}{2}, -\frac{1}{2}, 0\right\rangle_{1/2,1/2,1} + \right.$$
$$\left.\left.\left|-\frac{1}{2}, +\frac{1}{2}, 0\right\rangle_{1/2,1/2,1}\right)\right\} \quad (7)$$

in the spin subspace of $m_{b1} + m_{b2} + m_M = 0$ for the z-component of the total spin. The first and second terms in eq 7 represent complete cancellation of an $S = 1$ spin of the biradical ($S_b = 1$, $m_b = m_{b1} + m_{b2} = \pm1$) and that on the metal ion ($S_M = 1$, $m_M = \pm1$). The third term corresponds to the combination of $m_b = 0$ of $S_b = 1$ on the biradical and $m_M = 0$ of $S_M = 1$ on the metal ion, contributing to $S_T = 0$ as well. An antiparallel coupling of two $S = 1$ spins, $S_1 = 1$ and $S_2 = 1$, gives a singlet state

$$|S_T = 0(S_1 = 1, S_2 = 1)\rangle =$$
$$\frac{1}{\sqrt{3}}\{|+1, -1\rangle_{1,1} + |-1, +1\rangle_{1,1} - |0,0\rangle_{1,1}\} \quad (8)$$

in the spin subspace of $m_1 + m_2 = 0$ for the z-component of the total spin, where the basis kets $|m_1,m_2\rangle_{1,1}$ of the two spins, $m_1 = +1, 0, -1$ and $m_2 = +1, 0, -1$, are linearly combined. The $S_T = 0$ state (eq 7) of the biradical-metal ion pair is equivalent to that of ordinary ion pairs (eq 8) of $S = 1$ spins in terms of the spin angular momentum.

It is found from the eigenvector eq 7 that the expectation value of the biradical spin

$$\langle \mathbf{S}_b^2\rangle = \langle i|(\mathbf{S}_{b1} + \mathbf{S}_{b2})^2|i\rangle \quad (9)$$

TABLE 1: Energy Eigenvalue $E(i)$ and Total Spin S_T of the Spin Hamiltonian in Eq 4^a

state i	total spin S_T	energy eigenvalue $E(i)^b$
1	0	$1/2 (-J_1 + 4J_2 + 4J_3)$
2	1	$1/2 (J_1 + J_2 + J_3 - A)$
3	1	$1/2 (J_1 + J_2 + J_3 + A)$
4	2	$1/2 (-J_1 - 2J_2 - 2J_3)$

^{a} The ground state has $S_T = 0$ ($i = 1$) for $J_2/J_1 > (1+a)/4a$ or $S_T = 1$ ($i = 2$) for $J_2/J_1 < (1 + a)/4a$. ^{b} $A = \sqrt{4J_1^2+9J_2^2+9J_3^2-4J_1J_2-14J_2J_3-4J_3J_1}$.

amounts to two for the $S_T = 0$ ground state ($i = 1$) in the region of $J_2/J_1 > (1+a)/4a$. When the exchange interaction $|J_2|$ between the biradical and the metal ion predominates, the energy loss of $|J_1|$ due to the formation of triplet ($S_b = 1$) is overridden by the antiparallel alignment between the $S_b = 1$ and $S_M = 1$ spins, giving a spin-singlet ($S_T = 0$) in the whole three-spin system. In nonquantum terms, biradicals with a singlet ($S_b = 0$) ground state would seemingly have no contribution to the magnetization at low temperatures, $k_BT < |J_1|$. It is, however, shown that $S_b = 0$ is not necessarily a good quantum number for describing the biradical embedded in exchange-coupled systems. The deviation $\langle\mathbf{S}_b^2\rangle \neq 0$ for the ground-state singlet biradicals in the exchange-coupled system is an essential feature in the generalized ferrimagnetic system.[3,4] The momentless state in the three-spin system is indicative of a triplet-like state of the ground-state singlet biradical. The totally singlet state ($S_T = 0$) of the biradical-metal ion pair is discussed later on the basis of experimental results of the complex **1**.

For the other possible ground state, the eigenvector for $S_T = 1$ ($i = 2$) in the region of $J_2/J_1 < (1 + a)/4a$ was found to be a complicated function of J_2/J_1 and a. In the spin subspace of $m_{b1} + m_{b2} + m_M = 0$ for the z-component of the total spin, the eigenvector was found to have the form

$$|S_T = 1\rangle =$$
$$C_1\left(\left|+\frac{1}{2}, +\frac{1}{2}, -1\right\rangle_{1/2,1/2,1} - \left|-\frac{1}{2}, -\frac{1}{2}, +1\right\rangle_{1/2,1/2,1}\right) +$$
$$C_2\left(\left|+\frac{1}{2}, -\frac{1}{2}, 0\right\rangle_{1/2,1/2,1} - \left|-\frac{1}{2}, +\frac{1}{2}, 0\right\rangle_{1/2,1/2,1}\right) \quad (10a)$$
$$2C_1^2 + 2C_2^2 = 1 \quad (10b)$$

from the analytical diagonalization of the Hamiltonian eq 4. The C_1 term resembles a vector of the triplet state given by an antiparallel coupling of two $S = 1$ spins

$$|S_T = 1(S_1 = 1,S_2 = 1)\rangle =$$
$$\frac{1}{\sqrt{2}}\{|+1, -1\rangle_{1,1} - |-1, +1\rangle_{1,1}\} \quad (11)$$

which is represented by the same basis kets as in eq 8. The C_1 term seems to represent an $S = 1$ spin given by the coupling of a triplet biradical and an $S = 1$ metal ion. The eigenvector has, however, an additional term of C2, which shows only an $S = 1$ spin ($m_M = 0$) on the metal ion. Thus, in this $\{J_2/J_1, a\}$ region of $S_T = 1$, a simple interpretation of spin angular-momentum addition is no longer applicable to the eigenvector, eq 10, as found in eq 7 for the region of $S_T = 0$. The biradical has no definitive amplitude of spin in the region of $S_T = 1$, which is attributed to the noncommutativity between the biradical spin $\mathbf{S}_b^2$ and the Hamiltonian eq 4.[3,4]

A three-dimensional contour plot of the expectation value of the biradical spin $\langle\mathbf{S}_b^2\rangle$ is shown in Figure 3 as a function of the ratio of J_2/J_1 and the parameter a. In the region of $J_2/J_1 >$

Tripletlike Spin State in Singlet Biradicals

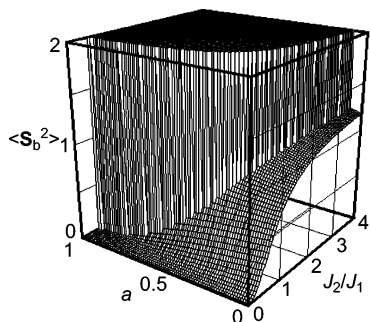*J. Phys. Chem. B, Vol. 110, No. 5, 2006* **2105**

Figure 3. Ground-state expectation value of the biradical spin $\langle S_b^2 \rangle$ $\equiv \langle (S_{b1} + S_{b2})^2 \rangle$ in the three-spin system of the biradical−Ni(II) pair (Figure 1a) as a function of the interaction ratios J_2/J_1 and a.

$(1+a)/4a$ with $S_T = 0$ ($i = 1$), the biradical always has $S_b = 1$ ($\langle S_b^2 \rangle = 2$), as described above. On the other hand, in the region of $J_2/J_1 < (1+a)/4a$ with $S_T = 1$ ($i = 2$), the expectation value $\langle S_b^2 \rangle$ depends on the relative amplitude of the exchange interactions. When the biradical is magnetically isolated with $J_2/J_1 \rightarrow 0$ or coupled with M through two equivalent exchange interactions ($a \rightarrow 1$) in the range of $0 \leq J_2/J_1 < 1/2$, a "pure" singlet, $\langle S_b^2 \rangle = 0$ appears. In the two limiting cases, an $S_b = 0$ is a good quantum number and the eigenvectors have the forms

$$\left| S_T = 1; \frac{J_2}{J_1} < \frac{1}{2}, a = 1 \right\rangle =$$
$$\frac{1}{\sqrt{2}} \left(\left| +\frac{1}{2}, -\frac{1}{2}, 0 \right\rangle_{1/2,1/2,1} - \left| -\frac{1}{2}, +\frac{1}{2}, 0 \right\rangle_{1/2,1/2,1} \right) \quad (12)$$

and

$$\left| S_T = 1; \frac{J_2}{J_1} \rightarrow \infty, a \rightarrow 0 \right\rangle = \frac{1}{\sqrt{3}} \left\{ \left| +\frac{1}{2}, +\frac{1}{2}, -1 \right\rangle_{1/2,1/2,1} - \right.$$
$$\left| -\frac{1}{2}, -\frac{1}{2}, +1 \right\rangle_{1/2,1/2,1} - \frac{1}{\sqrt{2}} \left(\left| +\frac{1}{2}, -\frac{1}{2}, 0 \right\rangle_{1/2,1/2,1} - \right.$$
$$\left. \left. \left| -\frac{1}{2}, +\frac{1}{2}, 0 \right\rangle_{1/2,1/2,1} \right) \right\} \quad (13)$$

Both are the special cases of eq 10; $C_1 = 0$, $C_2 = 1/\sqrt{2}$ (eq 12) and $C_1 = 1/\sqrt{3}$, $C_2 = 1/\sqrt{6}$ (eq 13). For arbitrary values of J_2/J_1 and a, a nonvanishing magnetic moment arising from $\langle S_b^2 \rangle \neq 0$ is predicted, as indicated in Figure 3.

2. Crystal Structure of Complex 1. The crystallographic data for the complex **1** are listed in Table 2. An ORTEP drawing of the asymmetric unit of the complex is depicted in Figure 4. The asymmetric unit consists of 1.5 mol of Ni(hfac)$_2$, 1 mol of bnn, and 1 mol of H$_2$O. Two Ni(II) ions, Ni1 and Ni2, are crystallographically independent. The biradical bnn chelates to one of the two nickel ions, Ni1, leading to a triangular motif of two $S = 1/2$ spins of bnn and an $S = 1$ spin of Ni1. The overlap between magnetic orbitals d_{z^2} and $d_{x^2-y^2}$ on Ni1 and SOMOs (SOMO: singly occupied molecular orbital) of bnn suggests that the $S = 1$ spin on Ni1 is antiferromagnetically coupled with the two $S = 1/2$ spins on bnn. Strong antiferromagnetic exchange interactions have been reported in complexes of Ni-(hfac)$_2$ and nitronyl nitroxide radicals[13] with coordination geometries similar to that of the complex **1**. The dihedral angle between the two nitronyl nitroxide radical moieties is 52.9° in the complex **1**, which is close to that in the metal-free, pristine bnn (55°).[7] Thus, the intramolecular antiferromagnetic exchange interaction in bnn, $2J/k_B = -448$ K,[7] should remain unchanged in the complex **1**. The triangular complex of bnn and Ni1 is

TABLE 2: Crystallographic Data for 1

formula	C$_{29}$H$_{29}$F$_{18}$N$_4$Ni$_{1.5}$O$_{11}$
fw	1039.59
crystal system	triclinic
space group	$P-1$ (#2)
a/Å	8.7852(1)
b/Å	14.5810(1)
c/Å	17.7406(5)
α/deg	73.052(7)
β/deg	86.854(9)
γ/deg	69.249(7)
V/Å^3	2029.83(6)
Z	2
D_{calc}/g cm^{-3}	1.701
T/K	193
no. of reflections measured	8814
no. of unique reflections used ($I>3\sigma(I)$)	7098
R, $R_w{}^a$	0.057, 0.183
goodness of fit	1.003

^{a} The function minimized is $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[0.0072F_o^2 + \sigma(F_o^2)]/(4F_o^2)$. The residuals are defined as $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.
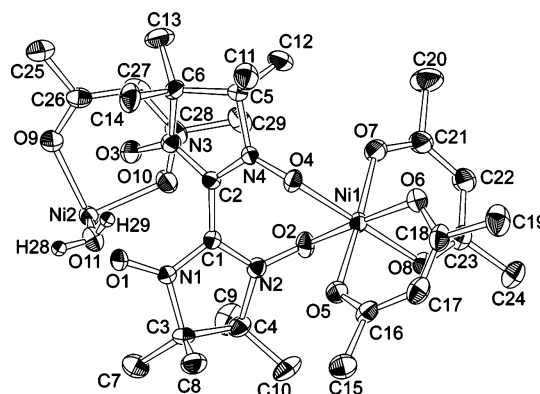

Figure 4. ORTEP drawing of the asymmetric unit of the complex [(bnn)(Ni(hfac)$_2$)$_{1.5}$(H$_2$O)] (**1**) with thermal ellipsoids of 50% probability. The hydrogen atoms are omitted for clarity except those participating in the intermolecular hydrogen bond (H28−H29−O11).

regarded as a model system for the three-spin system discussed in the theoretical calculations.

The other Ni(II) ion, Ni2, lies on an inversion center and is coordinated by four oxygen atoms of two hfac ligands and two oxygen atoms of H$_2$O molecules. The H$_2$O molecule (H28−H29−O11) and the Ni2(hfac)$_2$ moiety connect the triangular bnn−Ni1(hfac)$_2$ moieties, as shown in Figure 5a. Selected bond distances are summarized in Table 3. Weak exchange interactions are expected to be operative through hydrogen bonds around the bridging H$_2$O molecule, giving an alternating chain consisting of the Ni2 ions and two triangular bnn−Ni1(hfac)$_2$ moieties running along the a-axis as schematically shown in Figure 5b. The triangular three-spin moieties are bridged by the $S = 1$ spin on Ni2 in the chain. No short interatomic contact close to the van der Waals contact[14] was found between the chains. From the X-ray crystal structure analysis, the exchange pathway between the bnn molecules and the Ni ions is proposed as shown in Figure 5b; J_1 is the intramolecular exchange interaction within the biradical while J_2 and J_3 are the exchange couplings through the coordination bonds. The exchange interactions through the hydrogen bonds are represented by J_4 and J_5.

3. Magnetic Susceptibility of Complex 1. The temperature dependence of paramagnetic susceptibility χ_p for randomly oriented polycrystalline samples of the complex **1** is shown in Figure 6 in the $\chi_p T$ vs T plots. The $\chi_p T$ value decreases as the
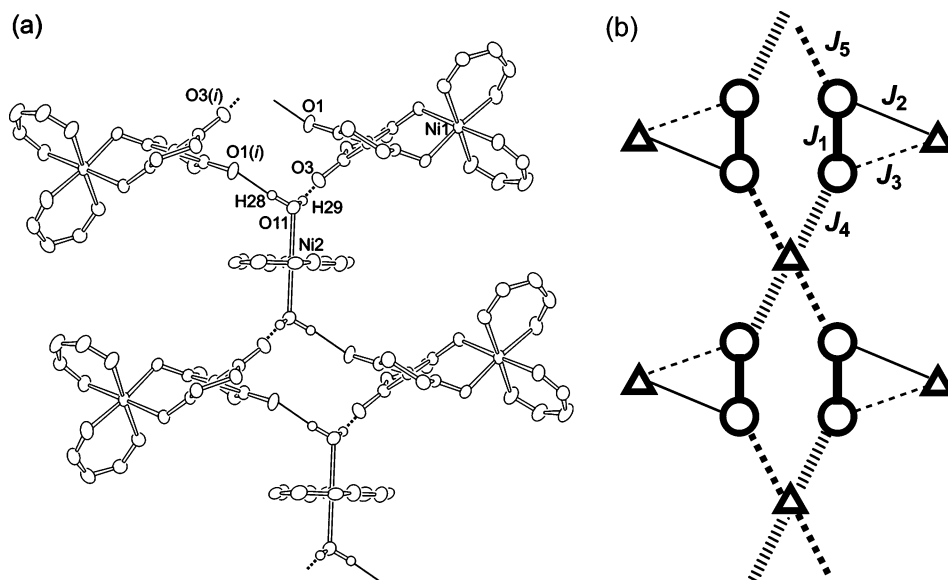
(a)

(b)

Figure 5. (a) One-dimensional chain structure of **1** along the *a*-axis. The trifluoromethyl groups, the methyl groups and the hydrogen atoms are omitted for clarity. (b) Schematic drawing of the exchange pathway. The coupling constants J_1, J_2, and J_3 represent the exchange interactions within the triangular bnn−Ni1(hfac)$_2$ moiety. The exchange couplings through the hydrogen bonds are denoted by J_4 and J_5.
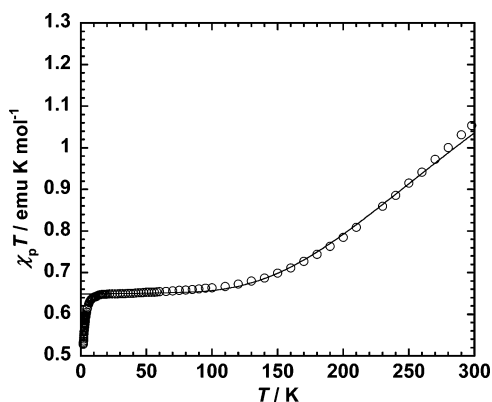

Figure 6. Temperature dependence of magnetic susceptibility χ_p of **1** measured on a SQUID magnetometer with $B = 0.1$ T in the $\chi_p T$ vs T plot. The solid line represents the theoretical calculations based on eqs 14−17.

TABLE 3: Selected Bond Distances (Å) for 1[a]

Ni1−O2	2.031(3)	Ni2−O9	2.038(2)
Ni1−O4	2.077(2)	Ni2−O10	2.077(2)
Ni1−O5	2.015(3)	Ni2−O11	2.074(3)
Ni1−O6	2.018(3)	O3−OH29	2.816(3)
Ni1−O7	1.990(3)	O1(*i*)−OH28	2.749(3)
Ni1−O8	2.025(2)		

[a] Symmetry operation *i*: $-x + 2, -y, -z + 1$.

temperature is lowered down to 100 K. The $\chi_p T$ exhibits a plateau in the temperature range of 100 and 16 K, and decreases further below 16 K. The $\chi_p T$ value of 0.65 emu K mol^{-1} in the plateau corresponds to a half mole of $S = 1$ spin with the *g*-factor of 2.28. Noting that the asymmetric unit contains 1 mol of Ni1, 1 mol of bnn, and 0.5 mol of Ni2 on the inversion center, the half mole of $S = 1$ spin surviving below 100 K is attributed to Ni2. It seems that the triangular bnn−Ni1(hfac)$_2$ moiety has no contribution to magnetic susceptibility below 100 K. This implies that the triangular complex moiety has an $S = 0$ ground state. The second decrease in $\chi_p T$ below 16 K is attributed to the weak exchange interactions through the hydrogen bonds, giving an antiparallel coupling between the $S = 1$ spins on the Ni2 ions.

The paramagnetic susceptibility above 16 K is analyzed by assuming the simple summation of the contributions from the Ni2 ion $\chi_p^{S=1}$ and the triangular bnn−Ni1 moiety χ_p^{tri}

$$\chi_p = \frac{1}{2}\chi_p^{S=1} + \chi_p^{tri} \quad (14)$$

The weak exchange interactions through the hydrogen bonds are neglected in the analysis of χ_p above 16 K. The Ni2 ions are assumed to obey the Curie law for $S = 1$

$$\chi_p^{S=1} = \frac{2N_A g_{Ni2}^2 \mu_B^2}{3k_B T} \quad (15)$$

The χ_p^{tri} of the triangular bnn−Ni1(hfac)$_2$ moiety is calculated from the spin Hamiltonian in a magnetic field **B** given by

$$H = H_{tri}(M = Ni1) + \sum_i g_i \mu_B \mathbf{S}_i \cdot \mathbf{B} \quad (i = b1, b2, Ni1) \quad (16)$$

where $\mathbf{S}_M = \mathbf{S}_{Ni1}$ is substituted in the three-spin Hamiltonian H_{tri} in eq 4. The spin Hamiltonian is diagonalized numerically to give energy eigenvalues $E_j(B)$ in a magnetic field B. The magnetic susceptibility χ_p^{tri} is calculated as

$$\chi_p^{tri} = \lim_{B \to 0} \frac{M_{tri}}{B} \quad (17a)$$

$$M_{tri} = \frac{N_A \sum_j \mu_j \exp(-E_j(B)/k_B T)}{\sum_j \exp(-E_j(B)/k_B T)} \quad (17b)$$

$$\mu_j = -\mu_B(g_{b1}m_{b1}^j + g_{b2}m_{b2}^j + g_{Ni1}m_{Ni1}^j) \quad (17c)$$

The *j*th eigenstate in a magnetic field is labeled by the *z*-component of the total spin

$$m_S^T(j) \equiv m_{b1}^j + m_{b2}^j + m_{Ni1}^j \quad (17d)$$

and the summation in eq 17b runs over $j = 1-12$. To avoid

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overparametrization, it is assumed that the intramolecular exchange interaction in bnn in the complex **1** is the same as that in the pristine metal-free molecule ($J_1/k_B = -224$ K[7]) and J_2 is assumed to be equal to J_3. The g values of the biradical spin are fixed to be $g_{b1} = g_{b2} = 2.006$ as found in an ESR spectrum of bnn in a solution. The best fit parameters $g_{Ni1} = 2.25 \pm 0.01$, $g_{Ni2} = 2.28 \pm 0.01$, and $J_2/k_B = J_3/k_B = -340 \pm 20$ K reproduced the observed temperature dependence of $\chi_p T$, as depicted in Figure 6. With the fixed value of $J_1/k_B = -224$ K, the sign and the ratio of $J_1:J_2$ (J_3) = $-224:-340$ are necessary for reproducing the curvature of the observed $\chi_p T$ vs T, showing the uniqueness of the solution. The g-value in the range $2.2-2.3$ is typical for Ni(II) in a similar coordination environment.[13,15]

The ratios of the exchange coupling constants are $J_2/J_1 \sim 1.51$ and $J_3/J_2 = a = 1$. It is found from the calculations described above that the ratios afford a singlet ($S_T = 0$) ground state for the triangular moiety. The spin eigenfunction for the singlet ground state as written in eq 7 tells us that the singlet state in the three-spin system is equivalent to that of ordinary antiparallel spin pairs of $S = 1$ (eq 8) in terms of the spin angular momentum: the biradical behaves as an $S = 1$ molecule with $\langle S_b^2 \rangle = 2$, which cancels the spin angular momentum of the Ni1 ion.

Another possible explanation of the half mole of $S = 1$ spin giving the plateau of $\chi_p T$ below 100 K is found for one surviving $S = 1$ spin in a repeating unit of the chain running along the a-axis. The repeating unit corresponds to two asymmetric units containing three $S = 1$ spins on the Ni ions, one from Ni2 on the inversion center and two from Ni1. Therefore, one resultant $S = 1$ spin from three $S = 1$ spins on the Ni1$-$Ni2$-$Ni1 triad seemingly explains the experimental result of $\chi_p T$ corresponding to a half mole of $S = 1$ spin. In this explanation, the biradical molecules lose their contribution to $\chi_p T$ owing to the intramolecular antiferromagnetic exchange interaction $J_1 < 0$. No communication between the bnn molecule and the Ni ions is needed. This explanation, however, requires large exchange interactions between the Ni ions; the exchange interactions through the hydrogen bonds should be larger than 100 K, $|J_4|/k_B$, $|J_5|/k_B > 100$ K. Such a large exchange interaction is not realistic for the exchange path based on the hydrogen bonds of the H$_2$O molecules. The temperature variation of $\chi_p T$ above 100 K should be explained by the exchange of $J_1/k_B = -224$ K through the covalent bonds and the exchange of $J_2/k_B = J_3/k_B = -340$ K due to the direct orbital overlap of nitroxide oxygen and the metal ions.

Conclusion

We have demonstrated from the theoretical calculations that the ground-state singlet biradical has a triplet-like spin state ($S_b = 1$) within the triangular geometry containing the competing exchange interactions with an $S = 1$ metal ion. The triplet-like state of the biradical affords a singlet state of the whole system of the triangular three-spin system, which is readily detectable in experiments for verifying the theoretical prediction. The nontrivial deviation of the biradical spin from $S = 0$ found for the pair of the biradical and the $S = 1/2$ molecule[3,4] is preserved in the present system of the biradical and the $S = 1$ ion. The result is ascribed to the noncommutativity of the biradical spin with the Hamiltonian.

As a model compound for the triangular three-spin system, the complex **1** has been synthesized from the ground-state singlet

biradical bnn and Ni^{II}(hfac)$_2$ and characterized by X-ray crystallographic analysis and magnetic susceptibility measurements. The compound has been found to have an alternating chain structure consisting of the triangular bnn$-$Ni(hfac)$_2$ moiety and another Ni(hfac)$_2$ unit. The two moieties are bound by hydrogen bonds of H$_2$O with negligibly weak exchange interactions. It has been found from the analysis of the temperature dependence of magnetic susceptibility for the crystalline solid of the complex **1** that the triangular bnn$-$Ni(hfac)$_2$ moiety has the singlet ($S = 0$) ground state. The singlet ground state corresponds to one of the ground states predicted in the calculations, in which the biradical has a triplet-like ($S = 1$) spin state. The triplet-like state in the ground-state singlet biradical has thus been verified experimentally, which is crucially important to realize the generalized ferrimagnetic spin alignment. Preparation of model complexes with extended chain structure composed of the triangular bnn$-$metal ion moiety is in progress.

Supporting Information Available: Crystallographic data (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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