Stabilization of a Nitroxide with a *β*-Hydrogen by Metals: Structure and Magnetic Properties of Adducts of *N*-Oxy-*N*-*tert*-butyl-(2-pyridyl)phenylmethanamine with Mn(II), Ni(II), and Co(II) Hexafluoroacetylacetonates†

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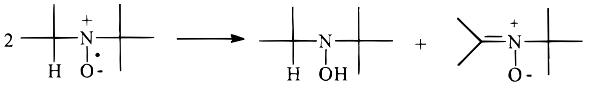
Transition metal hexafluoroacetylacetonate complexes of a nitroxide bearing a β-hydrogen, *N*-oxy-*N*-*tert*-butyl-(2-pyridyl)phenylmethanamine (2-PyBNO), were synthesized and characterized. X-ray analysis of the metal−nitroxide complexes M(2-PyBNO)(hfac)$_2$, where M(II) = Mn (**1**), Co (**2**), and Ni (**3**), revealed a distorted octahedral coordination geometry for the three metal centers. All complexes are isostructural and triclinic, $P\bar{1}$. Crystal data: **1**, $a = 7.996(2)$ Å, $b = 11.601(2)$ Å, $c = 17.105(4)$ Å, $\alpha = 91.287(1)°$, $\beta = 100.409\ (1)°$, $\gamma = 101.196(1)°$, $Z = 2$; **2**, $a = 7.932(4)$ Å, $b = 11.477(6)$ Å, $c = 17.395(8)$ Å, $\alpha = 92.780(1)°$, $\beta = 101.330(1)°$, $\gamma = 101.040(1)°$, $Z = 2$; **3**, $a = 7.862(5)$ Å, $b = 11.353(7)$ Å, $c = 17.423(10)$ Å, $\alpha = 93.583(1)°$, $\beta = 101.120\ (1)°$, $\gamma = 100.154(1)°$, $Z = 2$. SQUID magnetic susceptibility measurements over a temperature range of 2−300 K for complexes **1** and **3** showed antiferromagnetic coupling between the nitroxide and metal nucleus unpaired electrons, with $-J = 57(1)$ cm^{-1} for **1** and $-J = 181(15)$ cm^{-1} for **3**. EPR spectra of frozen solutions (115 K) show a weak signal centered at $g = 2.000$ for **1** and a doublet with $g_1 = 2.299$, $g_2 = 2.243$, and $g_3 = 2.193$ for **3**.

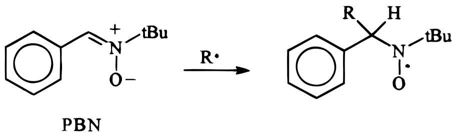
Introduction

New approaches in the design of novel molecular magnetic materials[1] have been the focus of active investigation during the past decade. Materials with metal−nitroxide interactions exhibit interesting magnetic behavior that may be useful for the design of inorganic−organic-based magnets. One goal has been to synthesize ferromagnetic materials that exhibit spontaneous magnetization at a critical temperature. A T_c of 46 K (the highest so far in its class) was observed for the complex of Mn(hfac)$_2$ with a trinitroxide.[2] Possible applications of molecular-based magnets include use as bulk magnets and in magnetic/magnetooptic recordings due to their anticipated properties such as low density, transparency, solubility, or photomagnetism.[1]

Stable nitroxides with α-carbons that are fully substituted or sp^2-hybridized are used for the preparation of metal−nitroxide complexes and for spin-labeling purposes. Nitroxide spin adducts are also widely used in mechanistic studies. However, nitroxides bearing a β-hydrogen are capable of undergoing disproportionation (eq 1) and therefore less suitable for such applications.[3] The present study was undertaken to determine whether nitroxides bearing a β-hydrogen could be stabilized by coordination to metal ions. It was expected that complexation of a nitroxide to a metal would inhibit disproportionation, since bimolecular interaction between nitroxides is less favored.


(1)

These complexes are of interest since most spin-trapping experiments employing *N*-*tert*-butyl-α-phenyl nitrone (PBN) yield relatively unstable spin adducts due to the β-hydrogen (eq 2). Since metal ions are often present in most spin-trapping experiments, such as Fenton reactions[4] and cellular[5] systems, a study of the interaction of metal ions with such nitroxyls would be useful in interpreting spin-trapping results.



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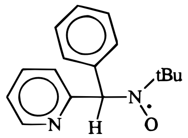
We now report our results on the synthesis, structure, magnetic properties, and EPR of metal (M(II) = Co, Ni, and Mn) hexafluroacetylacetonate (hfac) complexes of the nitroxide *N*-oxy-*N*-*tert*-butyl-(2-pyridyl)phenylmethanamine (2-PyBNO), which bears a β-hydrogen and is therefore similar to those commonly encountered in spin-trapping experiments with PBN.


2-PyBNO

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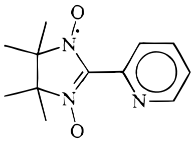
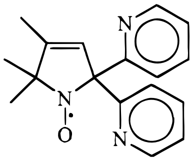
Although previous studies of metal complexes of nitroxyl radicals containing a 2-pyridyl moiety have been reported,[6] the nitroxides are generally in conjugation with a nitronyl group, e.g., M(NIT-2Py)(hfac)$_2$ (where M(II) = Mn and Ni), or have a fully substituted α-carbon, e.g., M(DTPI)$_2$(SbF$_6$)$_2$ (where M(II) = Zn, Fe, Co, and Cu).



NIT-2Py



DTPI

Experimental Section

Measurements. Infrared spectra were recorded on a MIDAC FTIR as KBr pellets. Microanalytical determinations were done by E + R Microanalytical Laboratory Inc. ESR spectra were recorded on a Varian E-4 X-band spectrometer. Spectra were referenced relative to DPPH ($g = 2.0037$).

Materials and Reagents. All metal hexafluoroacetylacetonate, M(hfac)$_2$, complexes were purchased from Aldrich as hydrates and stored over P_2O_5 under vacuum. *N-tert*-Butyl-α-(2-pyridyl) nitrone (2-PyBN) was prepared[7] by oxidation of 2-((*tert*-butylamino)methyl)pyridine with Na_2WO_4 and H_2O_2[8] in 92% yield as a colorless crystalline material. Mp: 67−68 °C. 2-((*tert*-Butylamino)methyl)pyridine was prepared[9] from equimolar amounts of *tert*-butylamine and 2-pyridinecarboxaldehyde in absolute ethanol. Catalytic hydrogenation of the imine with 5% Pd/C yielded a light brown oil, 90%. Bp: 92.5 °C/6 mmHg (lit.[9] bp 75−80 °C/1.2 mmHg). All chemicals used were reagent grade.

Preparation of Metal Nitroxides. *N*-Oxy-*N*-*tert*-butyl-(2-pyridyl)-phenylmethanamine (2-PyPBNO). *N*-Hydroxy-*N*-*tert*-butyl-(2-pyridyl)phenylmethanamine was prepared on the basis of the procedure described by Chang.[10] In a 200-mL, two-neck, round-bottom flask, 1.52 g (8.53 mmol) of *N-tert*-butyl-α-(2-pyridyl)nitrone was stirred in 100 mL of anhydrous ether at 0 °C under N_2, and 6.0 mL (18 mmol) of 3.0 M phenylmagnesium bromide (Aldrich) was added. The solution was refluxed for 1 h after which 50 mL of saturated aqueous of NH_4Cl was added slowly. The ether layer was separated and the aqueous layer washed 3 times with 50 mL of ether. The combined extracts were passed through K_2CO_3 and concentrated in vacuo. Yellow crystals were obtained, 2.00 g (92%). ^{1}H NMR showed no nitrone left and only the hydroxylamine present. Mp: 86−87 °C. ^{1}H NMR (CDCl$_3$): δ 1.07 (s, 9H, *t*-Bu), 5.35 (s, 1H, methine H), pyridyl H's 8.57 (d, 1H, $J = 6.15$ Hz), 7.64 (td, 1H, $J = 1.76$, 7.91, 7.47 Hz), 7.43 (d, 1H, $J = 7.91$ Hz), phenyl H's (with pyridyl H) 7.32−7.17. The nitroxide was prepared by following the procedure described by Rozantsev[11] by stirring 0.10 g (0.39 mmol) of the hydroxylamine in 1 mL of anhydrous ether with freshly prepared Ag_2O (0.18 g, 0.72 mmol) at −5 °C. As soon as the silver mirror covered the wall of the beaker, the solution was stirred for an additional 1 min at room temperature, after which N_2 gas was passed over the solution to evaporate ether. After addition of 10 mL of CH_2Cl_2, filtration gave a yellow filtrate having an EPR spectrum with $g = 2.005$, $a_N = 14.7$ G, and $a_\beta = 2.1$ G. This nitroxide solution was used immediately to complex with M(hfac)$_2$.

General Preparation of Metal−Nitroxide Complexes. M(2-PyPBNO)(hfac)$_2$ complexes (M = Mn, Co, and Ni) were prepared from a suspension of 193 mg (0.100 mol) of M(hfac)$_2$ in 10 mL of CH_2Cl_2 by adding freshly prepared nitroxide solution in one batch with vigorous stirring. The mixture was stirred an additional 5 min and filtered. Evaporation of solvent at room temperature gave crystals which were washed with heptane and dried over Drierite under vacuum with a typical yield of ca. 98%. Crystals suitable for X-ray analysis were obtained by recrystallization from methylene chloride−toluene inside a freezer.

Mn(2-PyPBNO)(hfac)$_2$ (1). The suspension of Mn(hfac)$_2$ turned from yellow to red during mixing with the nitroxide. Dark red crystals were obtained after recrytallization. Mp: 147−150 °C. IR (KBr): 1656 vs, 1603 s, 1554 s, 1527 s, 1501 vs, 1259 vs, 1197 vs, 1148 vs, 796 s, 770 m, 745 m, 700 m, 663 vs, 583 s cm^{-1}. Anal. Calcd for $MnC_{26}H_{21}F_{12}N_2O_5$: C, 43.11; H, 2.92; N, 3.87. Found: C, 43.08; H, 2.70; N, 3.77.

Co(2-PyPBNO)(hfac)$_2$ (2). The orange Co(hfac)$_2$ suspension turned deep green, and dark green crystals were obtained. Mp: 174−176 °C. IR (KBr): 1650 vs, 1604 s, 1554 s, 1527 s, 1501 s, 1259 vs, 1196 vs, 1148 vs, 795 s, 770 m, 746 m, 700 m, 668 vs, 585 vs cm^{-1}. Anal. Calcd for $CoC_{26}H_{21}F_{12}N_2O_5$: C, 42.87; H, 2.91; N, 3.85. Found: C, 43.08; H, 2.85; N, 3.86.

Ni(2-PyPBNO)(hfac)$_2$ (3). The suspension of Ni(hfac)$_2$ turned from cloudy green to dark green upon adding the nitroxide. Green crystals were isolated. Mp: 180−181 °C. IR (KBr): 1654 vs, 1606 m, 1553 s, 1525 s, 1501 s, 1257 vs, 1197 vs, 1148 vs, 794 s, 769 m, 745 m, 700 m, 671 s, 586 s cm^{-1}. Anal. Calcd for $NiC_{26}H_{21}F_{12}N_2O_5$: C, 42.89; H, 2.91; N, 3.85. Found: C, 43.01; H, 2.78; N, 3.76.

Magnetic Measurements. Polycrystalline samples of Mn(2-PyBNO)(hfac)$_2$ and Ni(2-PyBNO)(hfac)$_2$ (22.25 and 24.87 mg, respectively) were used. Magnetic susceptibility data were recorded over 2−300 K temperature range using a Quantum Design MPMS-5S SQUID susceptometer. The temperature-dependent magnetic data were measured at a magnetic field of 1000 G. A correction for the magnetization of the sample holder was applied; correction for the diamagnetism of the constituent atoms was made using Pascal's constants.

X-ray Data Collection. Crystals were mounted on glass fibers and placed in a nitrogen stream at 173(2) K on a Siemens SMART CCD single-crystal diffractometer equipped with Mo anode and graphite monochromator (wavelength = 0.710 73 Å). Further crystallographic data and pertinent experimental parameters are summarized in Table 1 for compounds **1**−**3**. A sphere of data was collected out to an effective 2θ value of 55°, using ω scans. Routine Lorentz and polarization corrections were applied. For **2** and **3** an empirical correction was used for absorption and other systematic error,[12] based on measured intensities of equivalent reflections at different ϕ and ω values. All structures were solved by direct methods. Hydrogen atoms were refined isotropically in observed positions. Full-matrix least-squares refinement was against F^2 over all reflections. Programs used were Siemens SMART, SAINT, and SHELXTL.[13]

Results and Discussion

X-ray Structures. When equimolar amounts of the nitroxide 2-PyBNO and M(hfac)$_2$ were mixed in CH_2Cl_2, crystalline products were formed in quantitative yield. The complexes showed no visible evidence of decomposition in the solid state after 15 months at room temperature in closed vials. X-ray analysis of the crystals revealed neutral, monomeric, isostructural

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Table 1. Crystallographic Data for $M(C_{16}H_{19}N_2O)(C_5HF_6O_2)_2$ Complexes

	compound		
	1	**2**	**3**
chem formula	$MnC_{26}H_{21}F_{12}N_2O_5$	$CoC_{26}H_{21}F_{12}N_2O_5$	$NiC_{26}H_{21}F_{12}N_2O_5$
fw	724.39	728.38	728.16
space group, *Z*	$P\bar{1}$ (No. 2), 2	$P\bar{1}$ (No. 2), 2	$P\bar{1}$ (No. 2), 2
a (Å)	7.996(2)	7.932(4)	7.862(5)
b (Å)	11.601(2)	11.477(6)	11.353(7)
c (Å)	17.105(4)	17.395(8)	17.423(10)
α (°)	91.287(1)	92.780(1)	93.583(1)
β (°)	100.409(1)	101.330(1)	101.120(1)
γ (°)	101.196(1)	101.040(1)	100.154(1)
unit cell vol ($Å^3$)	1528.06(6)	1517.79(13)	1494.6(2)
ρ_{calc} (g cm^{-3})	1.574	1.594	1.618
μ (cm^{-1})	5.43	6.78	7.63
T (°C)	−100	−100	−100
final R^a	$R_1 = 0.057$, $wR_2 = 0.132$	$R_1 = 0.050$, $wR_2 = 0.130$	$R_1 = 0.051$, $wR_2 = 0.124$

[a] $R_1 = \sum|F_o| - |F_c||/\sum|F_o|$ with $I > 2\sigma(I)$ and $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

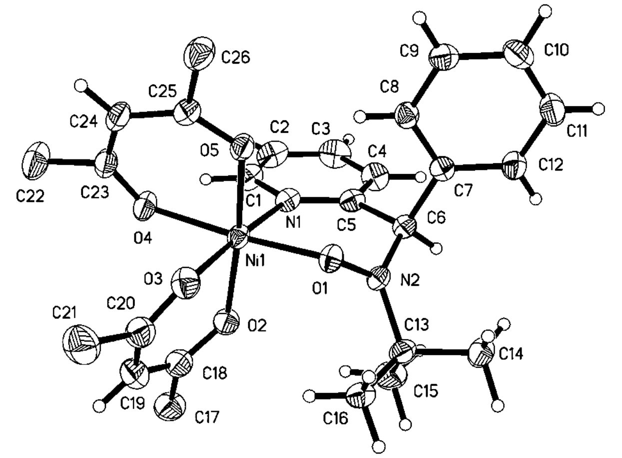

Figure 1. Full view of the $Ni(2\text{-PyBNO})(hfac)_2$ complex **3**. Anisotropic displacement ellipsoids are drawn at 50% probability. Hydrogen atoms are shown as circles of arbitrary radius, and fluorine atoms are omitted for clarity.

Table 2. Bond Distances (Å) and Angles (deg) for 2-PyBNO in Complexes **1**−**3**[a]

atoms	mean	Mn	Co	Ni
O1−N2	1.290[2]	1.292(2)	1.290(2)	1.287(3)
N2−C6	1.463[2]	1.466(3)	1.462(4)	1.462(3)
C6−C5	1.531[2]	1.531(3)	1.534(3)	1.529(3)
C5−N1	1.340[5]	1.336(3)	1.338(3)	1.346(3)
C6−C7	1.524[2]	1.522(3)	1.525(3)	1.525(4)
C7−C8	1.391[2]	1.392(3)	1.389(4)	1.393(4)
C8−C9	1.392[2]	1.394(3)	1.391(4)	1.390(4)
C9−C10	1.384[1]	1.383(4)	1.384(4)	1.384(4)
C10−C11	1.376[4]	1.373(4)	1.374(5)	1.381(5)
C11−C12	1.391[4]	1.388(4)	1.396(4)	1.390(4)
C12−C7	1.393[2]	1.391(3)	1.393(4)	1.395(4)
N1−C1	1.358[4]	1.353(3)	1.360(3)	1.360(3)
C1−C2	1.376[3]	1.377(4)	1.372(4)	1.378(4)
C2−C3	1.380[5]	1.376(4)	1.380(5)	1.385(5)
C3−C4	1.381[4]	1.382(4)	1.384(4)	1.376(4)
C4−C5	1.395[4]	1.390(3)	1.396(4)	1.398(4)
N2−C13	1.497[4]	1.495(3)	1.494(3)	1.501(3)
C13−C14	1.534[2]	1.534(3)	1.533(4)	1.536(4)
C13−C15	1.527[5]	1.532(4)	1.523(4)	1.526(4)
C13−C16	1.522[1]	1.521(4)	1.523(4)	1.523(4)
O1−N2−C13	120.2[1]	120.3(2)	120.2(2)	120.2(2)
C6−N2−O1	116.5[1]	116.4(2)	116.5(2)	116.6(2)
C5−C6−C7	111.2[4]	111.6(2)	111.2(2)	110.8(2)
C6−N2−C13	123.3[1]	123.3(2)	123.3(2)	123.2(2)
C7−C6−N2	112.4[4]	111.9(2)	112.5(2)	112.7(2)
N1−C5−C6	121.5[4]	121.2(2)	121.5(2)	121.9(2)
N2−C6−C5	113.0[2]	112.9(2)	112.8(2)	113.2(2)
N1−C1−C2	123.6[1]	123.6(3)	123.7(3)	123.6(3)
C1−C2−C3	118.7[2]	118.5(3)	118.8(3)	118.7(3)
C2−C3−C4	118.8[1]	118.7(3)	118.9(3)	118.7(3)
C3−C4−C5	119.6[4]	119.7(3)	119.1(3)	119.9(3)
C4−C5−N1	122.2[3]	122.0(2)	122.6(2)	122.0(2)
C5−N1−C1	117.2[2]	117.4(2)	117.0(2)	117.1(2)
C4−C5−C6	116.2[4]	116.7(2)	115.9(2)	116.1(2)
C6−C7−C8	121.2[2]	121.1(2)	121.4(2)	121.2(2)
C7−C8−C9	120.1[1]	120.0(2)	120.2(3)	120.0(3)
C8−C9−C10	120.2[1]	120.0(3)	120.2(3)	120.3(3)
C9−C10−C11	120.1[2]	120.3(2)	120.0(3)	120.0(3)
C10−C11−C12	120.2[1]	120.1(3)	120.3(3)	120.1(3)
C11−C12−C7	120.2[3]	120.4(3)	119.9(3)	120.3(3)
C12−C7−C8	119.3[1]	119.2(2)	119.4(2)	119.3(2)
C12−C7−C6	119.4[2]	119.6(2)	119.2(2)	119.5(2)
N2−C13−C14	107.5[3]	107.8(2)	107.6(2)	107.2(2)
N2−C13−C15	108.4[3]	108.1(2)	108.5(2)	108.7(2)
N2−C13−C16	107.9[2]	108.0(2)	108.0(2)	107.7(2)

[a] Calculated standard deviations of means are in brackets.

$M(hfac)_2(2\text{-PyBNO})$ complexes with M(II) = Mn (**1**), Co (**2**), and Ni (**3**) shown for Ni in Figure 1. The bidentate nitroxide ligand coordinates through the pyridine nitrogen atom and the nitroxyl oxygen forming a six-membered coordination ring. All three complexes exhibit a distorted octahedral geometry. Selected bond distances and angles for 2-PyBNO and the metal coordination spheres for each metal ion are shown in Tables 2 and 3, respectively.

Bond distances and angles are consistent with characterization of the complexes as M(II) nitroxyl adducts.[14] The N−O bond distances for all complexes vary little (all ca. 1.29(2) Å) and do not differ significantly from those of free nitroxides.[15] The O1, N2, C6, and C13 atoms are coplanar with an average angle of 120° around N2, which is consistent with a nitroxyl functionality. The M−O1−N2 bond angles for all complexes (average 118.90(13)°) and the dihedral angles (average 73.6(1)°) between planes of M−O1−N2 and C1−N1−C5 were consistent with those previously observed for nitroxyl complexes that exhibit antiferromagnetic behavior.[14]

Magnetic Properties. The temperature dependence of the molar susceptibility χ and effective magnetic moments μ_B for complexes $Mn(2\text{-PyBNO})(hfac)_2$ (**1**) and $Ni(2\text{-PyBNO})_2$ (**3**) are shown in Figures 2 and 3, respectively. Table 4 shows a summary of all important magnetic parameters for the two complexes. The χ vs *T* plots were fitted over the temperature ranges 20−300 and 1.76−300 K for **1** and **3**, respectively. The functions used were derived from the general isotropic exchange spin Hamiltonian for molecules with two coupled paramagnetic centers,[16] $\hat{H} = -2JS_1 \cdot S_2$. The *g* values and *J* were allowed to

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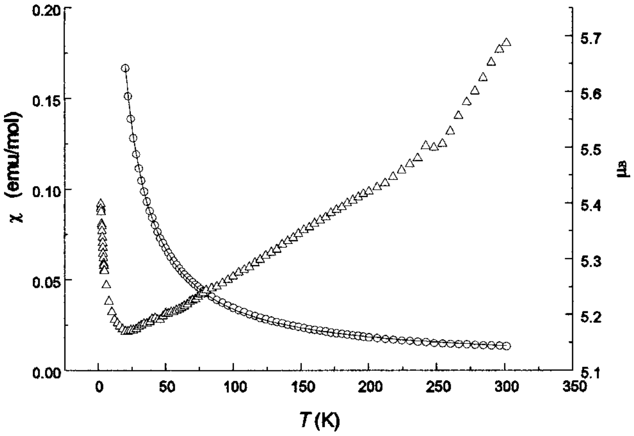

Figure 2. Plots of χ (observed (○); calculated (—)) and μ_B (△) vs T for complex **1**.

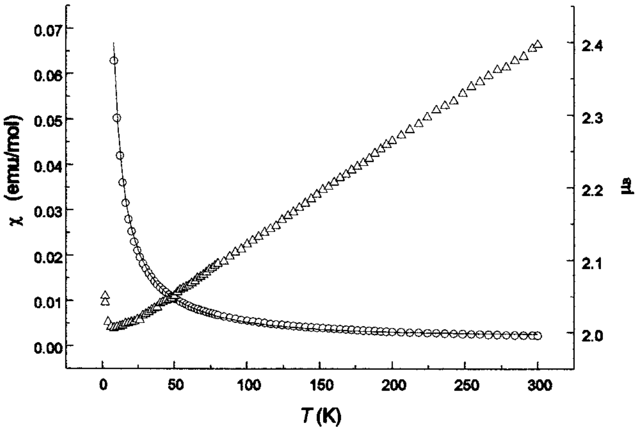

Figure 3. Plots of χ (observed (○); calculated (—)) and μ_B (△) vs T for complex **3**.

Table 3. Bond Distances (Å) and Angles (deg) for Metal Coordination Sphere in 2-PyBNO Complexes

atoms	Mn	Co	Ni
M−O1	2.041(2)	1.973(2)	1.973(2)
M−N1	2.236(2)	2.132(2)	2.082(2)
M−O2	2.155(4)	2.048(2)	2.021(2)
M−O3	2.146(2)	2.060(2)	2.026(2)
M−O4	2.147(2)	2.060(2)	2.045(2)
M−O5	2.149(2)	2.068(2)	2.037(2)
O4−M−O5	82.00(7)	85.99(7)	88.06(7)
O2−M−O3	81.90(7)	87.52(2)	88.91(8)
O1−M−O3	96.09(7)	92.47(8)	90.81(8)
O1−M−O2	104.21(7)	99.76(7)	98.04(8)
O1−M−O5	85.26(6)	85.31(7)	84.73(7)
O1−M−N1	84.66(6)	87.32(8)	88.68(8)
O2−M−N1	85.30(7)	87.32(8)	87.36(8)
N1−M−O5	103.38(7)	100.45(8)	98.16(8)
N1−M−O4	93.15(7)	93.93(8)	94.58(8)
O1−M−O4	166.21(7)	171.28(7)	172.45(7)
O3−M−N1	171.08(7)	174.70(8)	176.13(8)
O5−M−O3	85.53(7)	84.79(8)	85.61(8)
O4−M−O3	88.18(7)	87.20(8)	86.39(8)
O2−M−O4	89.35(5)	88.93(8)	88.93(8)
O5−M−O2	164.96(7)	170.98(7)	173.90(8)
N2−O1−M	117.4(3)	119.9(1)	118.9(1)
C5−N1−M	127.4(2)	127.1(2)	126.6(2)
C18−O2−M	124.2(2)	123.6(2)	122.8(2)
C20−O3−M	123.8(2)	123.1(2)	122.4(2)
C23−O4−M	126.7(2)	124.7(2)	124.0(2)
C25−O5−M1	126.5(2)	124.5(2)	124.0(2)
C1−N1−M1	115.1(2)	115.9(2)	116.3(2)

vary independently and were calculated using the constants $k = 0.695$ cm^{-1}/K and estimated TIP values of 10×10^{-6} and 100×10^{-6} for complexes **1** and **3**, respectively.

Table 4. Magnetic Parameters[a] of M(2-PyBNO)(hfac)$_2$

compd	g	J (cm^{-1})	TIP $\times 10^6$	μ_B (300 K)	μ_B (T)
1	2.118(1)	−57(1)	10	5.687	5.17 (20 K)
3	2.354(2)	−181(15)	100	2.397	2.01 (8 K)

[a] Units for TIP are emu mol^{-1}. χ^2 values for **1** and **3** are 2.48×10^{-7} and 5.34×10^{-7}, respectively.

Both complexes show evidence of antiferromagnetic behavior over the temperature range 10−300 K. The magnetic moments reach a minimum at low temperature with 5.17 μ_B for **1** and 2.00 μ_B for **3**. At 300 K, the magnetic moments increase to 5.69 and 2.40 μ_B for **1** and **3**, respectively. These values fall between the spin-only values for complete spin-pairing in **1** and **3** (4.90 and 1.73 μ_B for $S = 2$ and $S = {}^1/_2$, respectively) and those expected for uncorrelated spins (6.93 and 3.87 μ_B for $S = 3$ and $S = {}^3/_2$, respectively), consistent with thermal population of a mixture of spin states.[17] Increases in μ_B at very low temperature are probably due to small amounts of paramagnetic impurities.

The values of $-J$ found for **1** and **3** of 57(1) and 181(15) cm^{-1} are comparable to those found for NIT-2Py complexes,[6a] $-J = 65(2)$ cm^{-1} for Mn(NIT-2Py)(hfac)$_2$ and $-J = 167(6)$ cm^{-1} for Ni(NIT-2Py)(hfac)$_2$, but smaller than those found for other nonchelating nitroxyls,[1a] $-J = 158-330$ cm^{-1} for Mn−nitroxide complexes and $-J = 300-400$ cm^{-1} for Ni−nitroxide complexes.

EPR Spectra. A weak signal centered at $g = 2.00$ was observed for **1** as a frozen solution (115 K). At room temperature, no signal from Mn was observed, but a small amount of dissociated nitroxide was evident. The EPR spectrum of **3** showed anisotropic signals with rhombic **g**-tensors centered at $g_1 = 2.299$, $g_2 = 2.243$, and $g_3 = 2.193$ as a frozen solution (115 K) and a single isotropic peak at room temperature. Compound **2** was EPR silent.

Conclusion

X-ray analysis of M(2-PyBNO)(hfac)$_2$ complexes revealed distorted octahedral coordination around the metal ion. The bond distances and angles are typical of nitroxyls. Magnetic susceptibility measurements in the solid state (2−300 K) of the Mn and Ni complexes suggest antiferromagnetic coupling between the unpaired electrons of the metal and nitroxide. The extent of coupling in metal complexes of this chelating nitroxyl bearing a β-hydrogen is similar to those of metal complexes of chelating nitronyl nitroxides. Since nitroxyls bearing a β-hydrogen are commonly encountered in spin-trapping experiments such as the use of PBN as a spin trap, this study is not only significant to molecular magnetic researchers but also to spin-trapping experimentalists.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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(16) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

(17) A room-temperature crystal structure of **1** showed no evidence of nitroxyl oxygen disorder as seen in Mn(hfac)$_2$(tempo)$_2$: Dickman, M. H. Submitted for publication.