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^1H and ^{13}C NMR Studies of Electron Spin Delocalization in Nickel(II) Bis(alkyl xanthate) Complexes of Nitrogenous Bases and Comparison with Nickel–Nitroxyl Interactions in Analogous Spin-Labeled Complexes

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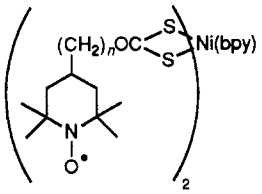
Spin delocalization into the alkyl chains of nickel(II) bis(alkyl xanthate) bipyridyl complexes was measured by ^1H and ^{13}C NMR. The trends in the spin delocalization are consistent with the previously reported observation that nickel–nitroxyl interaction in spin-labeled Ni(II) xanthates decreased rapidly as the number of carbons between the xanthate and nitroxyl rings increased. In a series of alkylamine derivatives of pyridine-2-carboxaldehyde coordinated to nickel bis(ethyl xanthate), the spin delocalization onto the first carbon of the *N*-alkyl group was larger than that for the first carbon of the *N*-alkyl xanthates. This is consistent with the observation of stronger nickel–nitroxyl interaction for a spin-labeled pyridine-2-carboxaldimine than for the spin-labeled xanthates. The ^1H NMR spectrum of a spin-labeled nickel(II) xanthate indicated that the Ni(II) provided an efficient relaxation mechanism for the nitroxyl protons. The contributions to the isotropic shifts of protons in the nitroxyl ring from the Ni(II) and nitroxyl unpaired electrons were approximately additive.

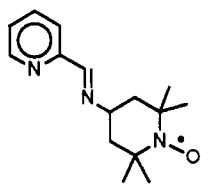
Introduction

Long-range interactions have been recognized with increasing frequency in several fields in recent years. For example, there is a rapidly developing body of work relating to nuclear–nuclear spin–spin splittings, electron–nuclear spin–spin splittings, electronic excited-state energy transfer, and electron transfer. Recent work has demonstrated long-range electron–electron spin–spin splitting.[1] These long-range interactions are inherently interesting for what they reveal about fundamental molecular processes. They also have immediate application to the study of the structure and function of macromolecular systems.

Continuing our interest in long-range electron–electron interaction, a recent study from this laboratory examined the EPR spectra of a series of spin-labeled nickel(II) xanthates, I, with



I



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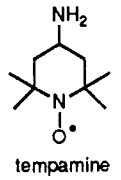

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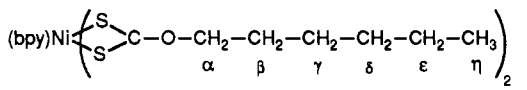
varying numbers of carbons between the nickel(II) and the nitroxyl.[2] The dominant feature in the EPR spectrum of I(n = 0) was broad and shifted 650 G away from g = 2 (to g = 2.5). For I(n = 1) the broad peak was shifted by about 250 G to g = 2.17. These shifted signals indicated substantial mixing of the nickel and nitroxyl wave functions due to electron–electron exchange interaction.[2] For the complexes with larger values of n there was less broadening of the nitroxyl signals and negligible effects on the g values, indicating much smaller exchange interaction through the longer alkyl chains. In Ni(Et-xan)$_2$·II[3] the nickel–nitroxyl exchange interaction was sufficiently strong that the dominant feature in the spectrum was shifted by about 1250 G from g = 2 to g = 3.25.[4] If it is assumed that greater shifts in the EPR spectra reflect a stronger nickel–nitroxyl exchange interaction, the EPR results indicate that the strength of the exchange interaction decreased in the order Ni(Et-xan)$_2$·II > $I(n = 0) > I(n = 1) > I(n \geq 2)$. To determine whether this order is consistent with the magnitude of Ni(II) spin delocalization into the alkyl chains, the present work uses NMR to investigate the electron spin densities on the nuclei of alkyl chains analogous to the bonding pathways in the spin-labeled nickel complexes. ^1H and ^{13}C NMR spectra were examined for a series of nickel(II) bis(alkyl xanthate) bipyridine complexes, Ni(R-xan)$_2$bpy, with varying lengths of the alkyl chain.[3] ^1H and ^{13}C isotropic shifts also were obtained for a series of *N*-alkylpyridine-2-carboxaldimines coordinated to Ni(Et-xan)$_2$.

Table I. Isotropic NMR Shifts for Ni(R-xan)$_2$bpy[a,b]



	^1H					
R	α-CH	β-CH	γ-CH	δ-CH	ε-CH	η-CH
Et	−2.2	2.5				
Pr	∼−2	2.6	1.1			
Bu	∼−2	2.7	0.7	0.2		
Pe	∼−2	2.7	0.7	0.0	0.1	
Hx	∼−2	2.7	0.7	0.0	0.0	0.0
Cyhx[c]	−16	6.4	0.4	0.1		
		0.8	0.1			

	^{13}C					
R	α-CH	β-CH	γ-CH	δ-CH	ε-CH	η-CH
Et	56	52				
Pr	51	48	6.3			
Bu	52	47	5.6	5.4		
Pe	51	47	5.1	4.8	1.1	
Hx	52	44	7.8	5.2	0.8	0.6
Cyhx	42	12	5.7	3.5		

[a] Isotropic shifts (ppm) were defined as chemical shift for Ni(R-xan)$_2$bpy − shift for Ni(R-xan)$_2$. Values were obtained at room temperature in $CDCl_3$. A positive value represents a downfield shift. [b] Isotropic shifts for the bpy protons: 3-H, 50 ± 1; 4-H, 8.4 ± 0.1; 5-H, 38 ± 0.5. [c] Pairs of values for the β- and γ-positions are for axial and equatorial protons.

Experimental Section

Physical Measurements. Visible spectra were recorded on a Beckman Acta V or on a Cary 14 with an OLIS modification. Spectra are reported with wavelengths in nanometers and log ε given in parentheses. IR spectra were obtained in Nujol mulls or in KBr disks on a Perkin-Elmer 283B spectrometer. EPR spectra were obtained on a Varian E-9 instrument interfaced to an IBM CS9000 computer. NMR spectra were recorded on a Chemagnetics A-200 instrument at the University of Denver or on an IBM WP-200SY instrument at Colorado State University. ^{13}C NMR were obtained with proton decoupling, except for a few spectra of diamagnetic compounds, which were recorded to facilitate signal assignments. Concentrations of samples for NMR studies were 10–300 mM in $CDCl_3$ solution. $CDCl_3$ was dried over 3A molecular sieves that had been activated by heating in vacuum for 8 h at 300 °C.

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(1) Eaton, G. R.; Eaton, S. S. *Acc. Chem. Res.* **1988**, *21*, 107.
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(3) Abbreviations used throughout the text: acac, acetylacetonate anion; bpy, 2,2′-bipyridine; R-xan, an alkyl xanthate.
(4) More, K. M.; Eaton, G. R.; Eaton, S. S. To be submitted for publication.

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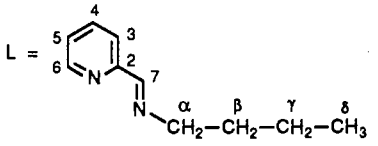
Table II. ^1H and ^{13}C NMR Isotropic Shifts for $Ni(Et\text{-}xan)_2L^{a-c}$



	^1H			
R	α-CH	β-CH	γ-CH	δ-CH
Me	94			
Et	149	~0		
	78			
n-Pr	170	~0	~0	
	79			
i-Pr	102	~0		
n-Bu	170	~0	~0	~0
	80			
t-Bu		~0		

	^{13}C		
R	β-CH	γ-CH	δ-CH
Et	83		
n-Pr	51	3	
i-Pr	37[d]		
n-Bu	48	4	5
t-Bu	123		

[a] Isotropic shifts (ppm) were defined as chemical shift for $Ni(R\text{-}xan)_2bpy$ − shift for $Ni(R\text{-}xan)_2$. Values were obtained at room temperature in $CDCl_3$. A positive value represents a downfield shift. [b] Values listed as ~0 were <1 ppm. [c] Isotropic shifts for ring protons and azomethine proton were as follows: H3, 45 ± 1; H4, 8 ± 0.5; H5, 38 ± 1; H6, 128 ± 2; H7, 250 ± 2 ppm, except that H7 in $Ni(Et\text{-}xan)_2(py\text{-}t\text{-}Bu)$ was 212 ppm. [d] Diastereotopic signals were expected, but only one peak was observed.

TMS was used as the internal standard.

Preparation of Compounds. The potassium salts of the alkyl xanthates were prepared by literature methods[5,6] and characterized by melting point, infrared spectroscopy, and ^1H NMR spectroscopy. I(n = 0)[2] and II[7] were prepared as previously reported.

The nickel bis(alkyl xanthates) were prepared by the method reported for nickel bis(ethyl xanthate).[8,9] $Ni(Et\text{-}d_{10}\text{-}xan)_2$ was prepared analogously from ethanol-d_{10}. The characterization data for the individual complexes are given below. The NMR chemical shift assignments use the designations shown in Tables I and II.

Nickel(II) Bis(ethyl xanthate), $Ni(Et\text{-}xan)_2$. Vis: 418 (3.48), 482 (3.23); lit,[9] 418 (3.49), 482 (3.24). ^1H NMR: 1.46 (6 H, t, CH_3 (β)), 4.37 (4 H, q, CH_2 (α)). ^{13}C NMR: 13.8 (CH_3 (β)), 68.4 (CH_2 (α)), 231.4 (CO).

Nickel(II) Bis(propyl xanthate), $Ni(Pr\text{-}xan)_2$. Vis: 418 (3.69), 479 (3.44). ^1H NMR: 1.02 (6 H, t, CH_3 (γ)), 1.88 (4 H, m, CH_2 (β)), 4.47 (4 H, t, CH_2 (α)). ^{13}C NMR: 10.2 (CH_3 (γ)), 21.6 (CH_2 (β)), 73.9 (CH_2 (α)), 231.2 (CO).

Nickel(II) Bis(butyl xanthate), $Ni(Bu\text{-}xan)_2$. Vis: 418 (3.52), 480 (3.28). ^1H NMR: 0.95 (6 H, t, CH_3 (δ)), 1.45 (4 H, m, CH_2 (γ)), 1.80 (4 H, m, CH_2 (β)), 4.50 (4 H, t, CH_2 (α)). ^{13}C NMR: 13.6 (CH_3 ((δ)), 18.9 (CH_2 (γ)), 30.1 (CH_2 (β)), 72.2 (CH_2 (α)), 231.4 (CO).

Nickel(II) Bis(pentyl xanthate), $Ni(Pe\text{-}xan)_2$. Vis: 416 (3.45), 479 (3.25). ^1H NMR: 0.90 (6 H, t, CH_3 (ε)), 1.39 (8 H, m, CH_2 (γ, δ)), 1.82 (4 H, m, CH_2 (β)), 4.50 (4 H, t, CH_2 (α)). ^{13}C NMR: 13.9 (CH_3 (ε)), 22.2 (CH_2 (δ)), 27.8, (CH_2 (β, γ)), 72.5 (CH_2 (α)), 231.3 (CO).

Nickel(II) Bis(hexyl xanthate), $Ni(Hx\text{-}xan)_2$. Vis: 423 (3.48), 483 (3.19). ^1H NMR: 0.90 (6 H, t, CH_3 (η)), 1.35 (12 H, m, CH_3 (γ, δ, ε)), 1.81 (4 H, m, CH_2 (β)), 4.46 (4 H, t, CH_2 (α)). ^{13}C NMR: 14.0 (CH_3 (η)), 22.5 (CH_2 (ε)), 25.3 (CH_2 (δ)), 28.1 (CH_2 (γ)), 31.3 (CH_2 (β)), 72.6 (CH_2 (α)), 231.3 (CO).

Nickel(II) Bis(cyclohexyl xanthate), $Ni(Cyhx\text{-}xan)_2$. Vis: 417 (3.49), 478 (3.48). ^1H NMR: 1.37 (4 H, m, CH_2 (δ)), 1.76 (8 H, m, CH_2 (γ)), 1.96 (8 H, m, CH_2 (β), 5.16 (2 H, CH (α)). ^{13}C NMR: 23.3 (CH_2 (γ)), 24.9 (CH_2 (δ)), 31.1 (CH_2 (β)), 82.6 (CH (α)), 230.2 (CO).

2-(Iminomethyl)pyridine, py-Me. First, 50 mL of 40% methylamine in water was extracted with four 25-mL portions of benzene. The resulting benzene solution was dried for 12 h over activated 3A molecular sieves. The dry benzene solution was added to pyridine-2-carboxaldehyde (0.030 mol). The solution was stirred for 7 h. The solvent was removed on a rotary evaporator and the residue was distilled at 36–38 °C/0.5 mmHg. ^1H NMR: 3.50 (3 H, s, CH_3 (α)), 7.23 (1 H, m, H5), 7.66 (1 H, m, H4), 7.77 (1 H, d, H3), 8.29 (1 H, s, H7), 8.56 (1 H, d, H6). ^{13}C NMR: 47.1 (CH_3), 120.0 (C3), 123.6 (C5), 135.5 (C4), 148.4 (C6), 153.5 (C2), 162.4 (C7).

2-(Iminoethyl)pyridine, py-Et. Ethylamine gas was bubbled slowly into a solution of pyridine-2-carboxaldehyde (0.021 mol) in 25 mL of absolute ethanol for 3 h. The resulting solution was stirred for 3 h. The solvent was removed on a rotary evaporator and the product was isolated by distillation at 38–44 °C/10 mmHg. ^1H NMR: 1.33 (3 H, t, CH_3 (β)), 3.71 (2 H, q, CH_2 (α)), 7.29 (1 H, m, H5), 7.72 (1 H, m, H4), 7.99 (1 H, d, H3), 8.39 (1 H, s, H7), 8.64 (1 H, d, H6). ^{13}C NMR: 16.0 (CH_3 (β)), 55.7 (CH_2 (α)), 121.1 (C3), 124.6 (C5), 136.6 (C4), 149.5 (C6), 154.9 (C2), 161.4 (C7).

Four of the pyridine imine derivatives were prepared by the following general procedure. To a solution of pyridine-2-carboxaldehyde (0.021 mol) in absolute ethanol was added, with stirring, 0.022 mol of alkylamine. The reaction was monitored by following the disappearance of the C=O stretch at 1715 cm^{-1}. The mixtures typically were stirred for 24 h. The solvent was removed on a rotary evaporator. The resulting oil was fractionally distilled. The characterization data for the products are given below.

2-(Imino-*n*-propyl)pyridine, py-*n*-Pr. Distilled at 80 °C/10 mmHg. ^1H NMR: 0.97 (3 H, t, CH_3 (γ)), 1.76 (2 H, m, CH_2 (β)), 3.65 (2 H, t, CH_2 (α)), 7.31 (1 H, m, H5), 7.74 (1 H, m, H4), 7.99 (1 H, d, H3), 8.38 (1 H, s, H7), 8.65 (1 H, d, H6). ^{13}C NMR: 11.8 (CH_3 (γ), 23.9 (CH_2 (β)), 63.3 (CH_2 (α)), 121.2 (C3), 124.6 (C5), 136.5 (C4), 149.4 (C6), 154.7 (C2), 161.7 (C7).

2-(Iminoisopropyl)pyridine, py-*i*-Pr. Distilled at 93–94 °C/18 mmHg. ^1H NMR: 1.23 (6 H, d, CH_3 (β)), 3.56 (1 H, m, CH (α)), 7.18 (1 H, m, H5), 7.61 (1 H, m, H4), 8.10 (1 H, d, H3), 8.47 (1 H, s, H7), 8.66 (1 H, d, H6). ^{13}C NMR: 24.0 (CH_3 (β)), 61.5 (CH (α)), 121.4 (C3), 124.6 (C5), 136.5 (C4), 149.4 (C6), 154.8 (C2), 159.2 (C7).

2-(Imino-*n*-butyl)pyridine, py-*n*-Bu. Distilled at 95–110 °C/10 mmHg. ^1H NMR: 0.94 (3 H, t, CH_3 (δ)), 1.39 (2 H, m, CH_2 (γ)), 1.72 (2 H, m, CH_2 (β)), 3.68 (2 H, t, CH_2 (α)), 7.30 (1 H, m, H5), 7.73 (1 H, m, H4), 7.98 (1 H, d, H3), 8.38 (1 H, s, H7), 8.65 (1 H, d, H6). ^{13}C NMR: 13.8 (CH_3 (δ)), 20.4 (CH_2 (γ)), 32.8 (CH_2 (β)), 61.2 (CH_2 (α)), 121.1 (C3), 124.5 (C5), 136.5 (C4), 149.4 (C6), 154.7 (C2), 161.7 (C7).

2-(Imino-*tert*-butyl)pyridine, py-*t*-Bu. Distilled at 102 °C/12 mmHg. ^1H NMR: 1.30 (9 H, s, CH_3), 7.29 (1 H, m, H5), 7.73 (1 H, m, H4), 8.03 (1 H, d, H3), 8.37 (1 H, s, H7), 8.64 (1 H, d, H6). ^{13}C NMR: 29.6 (CH_3), 57.7 (C (α)), 120.7 (C3), 124.1 (C5), 136.2 (C4), 149.0 (C6), 155.2 (C2), 156.1 (C7).

Assignment of NMR Spectra. The NMR spectra of diamagnetic $Ni(R\text{-}xan)_2$ and py-R were assigned on the basis of proton couplings and integrations (for the ^1H NMR) and by analogy with the assignments for aliphatic alcohols and 2,2′-bipyridine.[10,11] Peaks at 16.1, 45.7, and 59.7 ppm were present in the ^1H NMR spectra of $Ni(R\text{-}xan)_2bpy$, independent of R, and were assigned to the bpy protons by analogy with the reported shifts for $Ni(bpy)_3^{2+}$.[10,11] The assignments of the signals from the alkyl protons were based on three criteria: decreasing line widths for protons further from the Ni(II), integrations, and consistency within the set of substituents. The proton line widths were of the following orders: α, 100 Hz; β, 30 Hz; γ, 25 Hz. The 200 ppm window that was used for the ^{13}C spectra of $Ni(R\text{-}xan)_2bpy$ did not include the signals for the bpy carbons or the carbon in the xanthate ring. The assignments for the alkyl carbons were based on line widths and consistency within the series of substituents. The carbon line widths were of the following orders: α, 150 Hz; β, 25 Hz; γ, 15 Hz. In the ^1H NMR spectra of $Ni(Et\text{-}xan)_2L$, L = py-R, the peaks that were present independent of R were assigned to the pyridine ring protons, the azomethine proton, H7, and the ethyl groups on the xanthate. To facilitate the assignment of the resonances from the R groups, ^1H NMR spectra were obtained for $Ni(Et\text{-}d_{10}\text{-}xan)_2L$, L = py-R, in which the ethyl xanthate group was deuterated. The resonances from the R group were assigned on the basis of integrations and consistency within the series. The signals for the β- and γ-protons were broad although the isotropic shifts were small. In the ^{13}C NMR of $Ni(et\text{-}xan)_2L$, L = py-R, the signal from the α-carbon of the ligand was not observed within ±200 ppm of TMS. The signals for the other carbons were assigned on the basis of line widths and consistency within the series.

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Results and Discussion

2,2'-Bipyridine binds to diamagnetic four-coordinate Ni(R-xan)$_2$ to form paramagnetic six-coordinate Ni(R-xan)$_2$bpy. The equilibrium constants for formation of these complexes are on the order of 10^5,[12] and the rate of exchange between free and coordinated bpy is slow on the NMR time scale. In 1:1 mixtures of Ni(R-xan)$_2$ and bpy at millimolar concentrations, almost all of the Ni(II) is in the six-coordinate form.

Contributions to the Isotropic Shifts. The ^{1}H and ^{13}C isotropic shifts for the paramagnetic nickel complexes are summarized in Tables I and II. The diamagnetic four-coordinate Ni(II) complexes and the diamagnetic ligands were used as the reference compounds in the calculation of the isotropic shifts.

To relate the isotropic shifts to electron spin delocalization, it is necessary to determine the relative importance of the contact and dipolar contributions. Kurland and McGarvey pointed out that zero-field splitting (ZFS) could cause dipolar contributions to the isotropic shifts even for nuclei with nearly isotropic g values.[13] For S = 1 a zero-field splitting of 26 cm^{-1} is required to give a dipolar shift of 1 ppm for a proton at 5 Å from the paramagnetic center. Since ZFS for Ni(II) is typically smaller than this, they concluded that dipolar contributions were unlikely to be significant for Ni(II). Although it is generally argued that the dipolar contributions are negligible for 6-coordinate Ni(II),[14] it is important to check that assumption for particular molecules.

The contact term varies as T^{-1} and the dipolar term varies as T^{-2}, which suggests that the temperature dependence of the isotropic shifts can be used to estimate the importance of the dipolar contribution.[13] It has been noted that the T^{-2}-dependent contribution to the isotropic shifts may not be due to dipolar interaction.[15,16] Perry and Drago pointed out that deviation from simple T^{-1} behavior could arise from temperature-dependent interaction with a hydrogen-bonding solvent and recommended against the use of $CDCl_3$.[17] Due to the limited solubilities of these complexes, it was not possible to use an alternate solvent. Variable-temperature ^{1}H NMR spectra of Ni(R-xan)$_2$bpy were recorded between −30 and +50 °C. Three methods of analyzing the data indicated that the contribution to the isotropic shifts with T^{-2} dependence was detectable.[13,17] (1) In plots of the isotropic shift ($\Delta\nu$) vs T^{-1} the intercept at infinite temperature was nonzero. (2) Plots of $T\Delta\nu$ vs T^{-1} were sloped. (3) Least-squares fits of the data to the equation $\Delta\nu = A/T + B/T^2$ gave nonzero values of B. The magnitudes of A and B in the fit of the data to $A/T + B/T^2$ showed that the T^{-2} term contributed less than about 10% of the total shifts for the α- and β-protons at room temperature. Since the T^{-2} contribution is so small, the ^{1}H isotropic shifts were considered to be reasonable estimates of the extent of electron spin delocalization into the alkyl chains.

Bipyridine Proton Shifts. The similarity between the ^{1}H isotropic shifts for the bipyridine ring protons in Ni(R-xan)$_2$bpy (Table I) and the values reported for Ni(bpy)$_3^{2+}$ [10,11] suggests that the extent of electron spin delocalization into the aromatic ring is relatively insensitive to the nature of the other ligands bound to the nickel.

Alkyl Groups on Xanthate Rings. The large ratios of the ^{13}C isotropic shifts to the ^{1}H shifts for Ni(R-xan)$_2$bpy (Table I) are consistent with the argument above that the isotropic shifts in these complexes are dominated by the contact interaction.[18] The opposite signs for the shifts of the α-carbon and the protons attached to it and the difference in sign of the ^{1}H shifts for the α-proton than for the other protons in the alkyl chain indicate a contribution to the proton shift at the α-position[18] due to spin polarization by π spin density in the delocalized xanthate ring. Opposite signs of the isotropic shifts for the α- and β-positions of alkyl groups attached to delocalized rings have also been observed and attributed to spin polarization in alkoxy radicals,[19] iron(III) dithiocarbamates,[18,20,21] manganese(III) dithiocarbamates[22] and copper butyrate dimer.[23] The large difference in the isotropic shifts for the α proton in Ni(R-xan)$_2$bpy, R = Cyhx vs. linear alkyl, is consistent with the strong conformational dependence of the interaction with the spin density in the xanthate ring.[19] Another important feature of the isotropic shifts for these complexes is that the attenuation down the chain is approximately pairwise with comparable magnitudes of the shifts at the α- and β-positions and much smaller but similar shifts for the γ- and δ-positions. The nonuniform attenuation suggests the possibility that the contributions from σ delocalization and spin polarization tend to alternately reinforce and partially cancel along the chain.[24]

Alkyl Groups on a Coordinated Nitrogen. Large downfield ^{1}H isotropic shifts were observed for the protons on the α-carbon of the R groups in Ni(Et-xan)$_2$(py-R) (Table II). The difference in the shifts for diastereotopic α-protons and the variations as a function of R confirmed the importance of conformation in determining the magnitude of the spin delocalization. The importance of conformation in determining the magnitude of the isotropic shifts has been emphasized for cyclic amines coordinated to Ni(acac)$_2$.[25-27] The isotropic shifts for protons in the alkyl groups further from the coordinated nitrogen were negligible (Table II). The attenuation of the proton isotropic shifts in these complexes is more rapid than was observed for alkyl amines or cyclic amines coordinated to Ni(acac)$_2$,[25-27] although rapid attenuation was observed for the N-alkyl groups in Ni(N-R-salicylaldimine)$_2$[28] and Ni(N-R-aminotroponiminate)$_2$.[29] The signals from the α carbons were not detected within ±200 ppm of TMS. Large downfield shifts were observed for the β-carbons and much smaller, but significant, shifts were observed for the γ- and δ-carbons. Detectable ^{13}C isotropic shifts have also been observed for the γ- and δ-carbons of alkylamines coordinated to Ni(acac)$_2$.[25] The ^{1}H and ^{13}C shifts for Ni(acac)$_2$(RNH$_2$) were interpreted in terms of predominantly σ delocalization with some contribution of spin polarization at the α-carbon.[25]

Comparison of NMR Isotropic Shifts with EPR Data. The electron–electron spin–spin interaction in spin-labeled nickel complexes is expected to depend on the magnitude of the overlap of the orbitals containing the two unpaired electrons. Thus, if the nitroxyl portion of the molecule is kept constant, increasing the nickel unpaired electron spin density at the point of attachment of the nitroxyl is expected to increase the electron-electron spin-spin interaction. The data in Tables I and II and the discussion above support the conclusion that the spin density on the α-carbon of the R group in Ni(Et-xan)$_2$(py-R) is greater than the spin density on the α-carbon of the R group in Ni(R-xan)$_2$bpy. This result is in good agreement with the observation that the peak in the EPR spectrum of spin-labeled nickel complex of II is shifted

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Table III. Additivity of ^1H Isotropic Shifts

	CH		
Nitroxyl Radicals[a]	4	3	2
tempamine	+6.0	−19.5	−30
		−31.5	−3
Ni(Et-xan)$_2$·II	+5.0	−24	−34
		−40	+2

	CH			
Ni(II)[b]	α	β	γ	δ
Ni(Cyhx-xan)$_2$bpy	−16	6.4	0.4	0.1
		0.8	0.1	
I(n = 0)	−17	6		~0
		1		

[a] Isotropic shifts (in ppm) defined as shift for nitroxyl containing species − shift for reduced secondary amine analogue. [b] Isotropic shifts (in ppm) defined as shift for 6-coordinate bpy complex − shift for 4-coordinate complex without bpy.

further from the position expected for non-interacting nitroxyl than the peak in I(n = 0 or 1).

The data in Table I suggest that the spin densities on the α- and β-carbons of Ni(R-xan)$_2$bpy are similar. Why then is the electron–electron interaction greater for I with n = 0 than with n = 1? Electron–nuclear coupling constants in piperidinyl nitroxyl radicals indicate significant electron spin delocalization at the 3- and 4-positions of the ring.[30] In $I(n = 0)$, the α- and β-positions with respect to delocalization of the nickel unpaired electron are the 4- and 3-positions, respectively, of the nitroxyl ring so a substantial nickel–nitroxyl interaction is expected to result from overlap of the wave functions for the two unpaired electrons at these positions. In I(n = 1), the α-carbon with respect to delocalization of the nickel unpaired electron is outside of the nitroxyl ring and only the β-position provides overlap with the nitroxyl ring. For I($n \geq 2$), neither the α- nor the β-carbons are in the nitroxyl ring so electron-electron interaction is expected to be much less than for smaller values of n. Thus, the NMR measures of electron spin delocalization are consistent with the interpretation of the EPR spectra indicating that nickel–nitroxyl interaction decreases in the order Ni(Et-xan)$_2$·II > I(n = 0) > I(n = 1) ≫ I($n \geq 2$).

Additivity of Nickel and Nitroxyl Isotropic Shifts. Implicit in the discussion above is the aassumption that the nickel and nitroxyl isotropic shifts were additive—i.e., the isotropic shift in a nickel–nitroxyl complex is the sum of the contributions from the nickel and the nitroxyl wave functions. Additivity has been observed in the ^1H NMR isotropic shifts of diradicals.[31] To determine whether this occurs for nickel–nitroxyl complexes, comparisons were made for the nitroxyl isotropic shifts in the presence and absence of Ni(II) and for the Ni(II) isotropic shifts in the presence and absence of a nitroxyl.

The electron spin relaxation rates of nitroxyl radicals are too slow to obtain well-resolved NMR spectra in dilute solution. High concentrations (several molar) or paramagnetic solvents are used such that collisions cause increased relaxation rates and improved resolution of the NMR spectra.[19] Due to the intramolecular effect of the Ni(II) on the nitroxyl relaxation times, the resolution of the NMR spectra of I(n = 0), and Ni(Et-xan)$_2$·II at 0.1 M was as good as is usually obtained for nitroxyls at 1.0 M. Molin and co-workers have previously shown that complexes of nitroxyl radicals with paramagnetic metals could be used to obtain NMR spectra.[32,33] The nickel–nitroxyl distances in I(n = 0) and Ni(Et-xan)$_2$·II are substantially longer than the metal–nitroxyl distances in the complexes reported in ref 32 and 33, which suggests that intramolecular nickel–nitroxyl interaction that effects the narrowing of the NMR signals acts over a longer distance than had been revealed by the earlier work.

The ^1H isotropic shifts due to the nitroxyl unpaired electron in the presence and absence of Ni(II) are compared in Table III. For tempamine and Ni(Et-xan)$_2$·II the "diamagnetic" reference was the analogous compound with the nitroxyl reduced to the secondary amine. The isotropic shifts obtained for tempamine are in good agreement with the literature.[34] Due to the broad lines for the protons at the 2- and 3-positions of the nitroxyl ring, the uncertainty in these isotropic shifts is about ±5 ppm. The uncertainty for the 4-position is about ±2 ppm. An additional source of uncertainty in the comparison is that the conformation of the nitroxyl ring may be different for tempamine than for the coordinated nitroxyl. The large differences between the isotropic shifts for the axial and equatorial protons indicates strong dependence of the shifts on conformation so changes in ring conformations would be expected to impact the isotropic shifts. In spite of the uncertainties, there is substantial similarity in the values of the isotropic shifts for the two systems, indicating that the nitroxyl contributions to the isotropic shifts are independent of the presence of Ni(II). The isotropic shift at the 4-position of the nitroxyl ring is particularly significant since there is substantial delocalization of the nickel unpaired electron at this position.

The isotropic shifts for Ni(II) in the presence and absence of a nitroxyl also are compared in Table III. In these cases, the "diamagnetic" reference was the four-coordinate nickel complex prior to addition of bpy. The large shifts at the α-carbon were the same within experimental uncertainty in the two cases, which indicates additivity of the isotropic shifts.

Conclusions

Three conclusions emerge from this work. (1) The electron spin delocalization indicated by NMR electron–nuclear coupling constants is in qualitative agreement with the magnitude of electron–electron spin–spin interaction observed in the EPR spectra of I and Ni(Et-xan)$_2$·II. (2) Intramolecular nickel–nitroxyl interaction even over relatively long distances facilitates the observation of NMR spectra of nitroxyl radicals. (3) The isotropic shifts for nickel(II) and nitroxyl radicals are approximately additive in the complexes reported in this paper.

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Registry No. I (n = 0), 123540-98-7; Ni(et-xan)$_2$·II, 123540-97-6; py-Me, 7032-20-4; py-Et, 7032-21-5; py-n-Pr, 4206-52-4; py-i-Pr, 7032-23-7; py-n-Bu, 7032-24-8; py-t-Bu, 21478-42-2; Ni(Et-xan)$_2$, 3269-24-7; Ni(Pr-xan)$_2$, 52139-57-8; Ni(Bu-xan)$_2$, 52139-58-9; Ni(Pe-xan)$_2$, 61160-30-3; Ni(Hx-xan)$_2$, 53566-79-3; Ni(Cyhx-xan)$_2$, 53566-81-7; PrNH$_2$, 107-10-8; i-PrNH$_2$, 75-31-0; n-BuNH$_2$, 109-73-9; t-BuNH$_2$, 75-64-9; Ni(Et-xan)$_2$bpy, 29827-24-5; Ni(Pr-xan)$_2$bpy, 71597-04-1; Ni(Bu-xan)$_2$bpy, 71582-41-7; Ni(Pe-xan)$_2$bpy, 87635-53-8; Ni(Hx-xan)$_2$bpy, 123540-90-9; Ni(Cyhx-xan)$_2$bpy, 71582-44-0; Ni(Et-xan)$_2$L (R = Me), 123540-91-0; Ni(Et-xan)$_2$L (R = Et), 123540-92-1; Ni(Et-xan)$_2$L (R = n-Pr), 123540-93-2; Ni(Et-xan)$_2$L (R = i-Pr), 123540-94-3; Ni(Et-xan)$_2$L (R = n-Bu), 123540-95-4; Ni(Et-xan)$_2$L (R = t-Bu), 123540-96-5; methylamine, 74-89-5; pyridine-2-carboxaldehyde, 1121-60-4; ethylamine, 75-04-7; tempamine, 14691-88-4.

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