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Through-bond magnetic interaction between the 2p spin of the aminoxyl radical and the 3d spin of the metal ions in the complexes of bis(hexafluoroacetylacetonato)-manganese(II) and -copper(II) with 4-(*N*-*tert*-butyl-*N*-oxylamino)-2,2′-bipyridine †

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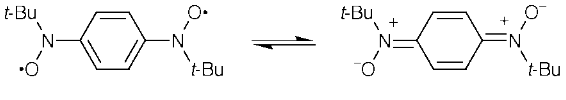
The crystal and molecular structures of 1 : 1 complexes of bis(hexafluoroacetylacetonato)-manganese(II), -copper(II) and -zinc(II) with 4-(*N*-*tert*-butylaminoxyl)-2,2′-bipyridine were studied by X-ray single crystal analyses to show their mononuclear structures in which the bipyridine moieties are coordinated with the metal ions in a *cis* configuration and the aminoxyl groups do not take part in the coordination. Their magnetic properties measured on a SQUID susceptometer/magnetometer revealed that the manganese(II) and copper(II) ions couple with the remote aminoxyl radical through the bipyridine ring antiferro- and ferro-magnetically by $J/k_B = -20.2$ and $+68.7$ K, respectively.

Introduction

When diradical **1** has no ring substituents which restrict a planar structure, the unpaired electrons of the two aminoxyl groups couple antiferromagnetically through the *p*-phenylene ring to give a closed-shell *p*-benzoquinonimine *N*,*N*′-dioxide.[1] The magnetic metal complexes coordinated with 4-pyridylaminoxyl derivative **2** having a topology similar to **1** show metal-dependency of the coupling: ferromagnetic in copper(II) and antiferromagnetic in Mn(II) and Cr(III) complexes.[2,3,4] The results are interpreted in terms of the symmetry of the magnetic orbitals of the metal ions with respect to the pπ orbital of the pyridyl nitrogens that carry positive spin density due to the aminoxyl radical at the 4-position. These findings have been used for designing and analyzing the magnetic interaction in hetero-spin polymeric chains.[5,6] Since the Lewis acidity of the bis(hexafluoroacetylacetonato)metal ions is limited, it seemed necessary to employ more strongly coordinating ligands. For this reason and in order to increase the structural dimensions of the polymeric high-spin complexes, we have paid attention to a 2,2′-bipyridine ligand that is known to form bis and tris complexes with suitable metal ions.[7] In this paper we studied the sign and magnitude of the exchange coupling between the metal ions and the aminoxyl radical through the bidentate 2,2′-bipyridine ligand[8] and compared the coupling parameters with those of corresponding monodentate pyridine metal complexes **2**.

Results and discussions

4-(*N*-*tert*-Butyl-*N*-oxylamino)-2,2′-bipyridine **3** and its 1 : 1 complexes of bis(hexafluoroacetylacetonato)-manganese(II), -copper(II), and -zinc(II), [Mn-, Cu- and Zn-(hfac)$_2$·**3**], were prepared in a manner similar to a procedure for **2** reported previously.[3,4]



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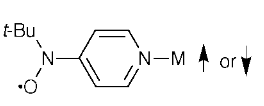

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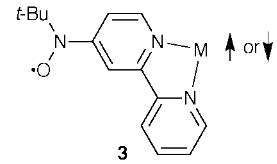

3

(A) X-Ray molecular and crystal structures

The molecular and crystal structures of [Mn-, Cu- and Zn-(hfac)$_2$·**3**] were investigated by X-ray single crystal analysis. Selected bond lengths, angles, and dihedral angles for [Mn-, Cu- and Zn-(hfac)$_2$·**3**] are given in Table 1. The three complexes [Mn(hfac)$_2$·**3**], [Cu(hfac)$_2$·**3**], and [Zn(hfac)$_2$·**3**] showed similar molecular structures in which the coordination geometries are distorted octahedra.

The molecular and crystal structure of [Cu(hfac)$_2$·**3**] is shown in Fig. 1. As listed in Table 1, the elongation axis is through O(5)–Cu–O(3). The dihedral angles between the planes of the bipyridine and the aminoxyl groups, O(1)N(1)C(3), are 18.1, 22.8, and 20.9° for [Mn(hfac)$_2$·**3**], [Cu(hfac)$_2$·**3**], and [Zn(hfac)$_2$·**3**], respectively. The crystal packings of the complexes are also similar to each other. As shown in Fig. 1b, the two 2,2′-bipyridine rings are layered on top of each other in a head-to-tail geometry to form a dimer structure (a pair of Δ and Λ isomers) and the dimers align along the *a* axis (the nearest contacts are 3.31, 3.30, and 3.30 Å for O(1)–C(14′) within the dimers and 3.57, 3.69, and 3.57 Å for C(10′)–C(12″) between the dimers in the manganese, copper, and zinc complexes, respectively). Since position 2 of the pyridine ring is considered to have only a small negative spin density, polarization of the spins on the unsubstituted pyridine ring in **3** should be negligible. The observed short contacts of the unsubstituted pyridine rings of 2,2′-bipyridine

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† Electronic supplementary information (ESI) available: ORTEP drawings of [Mn(hfac)$_2$·**3**] and [Zn(hfac)$_2$·**3**] and a χ_m^{-1} *versus T* plot for [Zn(hfac)$_2$·**3**]. See http://www.rsc.org/suppdata/dt/a9/a909564k/

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Table 1 Selected bond lengths (Å), angles, and dihderal angles (°) for [Mn(hfac)$_2$·**3**], [Cu(hfac)$_2$·**3**], and [Zn(hfac)$_2$·**3**]

	[Mn(hfac)$_2$·**3**]		[Cu(hfac)$_2$·**3**]		[Zn(hfac)$_2$·**3**]	
	Mn–N2	2.215(8)	Cu–N2	1.982(7)	Zn–N2	2.107(4)
	Mn–N3	2.229(9)	Cu–N3	2.012(7)	Zn–N3	2.119(4)
	Mn–O2	2.143(8)	Cu–O2	1.953(6)	Zn–O2	2.139(4)
	Mn–O3	2.191(7)	Cu–O3	2.347(5)	Zn–O3	2.078(4)
	Mn–O4	2.144(8)	Cu–O4	1.970(6)	Zn–O4	2.067(4)
	Mn–O5	2.192(7)	Cu–O5	2.314(5)	Zn–O5	2.139(4)
	N2–Mn–O2	93.5(3)	N2–Cu–O2	94.1(2)	N2–Zn–O2	93.3(2)
	N2–Mn–O3	96.7(3)	N2–Cu–O3	95.0(2)	N2–Zn–O3	95.9(2)
	N2–Mn–O4	172.1(3)	N2–Cu–O4	175.1(2)	N2–Zn–O4	174.4(2)
	N2–Mn–O5	94.7(3)	N2–Cu–O5	92.2(1)	N2–Zn–O5	92.5(2)
	N2–Mn–N3	73.1(2)	N2–Cu–N3	80.7(2)	N2–Zn–N3	77.6(2)
	O2–Mn–O3	82.6(3)	O2–Cu–O3	85.5(1)	O2–Zn–O3	86.1(1)
	O4–Mn–O5	82.2(3)	O4–Cu–O5	85.0(1)	O4–Zn–O5	85.7(1)
Dihedral Angles	O1N1C3–ClC3C5	18.07	O1N1C3–C1C3C5	22.76	O1N1C3–C1C3C5	20.89
	N2MnN3–N2C2C4	4.15	N2CuN3–N2C2C4	3.78	N2ZnNN3–N2C2C4	4.17
	N2MnO2–N2C2C4	1.44	N2CuO2–N2C2C4	5.18	N2ZnO2–N2C2C4	2.48
Within dimer	O1–C14′	3.305	O1–C14′	3.301	O1–C14′	3.295
Between dimer	C10′–C12″	3.573	C10′–C12″	3.686	C10′–C12″	3.567

within and between the dimers might therefore be ineffective for intermolecular magnetic couplings in crystals.

(B) Magnetic measurements

The temperature dependence of the molar paramagnetic susceptibilities (χ_m) for powder samples was investigated in the range 2–300 K at a constant field of 5 kOe. The $\chi_\mathrm{m}T$ *vs.* T plots for [Mn(hfac)$_2$·**3**] and [Cu(hfac)$_2$·**3**] are shown in Fig. 2a and 2b, respectively. The $\chi_\mathrm{m}T$ values at 300 K are 4.21 and 0.83 emu K mol^{-1} for [Mn(hfac)$_2$·**3**] and [Cu(hfac)$_2$·**3**], respectively, and already smaller and larger than the ones (4.75 and 0.75 emu K mol^{-1}, respectively) calculated for the spin-only values of isolated aminoxyl plus metal(II) ions. Their temperature-dependent profiles are in sharp contrast to each other. Upon the decrease of temperature from 300 to 2 K, $\chi_\mathrm{m}T$ for [Mn(hfac)$_2$·**3**] decreased gradually and reached a small plateau of 2.81 emu K mol^{-1} at *ca.* 13 K before decreasing steeply below 10 K. On the other hand, $\chi_\mathrm{m}T$ values for [Cu(hfac)$_2$·**3**] increased, reached a small plateau of 1.01 emu K mol^{-1} at *ca.* 40 K, and then increased steeply below 10 K. The $\chi_\mathrm{m}T$ values of the plateau observed in the low temperature region in [Mn(hfac)$_2$·**3**] and [Cu(hfac)$_2$·**3**] are close to the theoretical ones (3.0 and 1.0 emu K $^{-1}$) calculated for $S = 4/2$ and 2/2, respectively.

The eqn. (1)[9] and (2)[10] for a two-spin model ($H = -2J(S_1S_2)$) for the interaction between the two spin centers within a dimer were applied to the experimental data for [Mn(hfac)$_2$·**3**] and [Cu(hfac)$_2$·**3**] to give $J/k_\mathrm{B} = -20.2 \pm 0.26$ K, $\theta = -0.20 \pm 0.02$ K and $g = 1.95 \pm 0.07$, and $J/k_\mathrm{B} = +68.7 \pm 1.65$ K, $\theta = +0.40 \pm 0.01$ K and $g = 2.01 \pm 0.01$, respectively. The theoretical best fits are given by solid curves in Fig. 2. The $1/\chi_\mathrm{m}$ values increased linearly with T (Fig. S3, ESI) for [Zn(hfac)$_2$·**3**]. The Curie–Weiss equation $\chi_\mathrm{m} = C/(T - \theta)$ was fitted to the experimental data to give the Curie constant $C = 0.35$ emu K mol^{-1} and Curie–Weiss constant $\theta = 0.07$ K. This small θ value for [Zn(hfac)$_2$·**3**] suggests that intermolecular magnetic couplings between aminoxyl radical centers within the dimers should be weak also in [Mn(hfac)$_2$·**3**] and [Cu(hfac)$_2$·**3**].

$$\chi_\mathrm{m}T = \frac{Ng^2\mu_\mathrm{B}{}^2T}{k_\mathrm{B}(T-\theta)} \times \frac{2}{3 + \exp(-2J/k_\mathrm{B}T)} \qquad (1)$$

$$\chi_\mathrm{m}T = \frac{Ng^2\mu_\mathrm{B}{}^2T}{k_\mathrm{B}(T-\theta)} \times \frac{28 + 10\exp(-6J/k_\mathrm{B}T)}{7 + 5\exp(-6J/k_\mathrm{B}T)} \qquad (2)$$

where all symbols have their usual meanings.

It is concluded that the aminoxyl radicals in [Mn(hfac)$_2$·**3**] and [Cu(hfac)$_2$·**3**] interact antiferro- and ferro-magnetically with the manganese and copper ions through the 2,2′-bipyridine ring by $J/k_\mathrm{B} = -20.2$ and 68.7 K, respectively. Especially in [Cu(hfac)$_2$·**3**], intermolecular interaction (within dimer) is also ferromagnetic with $\theta = 0.40$ K.

(C) Comparison of magnetic coupling between [M(hfac)$_2$·3] and [{M(hfac)$_2$}·2$_2$]

When J/k_B values for both the complexes in this work are compared with those ($J/k_\mathrm{B} = -12.4$ and 60.4 K for Mn(II)[3] and Cu(II)[4] ions, respectively) of the corresponding 1 : 2 complexes, [{M(hfac)$_2$}·**2**$_2$], the signs of J/k_B are consistent; negative for the manganese and positive for the copper ion.

The 2pπ-orbital of the nitrogen atom at position 1 of the 2,2′-bipyridine ring contains a positive spin density due to the spin polarization of the pπ-orbitals by the 4-aminoxyl radical centers. The observed difference in the through-bond coupling between the manganese and copper complexes are understood by the overlap and the orthogonality between this 2pπ-orbital at the nitrogen atom and the half-filled 3d$_{xz}$ or 3d$_{yz}$ of Mn(II) and 3d$_{x^2-y^2}$ for Cu(II), respectively. This explanation is further corroborated by the difference in the magnitude of J/k_B between [M(hfac)$_2$·**3**] and [{M(hfac)$_2$}·**2**$_2$]. Since the coupling is due to π-type overlap in the Mn(II) complex, the magnitude should be dependent on the dihedral angle between the pyridine ring plane and the xy plane of the metal ion; J/k_B values are -20.2 and -12.4 K, for the dihedral angles of 6–5° and 17–15° in [Mn(hfac)$_2$·**3**] and [Mn(hfac)$_2$}·**2**$_2$] respectively. Since the magnetic orbital of Cu(II) is a σ-type, the ferromagnetic coupling of the 3d spin with that of 2pπ-orbital at the nitrogen atom should not be overly dependent on the dihedral angle; J/k_B values are 68.7 and 60.4 K for the dihedral angles of 3–0° and 25–24° in [Cu(hfac)$_2$·**3**] and [Cu(hfac)$_2$}·**2**$_2$], respectively.

The preparation and the investigation of the magnetic properties of bis- and tris-bipyridyl complexes with manganese and copper ions are in progress.

Experimental

General methods

Infrared spectra were measured on a Hitachi 270–30 IR spectrometer. ^{1}H NMR spectra were measured on a JEOL 270 Fourier transform spectrometer using CDCl$_3$ as solvent and referenced to TMS. EPR spectra were recorded on a Bruker

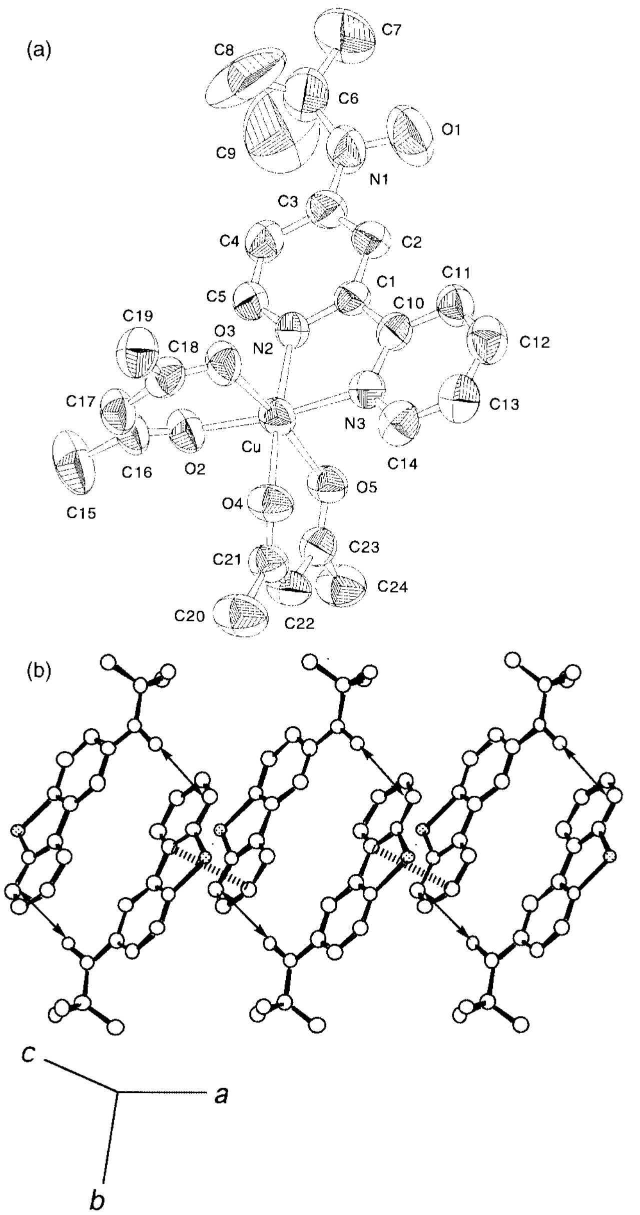

Fig. 1 Molecular and crystal structure of [Cu(hfac)$_2$·**3**]. Trifluoromethyl groups are omitted for clarity: (a) ORTEP[15] drawing of molecular structure with thermal ellipsoid plot at the 30% probability level. (b) Ball and stick model of the crystal structure. Hfac ligands are omitted for clarity. Shadow balls are copper ions and arrows and broken lines indicate short contacts of 3.30 and 3.69 Å within and between dimers, respectively.

ESP300 X-band (9.4 GHz) spectrometer equipped with a Hewlett Packard 5350B microwave frequency counter. FAB mass spectra (FAB MS) were recorded on a JEOL JMS-SX102 spectrometer. Melting points were obtained with a MEL-TEMP heating block and are uncorrected. Elemental analyses were performed at the Analytical Center of Faculty of Science in Kyushu University.

X-Ray crystal and molecular structural analyses

Diffraction data were collected using Cu-Kα and Mo-Kα radiations on Rigaku AFC5R for [Mn(hfac)$_2$·**3**] and [Cu(hfac)$_2$·**3**] and AFC7R four circle diffractometers for [Zn(hfac)$_2$·**3**]. The structures of these three complexes were solved in $P2_1/n$ (no. 14) by direct and Patterson methods[11] and refinement converged using a full-matrix least squares method of the teXsan[12] crystallographic software package (Ver. 1.9). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at standard positions (C–H 0.96 Å, C–C–H 120°) and refined isotropically using a rigid model. Pertinent crystallographic parameters and refinement data are collected in Table 2.

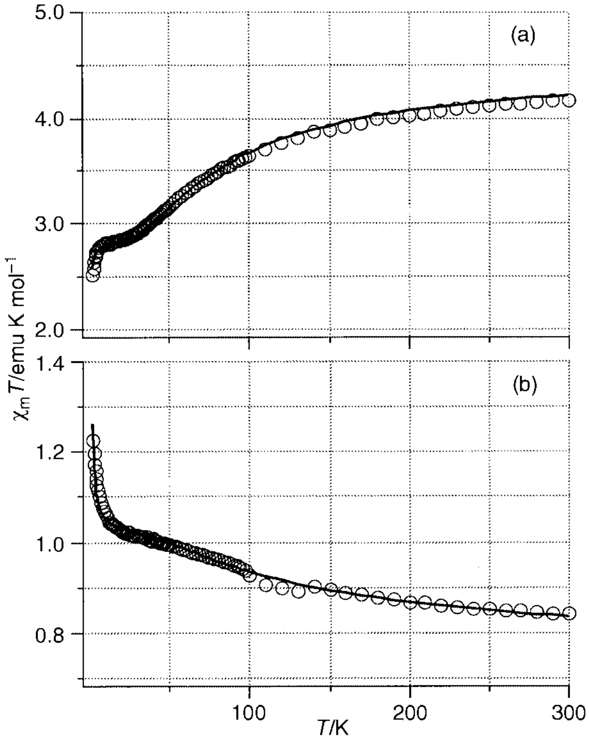

Fig. 2 Temperature dependence of molar magnetic susceptibility as expressed by $\chi_m T$ *vs.* T plots for (a) [Mn(hfac)$_2$·**3**] and (b) [Cu(hfac)$_2$·**3**]. The solid curves are theoretical ones as described in the text.

CCDC reference number 186/1846.

See http://www.rsc.org/suppdata/dt/a9/a909564k/ for crystallographic files in .cif format.

Magnetic measurements

Magnetic susceptibility data were obtained on Quantum Design MPMS$_2$ (0–10 kOe) and MPMS (0–50 kOe) SQUID magnetometer/susceptometers. The data were corrected for the diamagnetic contribution (-3.7×10^{-5}–-6.7×10^{-5} emu G) of sample capsules and holding straws used in the temperature range 2–300 K. The diamagnetic contributions of the samples were estimated by Pascal's constants.

Preparation of the ligand and the metal complexes

Unless otherwise stated, preparative reactions were carried out under a high-purity dry nitrogen atmosphere. Diethyl ether was distilled from sodium benzophenone ketyl. Bis(hexafluoroacetylacetonato)manganese-(II), -copper(II), -zinc(II) {M(hfac)$_2$, M = Mn(II), Cu(II), and Zn(II)}, 2-methyl-2-nitrosopropane,[13] and 4-bromo-2,2′-bipyridine[14] were prepared and purified by the literature procedures.

4-(*N-tert*-Butyl-*N*-hydroxylamino)-2,2′-bipyridine, 3-OH. To the solution of 4-bromo-2,2′-bipyridine (4.7 g, 20 mmol) in dry ether (75 ml) was added a 1.57 M solution of *n*-butyllithium (25.5 ml, 40 mmol) at −78 °C. After stirring for 30 min, a solution of 2-methyl-2-nitrosopropane (4.35 g, 50 mmol) in ether (15 ml) was added dropwise. The reaction mixture was stirred for 1 h at −78 °C and then the temperature was raised to 0 °C by the removal of a cooling bath. After the usual work-up, the mixture was chromatographed on aluminium oxide with *n*-hexane–CHCl$_3$ as eluent to afford hydroxylamine **3-OH** (0.85 g, 18%) as a white powder. Mp (from isopropanol) 129–130 °C (Found: C, 69.07; H, 7.04; N, 17.18. Calc. for $C_{14}H_{17}N_3O$: C 69.11; H, 7.04; N, 17.27%); ν_{max}/cm^{-1} 3170 (OH); δ_H (270 MHz; solvent CDCl$_3$; standard TMS) 8.68 (1H, d, J = 3.8 Hz,

Table 2 Crystal data and structure refinements for [Mn(hfac)$_2$·**3**], [Cu(hfac)$_2$·**3**], and [Zn(hfac)$_2$·**3**]

	[Mn(hfac)$_2$·**3**]	[Cu(hfac)$_2$·**3**]	[Zn(hfac)$_2$·**3**]
Empirical formula	$C_{24}H_{18}N_3O_5F_{12}Mn$	$C_{24}H_{18}N_3O_5F_{12}Cu$	$C_{24}H_{18}N_3O_5F_{12}Zn$
Formula weight	711.34	719.95	721.78
Crystal color, habit	Orange, prismatic	Green, plate	Red, prismatic
Crystal dimensions/mm	0.4 × 0.4 × 0.2	0.5 × 0.4 × 0.5	0.5 × 0.5 × 0.5
Crystal system	Monoclinic	Monoclinic	Monoclinic
a/Å	8.458(2)	8.496(2)	8.415(2)
b/Å	17.716(3)	17.305(3)	17.478(3)
c/Å	20.249(3)	20.100(3)	20.165(3)
β/°	98.83(2)	99.04(2)	99.19(2)
V/Å^3	2962(1)	2918.4(10)	2927(1)
T/°C	25	23	23
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
Z	4	4	4
D_{calc}/g cm^{-3}	1.595	1.638	1.637
No. of observations	2082	3135	4527
No. of variables	406	514	450
Residuals: R; Rw	0.074; 0.075	0.058; 0.046	0.067; 0.062

$C_{6'}$-H), 8.49 (1H, d, $J = 5.3$ Hz, C_6-H), 8.35 (1H, d, $J = 8.0$ Hz, $C_{3'}$-H), 8.25 (1H, d, $J = 1.8$ Hz, C_3-H), 7.80 (1H, dt, $J = 8.0$ and 1.8 Hz, $C_{4'}$-H), 7.30 (1H, ddd, $J = 7.5$, 4.8, and 1.1 Hz, $C_{5'}$-H), 7.18 (1H, dd, $J = 5.5$ and 2.0 Hz, C_5-H), 6.07 (1H, *s*, O-H), 1.25 (9H, *s*, C–H_3). FAB MS (in NOBA matrix) 244 (M + 1).

4-(*N*-*tert*-Butyl-*N*-oxylamino)-2,2′-bipyridine, 3. To the solution of hydroxylamine **3-OH** (0.11 g, 0.48 mmol) in ether (20 ml) was added freshly prepared Ag_2O (0.5 g, 4.0 mmol). The suspension was stirred for 1 h at room temperature and filtered. The filtrate was chromatographed on aluminium oxide. An EPR spectrum of the eluting red solution (in CH_2Cl_2) was characteristic of **3** with $a_N = 12.0$ G at $g = 2.0061$. When a solution of radical **3** was concentrated, it decomposed to give a complex mixture. A dilute solution of **3** in Et_2O was therefore used for the complexation with M(hfac)$_2$ without further purification.

Preparation of [M(hfac)$_2$·3]. A solution of **3** in Et_2O was mixed with solutions of Mn-, Cu-, and Zn-(hfac)$_2$ in *n*-heptane in a molar ratio of 1 : 1 and mixtures were left in a refrigerator. The single crystals of complexes [Mn(hfac)$_2$·**3**], [Cu(hfac)$_2$·**3**], and [Zn(hfac)$_2$·**3**] were obtained as orange prisms, green plates, and red prisms respectively.

[Mn(hfac)$_2$·**3**]: Anal. Calc. for $C_{24}H_{18}N_3O_5F_{12}Mn$: C 40.52; H, 2.56; N, 5.91. Found: C, 40.60; H, 2.60; N, 5.76%. [Cu(hfac)$_2$·**3**]: Anal. Calc. for $C_{24}H_{18}N_3O_5F_{12}Cu$: C 40.03; H, 2.52; N, 5.83. Found: C, 40.15; H, 2.57; N, 5.83%. [Zn(hfac)$_2$·**3**]: Anal. Calc. for $C_{24}H_{18}N_3O_5F_{12}Zn$: C 39.94; H, 2.51; N, 5.82. Found: C, 39.88; H, 2.59; N, 5.79%.

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