Ligand Structure Effects on Molecular Assembly and Magnetic Properties of Copper(II) Complexes with 3-Pyridyl-Substituted Nitronyl Nitroxide Derivatives

Tatiana Sherstobitova,† Kseniya Maryunina,‡,§,∥ Swyatoslav Tolstikov,‡,∥ Gleb Letyagin,∥⊥ Galina Romanenko,∥ Sadafumi Nishihara,‡,§,‡,∥ and Katsuya Inoue*†,‡,§

†Department of Chemistry, Graduate School of Science, ‡Chirality Research Center (CResCent), and §§Institute for Advanced Materials Research, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan
¶International Tomography Center SB RAS, Institutskaya Str. 3a, Novosibirsk 630090, Russian Federation
∥Novosibirsk State University, Pirogov Str. 1, Novosibirsk 630090, Russian Federation

ABSTRACT: Reaction of Cu(hfac)₂ with methyl- and bromo-3-pyridyl-substituted nitronyl nitroxides (L₅) leads to assemble a diverse set of coordination complexes: mononuclear [Cu(hfac)₂L₂Me], binuclear [(Cu(hfac)₂)₂(H₂O)₂Me₂], trinuclear [(Cu(hfac)₂)L₂Br]₂, pentanuclear [(Cu(hfac)₂)₃(L₂Me)]₃, and [(Cu(hfac)₂)L₂Me]₃, cocrys [Cu(hfac)₂(H₂O)₃]₂Cu(hfac)₂(H₂O)₃ and [Cu(hfac)₂(L₂Br)]₂Cu(hfac)₂H₂O, one-dimensional polymers [Cu(hfac)₂L₂Br]₃ and [Cu(hfac)₂L₂Me]₃, and cyclic dimers [Cu(hfac)₂L₂Me]₂, [Cu(hfac)₂L₂Br]₂, [Cu(hfac)₂L₂Me]₂, and [Cu(hfac)₂L₂Br]₂. The molecular structures of the obtained complexes are strongly affected by the substituent type and its location in the pyridine heterocycle. Occupation of the second position of the pyridine ring increases the steric hindrance of both imine and nitroxide coordination sites of L₂, which is favorable for the formation of various conformers and precipitation of complexes with different molecular structures. The pentanuclear [(Cu(hfac)₂)₃(L₂Me)]₃ and [(Cu(hfac)₂)L₂Me]₃ complexes do not have prior analogues and are valuable model objects for investigation of the mechanism of formation of various coordination polymers. The arrangement of long Cu–O_NO bonds in {CuL₄} square bipyramids due to the weakening nitroxide donor site in complexes, based on L₂Me, L₂Br, and L₆Br ligands, results in ferromagnetic exchange interactions between spins of Cu²⁺ ions and nitroxides. Complexes with substituents that do not considerably affect the coordination ability of ligands (L₅Mb, L₅Br, and L₆Me) exhibit strong antiferromagnetic exchange interactions between spins of Cu²⁺ ions and nitroxides.

INTRODUCTION

The study of the effect of ligand structure modification on molecular and crystal structures of the resulting complexes is an important aspect of the rational design of materials with desirable structure and functional properties. Copper(II) complexes with nitroxide radicals are unique objects for studying the peculiarities of magnetic exchange pathways between different types of paramagnetic centers. The magnetic behavior of Cu(II)–nitroxide heterospin systems strongly correlates with the geometry of the coordination sphere of Cu²⁺ Jahn–Teller ions, which is substantially affected by the molecular structure of the nitroxide ligand. The equatorial coordination of the nitroxide group (NO group) results in strong antiferromagnetic Cu²⁺-radical exchange coupling (J < 0), whereas axial binding leads to ferromagnetic exchange interactions (J > 0).¹⁻³ There are several well-known factors that may favor one of the geometries.¹ Equatorial coordination is often preferred because of the additional stabilization in the case of spin pairing. Presence of other strong coordination sites in the side chain of ligand forces the axial binding of the NO group. Steric factors and intermolecular interactions between uncoordinated NO groups can favor both axial and equatorial coordination types, depending on the molecular structure and crystal packing of the resulting compounds. In some cases, the energy gap between equatorial and axial coordination is very weak, which allows the magnetic exchange interactions to be switched by changing the temperature, pressure, or light irradiation.¹⁻¹² However, only a few Cu(II) complexes with nitroxides exhibit structural-magnetic anomalies under external stimuli.¹⁻二十四 Even a minor modification of a ligand leads to significant changes in the molecular and crystal structures of the resulting Cu(II) complexes. This strongly affects the parameters of magnetic transitions and can result in the assembly of phases that cannot exhibit any magnetostructural anomalies.⁵⁻⁷⁻¹³,⁻²³,⁻²⁴ Cu(hfac)₂ complexes with various derivatives of 3-pyridyl-substituted nitronyl nitroxide (L) are of particular interest due to the diversity of molecular species and their magnetic properties (Scheme 1).⁴⁻⁷⁻¹²⁻¹⁶⁻¹⁸⁻²⁵⁻²⁶ Introduction of a Me group in the 4th position of the pyridine ring

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for L^4-Me nitronyl nitroxide has led to the formation of Cu(II) complexes with structure and magnetic properties completely different from those of the [{Cu(hfac)}_2]_2 compound based on the unsubstituted ligand. Recently described copper(II) and mixed-metal copper(II)-lanthanide complexes with L^5-Br and L^6-OMe nitronyl nitroxides have demonstrated various topological structures and different magnetic behaviors in the absence of structural and magnetic transitions. However, the effect of substituents at different positions of the pyridine ring on the coordination ability of 3-pyridyl nitronyl nitroxide ligand, structure, and magnetic behaviors of the resulting Cu(II) complexes has not been studied systematically. Therefore, the Me group and Br atom were chosen as substituents for the 2nd, 5th, or 6th positions of the pyridine heterocycle of L^R, because both of them have the same spatial size but different electronic properties (Scheme 1). This approach allowed us to trace the general relationship between the donor ability of nitroxide coordination sites and the molecular structure of resulting complexes, as well as a substitution effect on magnetostructural correlations inherent in their nature.

## RESULTS AND DISCUSSION

Nitronyl nitroxides L^R (R = Me, Br) were synthesized by condensation of the corresponding aldehydes with 2,3-bis(hydroxyamino)-2,3-dimethylbutane and subsequent oxidation of the resulting adduct with PbO_2 according to a well-established approach derived from Ullmann’s work. The spin-labeled L^R (R = 2-Me, 2-Br, 5-Me, 5-Br, 6-Br) were successfully isolated as single crystals suitable for X-ray diffraction (XRD) analysis (Figures 1S–3S and Table 1S). It was shown that the N=O bond lengths are typical for nitronyl nitroxides (1.27–1.28 Å).

Reaction of synthesized Me- and Br-substituted nitronyl nitroxides with Cu(hfac)_2 resulted in obtaining new heterospin coordination complexes: mononuclear [{Cu(hfac)}_2L^2-Me], binuclear [{Cu(hfac)}_2(H_2O)L^2-Me], trinuclear [{Cu(hfac)}_3(L^6-Br)], pentanuclear [{Cu(hfac)}_4(L^6-Me)_2] and [{Cu(hfac)}_3L^6-Me], cocrystals [{Cu(hfac)}_2(L^2-Br)], [{Cu(hfac)}_2(H_2O)_2], and [Cu(hfac)_2(L^2-Br)_2][Cu(hfac)_2H_2O], one-dimensional polymers [Cu(hfac)_2L^2-Br], and [Cu(hfac)_2L^6-Br] and cyclic dimers [Cu(hfac)_2L^5-Me], [Cu(hfac)_2L^5-Br], and [Cu(hfac)_2L^6-Me]. Interestingly, only one main product was obtained in the reactions of the 5th- and 6th-substituted nitronyl nitroxides, whereas L^2-Me and L^2-Br radicals generated several different complexes depending on the synthetic conditions and reagent ratio. Some of the resulting complexes are kinetic products and crystallized as admixtures. The crystal structure comprises two crystallographically independent Cu(hfac)_2L^2-Me molecules (Figure 1a) with slightly different bond lengths and angles. The coordination environment of Cu atoms in both molecules is square pyramidal, where one of the O_hfac atoms is at the apex, and the base is formed by the other three O_hfac atoms and the N_py atom (Cu–N_py = 2.003(9) Å and 2.021(8) Å; Figure 1a and Table 2S). The nearest O_NO⋯O_NO distances between uncoordinated NO groups of neighboring [Cu(hfac)_2L^2-Me] molecules is 3.659(11) Å.

The χM(T) in the temperature range 15–300 K for [Cu(hfac)_2L^2-Me] is 0.81 cm^3 K mol^-1 (Figure 2a), in good agreement with the corresponding contribution of weakly correlated spins S = 1/2 of Cu^{2+} ion and nitroxide. The decrease of χM(T) below 15 K indicates weak antiferromagnetic exchange interactions between spin sites. According to the XRD data, J_{R=R} in the pair of neighboring [Cu(hfac)_2L^2-Me] complexes...
Cu(hfac)$_2$/L complex are reproducibly obtained when the ratio of reagents central Cu atom are occupied by the ONO atoms (Cu$_{cent}$ mol = 2.481(2) Å; Table 2S). The coordination environment cm intermolecular exchange interactions. good agreement with the hypothetical scheme of the Cu$_2+B}$ contribution of {Cu 2+...A-...Cu$^{2+}$} coordination units (Cuter = 1.30 cm$^3$ theoretical magnitude 1.30 cm$^3$...K mol$^{-1}$). At 300 K, the $x_M(T)$ for the Cu$_2$...L$_{2-Me}$ complex is 1.22 cm$^3$...K mol$^{-1}$ and does not change significantly when the temperature is lowered to 10 K (Figure 2b). The experimental dependence of $x_M(T)$ was analyzed using the PHI program$^{31}$ with the contribution of {Cu$_2$...A...-RA...-R...Cu$^{2+}$C...-C$^{2+}$...-RB...-RB...Cu$^{2+}$B} five-spin fragments ($H = -2J_{CuA}$($S_{CuA}$...$S_{CuA}$ + $S_{CuB}$...$S_{CuB}$) = 2$J_{CuA}$($S_{RA}$...$S_{RA}$ + $S_{RB}$...$S_{RB}$)). The weakly interacting spins of the Cu$^{2+}$ ions that coordinate with the donor NPy atoms were introduced in the analysis by using the Curie law. The optimal exchange parameters, $g_K$ = 2.00 (fixed), $g_{Cu^{2+}}$ = 2.25, $J_{CuA}$ = -2.49 cm$^{-1}$, and $zJ$ = -0.09 cm$^{-1}$ are in good agreement with the hypothetical scheme of the intermolecular exchange interactions.

Dark-red crystals of pentanuclear [{Cu(hfac)$_2$}$_5$(L$_{2-Me}$)$_2$] complex are reproducibly obtained when the ratio of reagents Cu$_2$(hfac)$_2$/L$_{2-Me}$ increases to 5:2. The molecular structure of the [{Cu(hfac)$_2$}$_3$(L$_{2-Me}$)$_2$] complex consists of five Cu(hfac)$_2$ fragments connected by two L$_{2-Me}$ (Figure 1b). The vertices of the square pyramidal coordination environment of the central Cu$_{cent}$ atom are occupied by the O$_{NO}$ atoms (Cu$_{cent}$...O$_{NO}$ = 2.481(2) Å; Table 2S). The coordination environment of the four terminal Cu$_{ter}$ atoms is a square pyramid, where the donor atom NPy of L$_{2-Me}$ occupies the axial position in the {Cu$_{O,N}$} coordination units (Cu$_{ter}$...N$_{Py}$ = 2.302(2) Å) and O$_{NO}$ atoms are in equatorial planes of the {Cu$_{O}$} square pyramids (Cu$_{ter}$...O$_{NO}$ = 1.953(2) Å).

At 300 K, the $x_M(T)$ for the [{Cu(hfac)$_2$}$_3$(L$_{2-Me}$)$_2$] is 1.22 cm$^3$...K mol$^{-1}$ and does not change significantly when the temperature is lowered to 10 K (Figure 2b). The experimental dependence of $x_M(T)$ was analyzed using the PHI program$^{31}$ with the contribution of {Cu$_2$...A...-RA...-R...Cu$^{2+}$C...-C$^{2+}$...-RB...-RB...Cu$^{2+}$B} five-spin fragments ($H = -2J_{CuA}$($S_{CuA}$...$S_{CuA}$ + $S_{CuB}$...$S_{CuB}$) = 2$J_{CuA}$($S_{RA}$...$S_{RA}$ + $S_{RB}$...$S_{RB}$)). The weakly interacting spins of the Cu$^{2+}$ ions that coordinate with the donor NPy atoms were introduced in the analysis by using the Curie law. The optimal exchange parameters, $g_K$ = 2.00 (fixed), $g_{Cu^{2+}}$ = 2.06, $J_{CuA}$ = -842 cm$^{-1}$, $J_{CuB}$ = +57 cm$^{-1}$, and $zJ$ = +0.01 cm$^{-1}$, indicate the strong antiferromagnetic exchange interactions between the spins of terminal Cu$^{2+}$ ions and nitrooxides in the {Cu$_{O}$} coordination units due to direct overlapping of their magnetic orbitals. The almost-constant $x_M$T value in the temperature range 10...300 K is in good agreement with the theoretical magnitude 1.30 cm$^3$...K mol$^{-1}$ for uncompensated spins of three Cu$^{2+}$ ions. In addition, we determined the molecular and crystal structures of pentanuclear [{Cu(hfac)$_2$}$_3$(L$_{2-Me}$)$_2$] and bimolecular [{Cu(hfac)$_2$}$_2$(H$_2$O)L$_{2-Me}$] complexes. The small amounts of these crystals were obtained as admixtures when synthesized with Cu(hfac)$_2$/L$_{2-Me}$ ratios exceeding 1:1. A pentanuclear molecule of the [{Cu(hfac)$_2$}$_2$(L$_{2-Me}$)$_2$] complex is a linear oligomer, where four bidentate nitroxide ligands bind five Cu(hfac)$_2$ units via the NPy and ONO atoms of the nitroxide ligands (Figure 1c). The vertices of the elongated octahedra of the {Cu$_{O}$} coordination units are occupied by O$_{NO}$ atoms (Cu$_{cent}$...O$_{NO}$ = 2.522(4) Å; Table 2S). The axial positions of the Cu$_{O}$ square pyramids are occupied by NPy donor atoms from two different ligands (Cu$_{i}$...N$_{Py}$ = 2.422(4) and 2.665(5) Å). The terminal Cu$_{O}$ square pyramids contain O$_{NO}$ atoms and aqua ligand in the axial positions (Cu$_{i}$...O$_{NO}$ = 2.461(3) Å and Cu$_{i}$...O$_{H,O}$ = 2.344(3) Å). The shortest O$_{NO}$...O$_{NO}$ contacts between uncoordinated NO groups of neighboring molecules for both [{Cu(hfac)$_2$}$_3$(L$_{2-Me}$)$_2$] and [{Cu(hfac)$_2$}$_2$(H$_2$O)L$_{2-Me}$] are quite long and are equal to 3.711(4) and 3.654(5) Å, respectively (Table 2S).

The main product in the [{Cu(hfac)$_2$}$_2$...L$_{2-Br}$]$_n$ synthetic system is a one-dimensional [{Cu(hfac)$_2$}$_2$...L$_{2-Br}$]$_n$ complex (Figure 3a). Nitroxide molecules carry out the bidentate bridging function via the O$_{NO}$ donor atoms of both NO groups in the coordination sphere of Cu atoms. The resulting polymer chains consist of two types of alternating [{Cu(hfac)$_2$}$_2$...L$_{2-Br}$] monomers, which slightly differ in bond lengths and angles (Table 3S). The vertices of [{Cu$_{O}$}] bipyrromidic are occupied by O$_{NO}$ atoms of NO groups (Cu...O$_{NO}$ = 2.554(3) and 2.619(2) Å), whereas the O atoms of the hfac anions are in the equatorial planes (Cu...O$_{hfac}$ = 1.92–1.93 Å). The experimental $x_M$T value for the [{Cu(hfac)$_2$}$_2$...L$_{2-Br}$]$_n$ polymer chain is 0.87 cm$^3$...K mol$^{-1}$ at 300 K, which is close to the theoretical value of 0.81 cm$^3$...K mol$^{-1}$ for two independent paramagnetic centers with $S = 1/2$. The $x_M$T value gradually increases to 2.74 cm$^3$...K mol$^{-1}$ upon lowering the temperature to 2 K, indicating weak ferromagnetic exchange interactions (Figure 4a) that are typical for complexes with axial coordination of NO groups.$^{1,12,10,13--15,18,24}$ The experimental dependence of $x_M$T($T$) was approximated using a high-temperature series...
expansion for the uniform chain model \(H = -J_{\text{Cur}} \sum_{A} S_A S_{A+n} \) on the assumption that the exchange interactions \(J_A\) and \(J_B\) are weakly ferromagnetic in nature and their magnitude should be approximately the same, i.e., \(J_{\text{Cur}} \approx J_A \approx J_B\). The estimated optimum parameters of magnetic exchange interactions, \(g_R = 2.00\) (fixed), \(E_{\text{Cur}} = 2.09\), \(J_{\text{Cur}} = 6.6 \text{ cm}^{-1}\), are in good agreement with the proposed scheme of the intrachain exchange interactions.

The reaction of \(\text{Cu(hfac)}_2\) with \(L^{2-}\)Br can often give products containing coordinated water molecules. Violet needle-shaped crystals of the \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\cdot[\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) complex were obtained from a 1:1 ratio of \(\text{Cu(hfac)}_2\) and \(L^{2-}\)Br. XRD revealed that their crystal structure is a cosynthetic of \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\) and \([\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) complexes (Figure 3b and Table 3S). The vertices of the square pyramidal of the Cu atom in the \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\) fragment are occupied by two \(\text{ONO}\) atoms (Cu–O = 1.92–1.93 Å). O atoms of the aqua ligands are located in the axial positions of a distorted octahedral \([\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) fragment (Cu–O = 2.413(2) Å). The distances between \(\text{ONO}\) atoms of the \([\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) molecules and uncoordinated NO groups and N atom of the pyridine ring from the \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\) complex fragment are short (2.898(4) and 2.954(5) Å), respectively. This indicates the presence of weak O–H…NPy hydrogen bonds, which connect these \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\) and \([\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) fragments into layers (Figure 3b).

After increasing the ratio of \(\text{Cu(hfac)}_2\) and \(L^{2-}\)Br to 3:2, a small amount of the \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\cdot[\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) compound was precipitated (Figure 3c). The molecular structure of \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\) complex is similar to that described above. There are \(\text{ONO}\) atoms in the axial positions of the \(\text{CuO}_4\) units (Cu–O = 2.651(9) Å). \(\text{ONO}\) atoms occupy the vertices of \(\text{CuO}_4\) complexes pyramids of the \([\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) fragments (Cu–O = 2.250(8) Å). Each \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\) fragment is connected with two \([\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) via hydrogen bonds (O–H…O = 2.841(10) Å), whereas other hydrogen bonds (O–H…NPy = 2.897(12) Å) are linked resulting in linear \([\text{Cu(hfac)}_2(L^{2-}\text{Br})_2]\cdot[\text{Cu(hfac)}_2(\text{H}_2\text{O})_2]\) chains forming ribbons (Figure 3c and Table 3S).

The reactions of \(\text{Cu(hfac)}_2\) with nitroxides bearing substituents at the 5th position of the pyridine ring produce the cyclic dimer complexes \([\text{Cu(hfac)}_2L_5^{5}\text{Me}\big(\text{Me}\big)_2\] and \([\text{Cu(hfac)}_2L_5^{5}\text{Br}\big(\text{Br}\big)_2\] with similar molecular structures and crystal packing. These dimer molecules consist of two \(\text{Cu(hfac)}_2\) fragments bridged by two nitroxide molecules via NPy and \(\text{ONO}\) donor atoms (Figures 5a and 3ba). The coordination sphere of both crystallographically identical Cu atoms includes the \(\text{ONO}\) and \(\text{ONO}\) atoms from two paramagnetic ligands and two \(\text{hfac}\) anions in cis positions. The vertices of a square pyramidal are occupied by two \(\text{ONO}\) atoms (Cu–O = 2.358(3) Å) and \(\text{ONO}\) atoms are located in the equatorial plane (Table 4S). The remaining \(\text{ONO}\) atom, the \(\text{ONO}\) atom, and \(\text{NPy}\) atoms from two paramagnetic ligands and two \(\text{hfac}\) anions are in cis positions. The vertices of a square pyramidal are occupied by two \(\text{ONO}\) atoms (Cu–O = 2.358(3) Å) and \(\text{ONO}\) atom are located in the equatorial plane (Table 4S).

The temperature dependence of the molar magnetic susceptibility shows a similar magnetic behavior for both \([\text{Cu(hfac)}_2L_5^{5}\text{Me}\big(\text{Me}\big)_2\] and \([\text{Cu(hfac)}_2L_5^{5}\text{Br}\big(\text{Br}\big)_2\] complexes (Figures 6a and 4Sc). At 300 K, \(\chi M\) values are equal to 0.04 and 0.06 cm$^3$K$^{-1}$mol$^{-1}$ for \([\text{Cu(hfac)}_2L_5^{5}\text{Me}\big(\text{Me}\big)_2\] and \([\text{Cu(hfac)}_2L_5^{5}\text{Br}\big(\text{Br}\big)_2\] complexes, respectively, much smaller than the theoretical spin value (1.62 cm$^3$K$^{-1}$mol$^{-1}$) for four independent paramagnetic centers with spins.
$S = 1/2$. By lowering the temperature to 2 K, the $\chi_M T$ decreases to 0.01 cm$^3$·K·mol$^{-1}$ for both complexes. The strong suppression of paramagnetic properties correlates well with the short Cu–ONO distances in the molecular structure of [Cu(hfac)$_2$L$_5$-R]$_2$ (R = Me, Br) dimers. The equatorial coordination of the nitroxide group to the central Cu$^{2+}$ ion should lead to direct overlapping of their magnetic orbitals and mutual compensation of the spins in the {Cu–O•–N<} exchange clusters. The $\chi_M T(T)$ dependences are well described by the dimer model with the Hamiltonian $H = -2J_{CuR}(S_{Cu}S_R)$ using the PHI program. The optimum values of the fitted exchange parameters are as follows: $g_R = 2.15$ (fixed), $g_{Cu} = 2.00$, $J_{CuR} = -0.11$ cm$^{-1}$ for [Cu(hfac)$_2$L$_5$-Me]$_2$. The residual $\chi_M T$ value is 0.01 cm$^3$·mol$^{-1}$ at 2 K for both the dimers, attributed to the free spin defects being less than 0.6%.

Dark-red crystals of the [Cu(hfac)$_2$L$_6$-Me]$_2$ dimer complex were isolated in the synthesis containing equimolar amounts of Cu(hfac)$_2$ and L$_6$-Me. The [Cu(hfac)$_2$L$_6$-Me]$_2$ complex shows the same molecular structure with short Cu–N$_{Py}$ and Cu–ONO bond lengths (Cu–ONO ∼1.97 Å and Cu–N$_{Py}$ ∼2.04 Å; Figure 4Sb and Table 4S) as the above-mentioned Cu(II) compounds with nitroxide derivatives containing Me and Br substituents in the 5th position of the pyridine ring. The mutual arrangement of [Cu(hfac)$_2$L$_5$-R]$_2$ dimer molecule is different from that in the crystal structure complexes with 5-Me- and 5-Br-substituted nitroxides. However, the magnetic behavior, mainly caused by intramolecular magnetic exchange interactions, is similar to the above-described one for [Cu(hfac)$_2$L$_5$-R]$_2$ (R = Me, Br). The optimum values of the fitted exchange parameters $g_R = 2.15$ (fixed), $g_{Cu} = 2.15$, $J_{CuR} = -460$ cm$^{-1}$, $J' = -0.10$ cm$^{-1}$ ($H = -2J_{CuR}(S_{Cu}S_R)$) show totally suppressed paramagnetism due to strong antiferromagnetic exchange interactions between spins in the {Cu–O•–N<} exchange clusters (Figure 4Sd).

The molecular structures of the obtained [Cu(hfac)$_2$L$_5$-Me]$_2$, [Cu(hfac)$_2$L$_5$-Br]$_2$, [Cu(hfac)$_2$L$_6$-Me]$_2$ cyclic dimers and the previously described [Cu(hfac)$_2$L$_5$-Me]$_2$ complex are similar. [Cu(hfac)$_2$L$_6$-Me]$_2$ undergoes ferromagnetic exchange interactions in the temperature range 2–300 K, whereas [Cu(hfac)$_2$L$_5$-Br]$_2$, [Cu(hfac)$_2$L$_5$-Me]$_2$, and [Cu(hfac)$_2$L$_6$-Me]$_2$ exhibit suppressed paramagnetism that strongly correlates with the axial and equatorial type of the NO group bonding to the Cu$^{2+}$ central ion. As the increasing of intermolecular Cu–ONO distances, associating with the change-over of spin multiplicity,
can be initiated by increasing the temperature, we performed the differential thermal and thermogravimetric analysis of the obtained dimer complexes. However, the TG-DTA curves for \([\text{Cu(hfac)}_2\text{L}_5\text{Me}_2], \text{Cu(hfac)}_2\text{L}_5\text{Br}_2\] and \([\text{Cu(hfac)}_2\text{L}_6\text{Me}_2] \), (Figure 5S) did not show any specific heat effects associated with phase transitions up to the samples’ decomposition temperature. Thus, the strongly coupled state is the most stable one for the \([\text{Cu(hfac)}_2\text{L}_5\text{Me}_2], \text{Cu(hfac)}_2\text{L}_5\text{Br}_2\] and \([\text{Cu(hfac)}_2\text{L}_6\text{Me}_2] \) dimer complexes in the temperature range 2–380 K.

The reaction of \(\text{Cu(hfac)}_2\) with the 6-Br-substituted derivative of nitronyl nitroxide yielded the one-dimensional \([\text{Cu(hfac)}_2\text{L}_6\text{Br}_2\] and trinuclear \([\text{Cu(hfac)}_2\text{L}_6\text{Br}_3\] complexes (Figure 5b) and Table 4S). The trinuclear molecule of the \([\text{Cu(hfac)}_2\text{L}_6\text{Br}_3\] complex is a linear oligomer, where two nitroxide ligands bind with three \(\text{Cu(hfac)}_2\) via ONO atoms. The vertices of the square bipyramid of the central \(\text{Cu}_{\text{Cn}}\) atom in the \([\text{CuO}_6\) coordination unit are occupied by the ONO atoms \((\text{Cu}_{\text{Cn}}\text{ONO} = 2.577(2) \) Å). The coordination sphere of the \(\text{Cu}_{\text{Cn}}\) atom of the terminal \{CuO \} square pyramids contains an ONO atom in the equatorial plane \((\text{Cu}_{\text{Cn}}\text{ONO} = 1.953(2) \) Å).

The structure of the \([\text{Cu(hfac)}_2\text{L}_6\text{Br}_2\] polymer chain complex results from the bridging bidentate coordination of \(\text{L}_6\text{Br}\) (Figure 5b). Each \(\text{Cu}\) atom is surrounded either by two ONO atoms or by two NPy atoms from two different \(\text{L}_6\text{Br}\), leading to a head-to-head motif of infinite chains. Both donor atoms of the ligands occupy the axial positions in the alternating \{CuO \} and \{CuO,N \} square bipyramids \((\text{Cu}_{\text{Cn}}\text{ONO} = 2.385(3) \) Å and \(\text{Cu}_{\text{Cn}}\text{NPy} = 2.955(3) \) Å), whereas the equatorial planes are formed by the \(\text{ONO}\) atoms of the hfac anions (Table 4S). The shortest distances between \(\text{ONO}\) atoms from uncoordinated nitroxide groups of the ligands from neighboring chains are more than 4 Å.

The \(\chi M T\) for \([\text{Cu(hfac)}_2\text{L}_6\text{Br}_2\] is 0.80 cm\(^{-1}\)Kmol\(^{-1}\) at 300 K, in good agreement with the theoretical value \((0.81 \) cm\(^{-1}\)Kmol\(^{-1}\)) for two independent spins \(S = 1/2\) of \(\text{Cu}^{2+}\) ion and nitrooxide radical per formula fragment \([\text{Cu(hfac)}_2\text{L}_6\text{Br}_2\] (Figure 6b). \(\chi M T\) gradually increases with decreasing temperature and reaches 1.68 cm\(^{-1}\)Kmol\(^{-1}\) at 2 K, indicating the domination of ferromagnetic exchange interactions, which are typical for axial coordination of NO groups to central \(\text{Cu}^{2+}\) ions. \(\chi M T\) is well described by the model including the contribution of the three-spin \((\text{RA-J}_{\text{Cn}}\text{ Cu}^{2+}\text{ A-J}_{\text{Cn}}\text{ RA})\) exchange cluster \((H = −2\text{J}_{\text{Cn}}\text{ S}_{\text{Cn}}\text{S}_{\text{RA}} + \text{S}_{\text{RA}}\text{S}_{\text{Cn}})\) and isolated \(\text{Cu}^{2+}\) ions from coordination units \{CuO \} according to the Curie law, with the best fit parameters as follows: \(g_{\text{R}} = 2.00\) (fixed), \(g_{\text{Cn}} = 2.10, \text{J}_{\text{Cn}} = +16 \) cm\(^{-1}\), and \(zJ = +0.07 \) cm\(^{-1}\).

General Comparisons. Comparing data of the Cu(hfac)\(_2\) complexes with substituted derivatives of 3-pyridyl nitronyl nitroxides obtained within the scope of the current study and previously described elsewhere showed that the substituent type and its position in the pyridine heterocycle considerably affect the structure and magnetic behavior of the resulting compounds. Initially, we suspected that a substituent at the 2nd position of the pyridine ring should sterically hinder the coordination of both imine and nitroxide donor sites. Occupation of the 4th or 6th positions should mainly weaken the donor properties of only the nitroxide or the imine, respectively. The location of the substituent at the 5th position of the pyridine heterocycle should have a much smaller effect on donor abilities of a ligand. Additionally, we assumed that Br substituent should considerably weaken the nearest donor site due to a strong negative inductive effect. However, the ability of ligand donor sites to allow coordination is only one of the factors affecting the molecular structures of complexes. The spatial arrangements of hfac and nitrooxide ligands in different types of coordination units and the number of coordinated donor sites of ligands are strongly influenced by the reagents ratio, their concentration, the solvent used, ambient temperature, and humidity. The low solubility of the resulting solids and the strong antiferromagnetic exchange interactions between paramagnetic centers can result in some particular molecular and high-dimensional species. The angle between the planes of the nitronyl nitroxide \(\text{O}^\cdots\text{N}−\text{C}−\text{N}→\text{O}\) fragment and the pyridine ring is one of the key indicators of steric hindrance for 3-pyridyl-substituted nitronyl nitroxides (Scheme 2 and Table 5S). It is 36 and 53° for crystallographically independent molecules in the crystal structure of L\(_4\) showing a broad range of possible conformations of the substituted derivatives. The smallest values of the CN\(_{1,2}\)-Py angle (10–19°) were found for nitroxides with the Me group or Br atom at the 5th position of the pyridine ring. This angle increases to ∼37° when the Br atom is shifted to the 6th position of the pyridine heterocycle. The largest values were found for L\(^{2-R}\) and L\(^{4-Me}\) derivatives (47–72°), which are in perfect agreement with the expected increased steric hindrance.

A similar correlation between the CN\(_{1,2}\)-Py interplanar angle and the arrangement of substituents in L\(^R\) (\(R = \text{Me}, \text{Br}\)) is found for the molecular structures of the complexes (Table 6S). However, this relationship is much more complicated and required consideration of the steric properties of bulky Cu(hfac)\(_2\) fragments in the different types of coordination units and the variation of a number of coordinated donor sites of ligands. Notably, the most sterically hindered L\(^{2-R}\) and L\(^{4-Me}\) radicals produce the largest number of complexes, whereas the use of ligands bearing substituents at the 5th and 6th positions of the pyridine heterocycle produces only one main coordination complex for each paramagnetic ligand. Apparently, a high steric hindrance for complexes with L\(^{2-R}\) and L\(^{4-Me}\) derivatives induces the formation of many conformers with various CN\(_{1,2}\)-Py angles in a solution, leading to the precipitation of compounds with different molecular structures.

The comparison of distances between Cu atoms and imine and nitroxide donor sites allowed us to clarify the key correlations between the type and position of the substituent in the pyridine heterocycle and the coordinating ability of nitrooxide ligands (Table 6S). The short Cu–N\(_{NPy}\) (∼2.00 Å) and Cu–ONO (∼1.97 Å) distances have been found for dimer complexes containing ligands bearing Me and Br substituents.
at the 5th position of the pyridine ring. Similar cyclic dimers were obtained for Cu(hfac)$_2$ complexes with L$^{1-Me}$ and L$^{6-Me}$ ligands. Shift of the Me group to the 6th position of the pyridine ring does not considerably change the donor ability of the imine site and Cu–N$_{Py}$ distance (≈2.04 Å). In contrast, the nitroxide donor site for L$^{4-Me}$ is more sterically hindered, which results in lengthening of the Cu–ONO bond (≈2.43 Å).

The complexes with L$^{6-Br}$ ligand are the one-dimensional polymer [Cu(hfac)$_2$]L$^{6-Br}$_n and the trinuclear molecule [Cu(hfac)$_3$]$_2$(L$^{6-Br}$)$_2$. These are completely different from the [Cu(hfac)$_3$L$^{6-Me}$] cyclic dimer based on a Me-substituted analogue. The replacement of the Me group by a Br atom at the 6th position of the pyridine heterocycle substantially weakens the imine donor site due to a strong negative inductive effect, as indicated by the Cu–N$_{Py}$ bond lengths in the resulting complexes. Chains with a head-to-head motif of [Cu(hfac)$_2$]L$^{6-Br}$$_n$ are similar to the previously described coordination polymers for complexes based on pyrazolyl-substituted derivatives of nitroxides. 9,10,23,24 Alternating octahedral {CuO$_6$} and {CuO$_5$N} coordination units contain chelate hfac ligands in a coplanar arrangement. This arrangement should be less spatially crowded compared with the cis position spacing in {CuO$_4$N} units for the [Cu(hfac)$_2$L$^{6-Me}$]$_2$ dimer complex. Both N$_{Me}$ and ONO atoms are situated in axial positions of elongated octahedra [Cu–N$_{Me}$ = 2.954(3) Å and Cu–O$_{ONO}$ = 2.385(2) Å]. The structure of [Cu(hfac)$_3$]$(L^{6-Br})_2$ is similar to the previously described [Cu(hfac)$_3$L$^{6-Me}$]. 2,6 The weak donor ability of the imine site leads to the absence of coordination to the central Cu$^{2+}$ ion in both trinuclear complexes with L$^{6-Br}$ and L$^{6-Me}$. The negative inductive effect inherent in L$^{6-Br}$ is comparable to the steric hindrance of L$^{6-Me}$. The pentacoordinated terminal {CuO$_5$} units have reduced spatial bulkiness and provide shorter Cu–ONO (1.953(2) Å) distances than those in the central {CuO$_6$} coordination unit (2.577(2) Å).

The introduction of substituents at the 2nd position of the pyridine heterocycle sterically hinders both imine and nitroxide donor sites of the L$^{2-R}$ ligand. Nevertheless, it turned out to be favorable for the formation of various conformers of L$^{2-R}$ and complexes with different molecular structures. This is similar to some other stereochemically flexible Cu(II)–nitrooxide systems, where a reaction of Cu(hfac)$_2$ with polyfunctional nitroxides yields various solids with different structures and compositions. 1,2,7,9,12 At the same time, a variety of structural motifs generates the diversity of magnetic properties. 1,2,10,11,23,24 The short Cu–N$_{Py}$ bonds (2.003(9) and 2.021(8) Å) were observed only for the mononuclear [Cu(hfac)$_2$L$^{2-Me}$]$_2$ complex due to the reduced spatial bulkiness of pentacoordinated {CuO$_5$N} units. For the [Cu(hfac)$_2$L$_2$(H$_2$O)L$^{2-Me}$]$_2$ complex with two Cu(hfac)$_2$ fragments, which coordinate the same L$^{2-Me}$ ligand, the Cu–N$_{Py}$ bond in the {CuO$_4$N} units becomes longer (2.298(3) Å), whereas the coordination sphere of the other Cu atom tends to a distorted octahedral environment {CuO$_6$} by including an ONO atom and H$_2$O molecule in axial positions (Cu–O$_{ONO}$ = 2.461(3) Å and Cu–O$_{H_2O}$ = 2.344(3) Å).

The reproducibly obtained [Cu(hfac)$_2$L$_2$(L$^{2-Me}$)$_2$] complex is supposedly the most thermodynamically stable product in the {Cu(hfac)$_2$}$_2$ system. In spite of steric hindrance, both L$^{2-Me}$ ligands can perform tridentate coordination. As expected, Cu–ONO distances in central {CuO$_4$} square bipyramids are long (2.481(2) Å). Long Cu–N$_{Py}$ (2.302(2) Å) and short Cu–ONO (1.953(2) Å) bonds in pentacoordinated {CuO$_N$} and {CuO$_3$} units, respectively, indicate the higher steric effect on the imine donor site, comparable with nitroxide. Similar bond lengths for the L$^{2-Me}$ ligand donor sites are found for the linear pentanuclear [Cu(hfac)$_3$(L$^{2-Me}$)$_2$] complex (Cu–N$_{Py}$ = 2.422(4) and 2.665(5) Å, Cu$_{nit}$–ONO = 2.522(4) Å, and Cu$_{cent}$–ONO = 1.947(2) Å). Linear trinuclear complexes are often obtained using an excess of Cu(hfac)$_2$ in the reaction mixture. 1,2,12 Recently, another linear pentanuclear complex with a different arrangement of coordination units was reported. 10 Reducing the spatial bulkiness of [Cu(hfac)$_3$L$^{2-Me}$]$_2$ and [Cu(hfac)$_3$(L$^{2-Me}$)$_2$] complexes via formation of terminal pentacoordinated {CuO$_5$} or {CuO$_3$} units prevents the assembly of high-dimensional species. However, the precipitation of intermediate oligomers in the form of new pentanuclear [Cu(hfac)$_3$(L$^{2-Me}$)$_2$] and [Cu(hfac)$_3$L$^{2-Me}$]$_4$ complexes could clarify the mechanism for obtaining various polymers with chain, layered, or framework structures.

Location of the Br atom at the 2nd position of the pyridine heterocycle leads to considerable weakening of the imine site of L$^{6-Br}$ because of both the increasing steric hindrance and the negative inductive effect. Therefore, coordination of an imino atom to a Cu$^{2+}$ ion is absent for the molecular structure in the [Cu(hfac)$_2$L$^{6-Br}$]$_2$, [Cu(hfac)$_2$L$^{6-Me}$]$_2$-[Cu(hfac)$_2$(H$_2$O)$_2$], and [Cu(hfac)$_3$L$^{6-Me}$]$_2$[Cu(hfac)$_2$(H$_2$O)$_2$] complexes. The chain polymer structure of [Cu(hfac)$_2$L$^{6-Me}$]$_n$ consists of alternating nitroxide and Cu(hfac)$_2$ fragments, with long Cu–O$_{ONO}$ distances (2.554(2) and 2.619(2) Å) in distorted octahedral {CuO$_6$} units. Despite the possibility of the existence of trinuclear oligomers like [Cu(hfac)$_3$L$^{6-Me}$]$_2$, the molecular structures of the other two complexes includes mononuclear [Cu(hfac)$_2$L$^{6-Me}$]$_2$, which are bound by weak hydrogen bonds with [Cu(hfac)$_2$(H$_2$O)$_2$] or [Cu(hfac)$_2$(H$_2$O)] fragments containing coordinated water molecules.

The magnetic properties of complexes correlate with their structural characteristics. The character of the magnetic exchange interactions for cyclic dimers with {CuO$_N$} coordination units mainly depends on the steric properties of the ligand. The strong antiferromagnetic coupling between spins of Cu$^{2+}$ ions and nitrolyl nitroxides is observed for the [Cu(hfac)$_2$L$^{5-Me}$]$_2$, [Cu(hfac)$_2$L$^{5-Me}$], and [Cu(hfac)$_2$L$^{6-Me}$]$_2$ dimers with short Cu–ONO bonds due to a weak steric effect. Ferrimagnetic exchange interactions in the two-spin-coupled {Cu$^{2+}$–O$^\cdot$–N$^\cdot$–Cu$^{2+}$} exchange clusters for [Cu(hfac)$_2$L$^{5-Me}$]$_2$ results from lengthening of the Cu–ONO bond due to steric hindrance of the nitroxide donor site of L$^{5-Me}$. The appearance of {CuO$_5$} coordination units with short Cu–ONO in complexes based on L$^{2-R}$ and L$^{6-Br}$ ligands provides strong antiferromagnetic exchange interactions. This leads to full compensation of spins of Cu$^{2+}$ ions and coordinated nitrolyl nitroxides already at room temperature, as was found for {[Cu(hfac)$_3$L$^{2-Me}$]$_2$}. Coordination of a nitroxy group to the axial position of elongated {CuO$_5$} octahedra is favorable for the formation of exchange channels with ferrimagnetic interactions between spins of Cu$^{2+}$ ions and nitroxides, as takes place for [Cu(hfac)$_2$L$^{6-Br}$]$_n$ and [Cu(hfac)$_2$L$^{6-Me}$]$_n$ species.

**CONCLUSIONS**

Tuning of the donor ability of nitroxyde coordination sites is a powerful tool for the formation of Cu(II) complexes with diverse molecular and crystal structures and therefore various
magnetic behaviors. Introduction of a methyl group or bromine atom at different positions of the pyridine heterocycle affects the donor abilities of the nitroxide ligand due to steric or/and electronic effects of substituents. Complexes in which substituents do not strongly reduce the coordination ability of ligands (L\(^{5\text{Me}}\), \^{5\text{Br}}\), \^{6\text{Me}}\) exhibit strong antiferromagnetic exchange interactions in two-spin-coupled \(\{\text{Cu}^{2+}-\text{O}^\cdot-\text{N}^\cdot-\text{N}\}\) clusters when NO groups are equatorially coordinated in \(\{\text{CuO}_5\}\) units. The arrangement of long Cu–O=NO bonds in \(\{\text{Cu}_2\}\) square bipyramids due to the weakening of the ONO distances allows the assembly of low-dimensional species with strong antiferromagnetic exchange interactions in two-spin-coupled \(\{\text{Cu}^{2+}-\text{O}^\cdot-\text{N}^\cdot-\text{N}\}\) clusters.

The high steric hindrance for \(\text{L}^{2-}\text{Br}\) ligands can lead to various conformers in solution, which provides additional diversity of molecular structures of the resulting complexes. This allows pentanuclear \(\{[\text{Cu(hfac)}_2]_2\text{L}^{2\text{Me}}\}\) and \(\{[\text{Cu(hfac)}_2]_2\text{L}^{2\text{Me}}\}_2\) complexes to be obtained with unique molecular structures. The \(\{[\text{Cu(hfac)}_2]_2\text{L}^{2\text{Me}}\}\) and \(\{[\text{Cu(hfac)}_2]_2\text{L}^{2\text{Me}}\}_2\) oligomers are suggested to be intermediate species in the formation of various chain polymers, as well as layered and framework complexes. We have plans for further investigations on the effect of bulky substituents in the pyridine heterocycle of nitroxide on the structure and magnetic properties of complexes. This will create additional opportunities in the design of complexes with novel molecular structures and desired magnetic properties.

## EXPERIMENTAL SECTION

### General Procedures

The reactions were monitored by TLC using Merck “Aluminum oxide 60 F 254” neutral, aluminum sheets and Merck “Silica gel 60 F 254” aluminum sheets. Column chromatography was carried out with the use of Al\(^2\text{O}_3\) (Alumina activated 300, Nacalai Tesque). The reagents used without additional purification included 2-bromo-3-formylpyridine (96%, Sigma-Aldrich), 5-bromonicotinaldehyde (97%, Sigma-Aldrich), 3-bromo-2-methylpyridine (97%, Sigma-Aldrich), 5-bromo-2-methylpyridine (99%, Sigma-Aldrich), n-butyllithium (1.6 M in n-hexane, Kanto Chemical Co., INC), ethyl formate (FUJIFILM Wako Pure Chemical Corporation), and PbO\(_2\) (FUJIFILM Wako Pure Chemical Corporation). Cu(hfac)\(_2\), 2,3-bis(hydroxymino)-2,3-dimethylbutane, and 2-methylnicotin aldehyde, 5-methylnicotin aldehyde, and 6-methylnicotin aldehyde were synthesized by standard procedures. C, H, and N elemental analyses were carried out on a 2400 CHNS/O Series II System (100V) analyzer. Thermogravimetric and differential thermal analysis (TG-DTA) for polycrystalline samples \(\{\text{Cu(hfac)}_2\text{L}^{5\text{Me}}\}_2\), \(\{\text{Cu(hfac)}_2\text{L}^{5\text{Br}}\}_2\), and \(\{\text{Cu(hfac)}_2\text{L}^{6\text{Me}}\}_2\) were performed using SII EXSTAR TGA operating under dry nitrogen with heating from 300 to 500 K at a rate of 5 K/min.

2-(2-Bromopyridin-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl \((\text{L}^{2\text{Br}})\). 2-Bromo-3-formylpyridine (249.8 mg, 1.34 mmol) was added to a solution of 2,3-bis(hydroxymino)-2,3-dimethylbutane (207.4 mg, 1.40 mmol) in MeOH (7.0 mL) at room temperature. The reaction mixture was stirred for 30 h; then, the precipitate was filtered off, washed with MeOH, and dried in air. This gave 3-(1,3-dihydropyrrole-4,4,5,5-tetramethyl-imidazolidin-2-yl)-2-bromopyridine (394.9 mg) as a white powder, which was subsequently used without additional purification. PbO\(_2\) (1.9 g) was added to a suspension of the adduct in MeOH (10.0 mL) and the mixture was stirred for 2 h. The resulting violet solution was filtered, the filtrate was evaporated, and the residue purified by column chromatography (Al\(^2\text{O}_3\), EtOAc) followed by recrystallization from a CH\(_2\)Cl\(_2\)/n-hexane mixture. Yield: 271.0 mg (64%). Found (%): C 45.7; H 4.5; N 13.3. Calculated for C\(_{13}\)H\(_{18}\)N\(_3\)O\(_2\Bbox{ Br}\): C 46.0; H 4.8; N 13.4. Other bromo- and methyl-substituted 4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyls were obtained by an analogous procedure. 2-(2-Methylpyridin-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl \((\text{L}^{2\text{Me}})\). Yield: 820.0 mg (53%). Found (%): C 62.8; H 7.5; N 16.9. Calculated for C\(_{13}\)H\(_{18}\)N\(_3\)O\(_2\): C 62.9; H 7.3; N 16.9. 2-(5-Bromopyridin-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl \((\text{L}^{5\text{Me}})\). Yield: 1610.0 mg (51%). Found (%): C 46.1; H 4.7; N 13.4. Calculated for C\(_{14}\)H\(_{19}\)N\(_3\)O\(_2\Bbox{ Br}\): C 46.0; H 4.8; N 13.4. 2-(Methylpyridin-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl \((\text{L}^{2\text{Me}})\). Yield: 210.0 mg (36%). Found (%): C 62.2; H 7.6; N 16.9. Calculated for C\(_{14}\)H\(_{19}\)N\(_3\)O\(_2\): C 62.9; H 7.3; N 16.9. 2-(5-Bromopyridin-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl \((\text{L}^{5\text{Me}})\). Yield: 2610.0 mg (41%). Found (%): C 46.0; H 4.5; N 13.2. Calculated for C\(_{14}\)H\(_{19}\)N\(_3\)O\(_2\Bbox{ Br}\): C 46.0; H 4.8; N 13.4. 2-(2-Methylpyridin-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl \((\text{L}^{2\text{Me}})\). Yield: 2930.0 mg (61%). Found (%): C 62.4; H 7.3; N 16.9. Calculated for C\(_{14}\)H\(_{19}\)N\(_3\)O\(_2\): C 62.9; H 7.3; N 16.0.

2-[3-(2-Bromopyridin-3-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl \((\text{L}^{2\text{Br}})\) and \([\text{Cu(hfac)}_2]_4\text{L}^{2\text{Me}}\)_n-Hexane (3 mL) was added to a solution of Cu(hfac)\(_2\) (59.2 mg, 0.125 mmol) and L\(^{2\text{Me}}\) (1.25 mg, 0.050 mmol) in a mixture of Et\(_2\)O (0.5 mL) and CH\(_2\)Cl\(_2\) (1.0 mL). The volume of the dark-red solution was decreased to ~2 mL with a slow flow of nitrogen. The reaction mixture was kept in a sealed flask at ~5 °C for 12 h. The dark-red crystals suitable for XRD analysis were filtered off, washed with hexane, and dried in air. Yield: 63.7 mg (89%). Found (%): C 31.2; H 1.6; N 2.9. Calculated for Cu\(_3\)C\(_7\)H\(_{46}\)N\(_6\)O\(_{24}\): 62.9; H 7.3; N 16.0.

\([\text{Cu(hfac)}_2]_3\text{L}^{2\text{Me}}\] crystals were precipitated together with \([\text{Cu(hfac)}_2]_3\text{L}^{2\text{Me}}\] when the above-described reaction mixture was kept in an open flask at room temperature for 12–24 h. The crystals of \([\text{Cu(hfac)}_2]_3\text{L}^{2\text{Me}}\] and \([\text{Cu(hfac)}_2]_3\text{L}^{2\text{Me}}\] compounds are difficult to distinguish because they are similar in both color and habit. We could not collect enough \([\text{Cu(hfac)}_2]_3\text{L}^{2\text{Me}}\] manually with SC XRD identification for an extensive SQUID analysis and studied only the crystal structure.
crystals suitable for XRD analysis were filtered off, washed with hexane, and dried in air. Yield: 65.1 mg (72%). Found (%): C 37.0; H 2.7; N 5.7. Calculated for \(\text{Cu}_2\text{H}_6\text{N}_3\text{O}_6\text{F}_{12}\%): C 38.1; H 2.8; N 5.7.

\[\text{[Cu(hfac)}_2\text{]}_2\text{(H}_2\text{O})\text{L}^2\text{-Me}\]. A solution of Cu(hfac)\(_2\) (48.0 mg, 0.100 mmol) in \(n\)-heptane (20.0 mL) was placed in a 50 mL flask and was refluxed until the volume of the reaction mixture decreased to \(\sim 8\) mL. Then, a solution of \(L^2\text{-Me}\) (12.5 mg, 0.050 mmol) in \(\text{CH}_3\text{Cl}_2\) (2.0 mL) was added and the volume of the reaction mixture was reduced to \(\sim 4\) mL with a slow flow of nitrogen. The reaction mixture was kept in a sealed flask at \(-5°C\). After 12 h, a mixture of agglomerates of green crystals and violet powder was filtered off, washed with cold hexane, and dried in air. Several green crystals suitable for XRD analysis were collected manually.

\[\text{[Cu(hfac)}_2\text{]}_2\text{(L}^2\text{Br)}_2\text{)}\text{. n-Hexane (3.0 mL) was added to a solution of Cu(hfac)}_2\text{)}_2\text{(L}^2\text{Br)}_2\text{)}\text{. 2[Cu(hfac)}_2\text{(L}^2\text{Br)}_2\text{]}_2\text{H}_2\text{O}\text{. [Cu(hfac)}_2\text{(L}^2\text{Br)}_2\text{]}_2\text{H}_2\text{O}\]. A solution of Cu(hfac)\(_2\) (71.9 mg, 0.150 mmol) in CH\(_3\)Cl\(_2\) (2.0 mL) was placed in a 50 mL flask and was refluxed until the volume of the reaction mixture reduced to \(\sim 8.0\) mL. Then, a solution of L\(^6\text{-Br}\) (31.5 mg, 0.100 mmol) in CH\(_3\)Cl\(_2\) (1.0 mL) was added and the volume of the reaction mixture was reduced to \(\sim 3\) mL with a slow flow of nitrogen. The reaction mixture was kept at \(-5°C\) in a sealed flask for 10–16 h. Resulting dark-blue crystals were filtered off, washed with cold hexane, and dried in air. Yield: 46.1 mg (39%). Found (%): C 33.0; H 1.7; N 5.2. Calculated for \(\text{Cu}_2\text{H}_3\text{N}_3\text{O}_{12}\text{F}_{42}\text{Br}_2\%): C 33.4; H 2.2; N 5.3.

The crystals of \([\text{Cu(hfac)}_2\text{]}_2\text{(L}^6\text{-Br)}_2\] complex were obtained as an admixture by quickly decreasing the volume of the reaction mixture with a flow of nitrogen. Because of the small size of \([\text{Cu(hfac)}_2\text{]}_2\text{(L}^6\text{-Br)}_2\] crystals, we collected only several of them manually for SC XRD study.

X-ray Crystallography (XRD). X-ray diffraction intensities were collected for the selected single crystals individually mounted on glass fibers using Bruker diffractometers—SMART-APEX II with a CCD and D8-QUEST with a CMOS area detector (Mo K\(\alpha\) radiation). Data reduction was performed using SAINT, and intensities were corrected for absorption by using SADABS. The structures were solved by direct methods and refined by the full-matrix least-squares procedure anisotropically for nonhydrogen atoms. The H atoms were calculated geometrically and included in the refinement as riding groups. All calculations were fulfilled with the program package SHELXT 2014/5 and SHELXTL 2018/3. The crystallographic data and details of experiments are presented in Tables 1S–4S in the Supporting Information.

Magnetic Measurements. The magnetic susceptibility measurements were performed using an MPMS-5 SQUID magnetometer (Quantum Design) in the temperature range 2–350 K in a 5 kOe magnetic field. The molar magnetic susceptibility was calculated using diamagnetic corrections for the complexes according to the Pascal scheme. Analysis and fitting of magnetochemistry data for heterospin complexes was performed with the PHI program.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01575.

M magnetochemistry and thermogravimetric analysis data, detailed SC XRD experimental data (PDF)

Crystallographic information files (ZIP)

Accession Codes

Accession Codes CCDC 1916610–1916626 contain the supplementary crystallographic data in the form of CIF files.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: mks@tomo.nsc.ru (K.M.).
*E-mail: kxi@hiroshima-u.ac.jp (K.I.).

ORCID

Kseniya Maryunina: 0000-0003-4332-6054
Galina Romanenko: 0000-0001-8852-2759
Sadafumi Nishihara: 0000-0003-4030-786X

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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Cu(hfac)$_2$, copper(II) hexafluoracetacetonate; MeOH, methanol; Et,O, diethyl ether; PbO$_2$, lead(IV) oxide; EtOAc, ethyl acetate; CH$_2$Cl$_2$, dichloromethane; Al$_2$O$_3$, aluminum(III) oxide

**ABBREVIATIONS**

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