appears that the room-temperature-solution EPR data are reasonably interpreted as a measure of exchange interactions. The values of J measured from frozen-solution spectra did not correspond to linear extrapolation of fluid-solution data, but there is no reason to expect them to correspond to the extrapolation, although the values are similar. Interpretation of the frozen-solution EPR splitting as pure dipolar interactions permits calculation of a copper–nitroxyl distance using the simple point–dipole formula for nonequivalent spins[25,26] $r = (2g\beta/|2D|)^{1/3}$, where $|2D|$ denotes the observed splitting. If the observed splittings in the frozen-solution spectra of $\text{Cu(hfac)}_2\cdot\text{I}$ and $\text{Cu(hfac)}_2\cdot\text{II}$ were assumed to be purely dipolar, then the calculated copper–nitroxyl distances would be 8.1 and 6.3 Å, respectively. However, using CPK molecular models and assuming various molecular conformations which seemed reasonably strain free, we estimated copper–nitroxyl distances of 12 and 10 Å, respectively. At these distances the calculated dipolar couplings would be 22 and 37 G, respectively. Although the calculated numbers are very approximate, they are probably reasonable estimates for the upper limits on the dipolar contribution to the coupling. Even if the molecules were to adopt rather different conformations, it appears unlikely that the dipolar contributions could be greater than half the observed splittings.[27] Consequently considerable caution must be exercised in attributing all splittings in frozen solution to dipolar coupling and in assuming that the splitting can be used to calculate metal–nitroxyl distances in rigid-media spectra.

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Registry No. I, 64013-19-0; II, 72442-95-6; III, 72453-28-2; IV, 72442-96-7; V, 72442-97-8; VI, 72442-98-9; VII, 64071-78-9; VIII, 72057-28-4; IX, 72442-72-9; X, 72442-73-0; XI, 72442-74-1; XII, 72442-75-2; $\text{Cu(hfac)}_2\cdot$XIV, 72442-76-3; $\text{Cu(hfac)}_2\cdot$XV, 72442-77-4; $\text{Cu(hfac)}_2\text{(py)}_2$, 38496-50-3; Cu(hfac)_2(DTBN), 35164-63-7; Cu(hfac)_2, 14781-45-4; 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy, 14691-88-4; pyridine-4-carboxaldehyde, 872-85-5; pyridine-3-carboxaldehyde, 500-22-1; pyridine-2-carboxaldehyde, 1121-60-4; $\text{Cu(hfac)}_2\cdot$XIII, 72442-78-5.

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Metal–Nitroxyl Interactions. 17. Spin-Labeled Adducts of Bis(hexafluoroacetylacetonato)copper(II)

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Spin-labeled ligands have been prepared by condensing pyridine-4-carboxaldehyde, pyridine-3-carboxaldehyde, and pyridine-2-carboxaldehyde with 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy and by condensing pyridine-4-carboxaldehyde with 3-aminomethyl-2,2,5,5-tetramethylpyrrolidinyl-1-oxy. The equilibrium constants have been obtained for the coordination of these ligands to bis(hexafluoroacetylacetonato)copper(II) in CCl_4 at 20 °C. The EPR spectra of the 1:1 complexes exhibit electron–electron coupling in CCl_4 at room temperature with values of the coupling constant ranging from ca. 30 to >2000 G.

Introduction

The utility of the spin-label and spin-probe techniques in the study of biological systems has generated substantial interest in the interactions which may occur if a metal ion is present in the spin-labeled system.[1] We have demonstrated that in a variety of copper complexes with ligands which contain nitroxyl radicals, electron spin–electron spin coupling is observed in the room-temperature solution EPR spectra.[2-5] Values of the coupling constant, J, ranging from 4.8[4] to >2650 G[2] have been found. We have recently reported equilibria and EPR studies of the interaction of the homologous series of spin-labeled pyridines (I–III) with Cu(hfac)_2.[5,6] Values of J from 37.0 to >1000 G were observed. In order to elucidate the effect of the nitroxyl ring size on J, we now report analogous studies with the spin-labeled pyridines IV–VI. To explore the effect of the linkage between the pyridine and nitroxyl rings, we examined ligand VII.

Experimental Section

Physical Measurements. Infrared spectra were obtained in halocarbon and Nujol mulls on a Perkin-Elmer 337 grating spectrometer. Magnetic susceptibilities were measured on a Bruker Faraday balance with 1-μg sensitivity using HgCo(SCN)_4 as calibrant.[7] Values of μ_{eff} in Bohr magnetons (μ_β) are reported below with the temperature at which the measurement was made and the diamagnetic correction (χ^{dia})[8] used in the calculation given in parentheses. The cgs emu units

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(6) The following abbreviations are used throughout the text: Cu(hfac)_2, bis(hexafluoroacetylacetonato)copper(II); NO, a nitroxyl group; py, pyridine; py⁓NO, a ligand which contains both a pyridine and a nitroxyl group; Cu(hfac)_2(NO), Cu(hfac)_2 bonded to a nitroxyl oxygen; Cu(hfac)_2(py⁓NO), Cu(hfac)_2 bonded to the pyridine end of py⁓NO; Cu(hfac)_2(NO⁓py), Cu(hfac)_2 bonded to the nitroxyl group of py⁓NO; Cu(hfac)_2(py⁓NO)Cu(hfac)_2, a dimer with one Cu(hfac)_2 bonded to the pyridine end and one Cu(hfac)_2 bonded to the nitroxyl end of py⁓NO; ϵ, molar extinction coefficient at 775 nm; ϵ_{Cu}, ϵ for Cu(hfac)_2; ϵ_{py}, ϵ for Cu(hfac)_2py or Cu(hfac)_2(py⁓NO); $\epsilon_{(\text{py})_2}$, ϵ for $\text{Cu(hfac)}_2\text{(py)}_2$ or Cu(hfac)_2(py⁓NO)$_2$; ϵ_{NO}, ϵ for Cu(hfac)_2(NO) or Cu(hfac)_2(NO⁓py).

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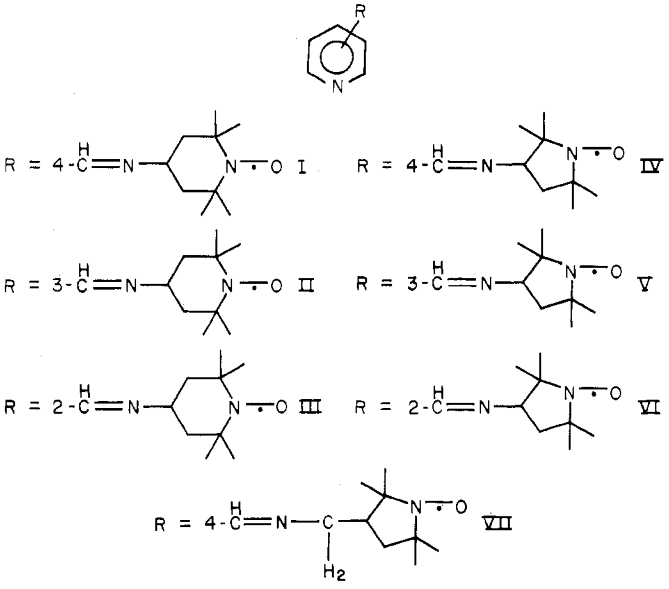

are used for all the susceptibilities. A value of 60×10^{-6} was assumed for the temperature-independent paramagnetism of copper.[2] Electronic spectra were recorded on a Beckman Acta V spectrometer with digital readout. The sample compartment was thermostated at 20 °C. $Cu(hfac)_2$ and the ligands were sublimed under vacuum before use for spectral studies. CCl_4 and toluene were dried over CaH_2 and distilled under nitrogen. Solutions were prepared in a Kewaunee glovebox. For minimum dissociation and interference from remaining traces of water, concentrations of 5.0×10^{-3}–1.0×10^{-2} M were used for the visible and EPR spectra. Although the dissociation was greater at lower concentrations, the EPR line shape for the spin-coupled species remained the same. Thus intermolecular contributions to the line shape were negligible. EPR spectra in CCl_4 and toluene solutions were obtained on a Varian E-9 spectrometer as previously described.[2] g values were measured relative to DPPH. All coupling constants are given in gauss except in Table II where values are also given in cm^{-1}.

Preparation of Compounds. All starting materials were commercially available and were used as received unless specified otherwise. $Cu(hfac)_2$ was prepared by the literature methods.[9]

3-Aminomethyl-2,2,5,5-tetramethylpyrrolidinyl-1-oxy (VIII). The previously reported preparation of this nitroxyl[10] was modified by analogy with the procedure reported for the corresponding pyrrolidine derivative.[11] A 1.5-g sample (8.1×10^{-3} mol) of 3-carboxamide-2,2,5,5-tetramethylpyrrolidinyl-1-oxy in 50 mL of anhydrous ether was added dropwise to an ice-cold slurry of $LiAlH_4$ (0.30 g, 3.5×10^{-2} mol) in 50 mL of anhydrous ether. After the addition was complete, the mixture was warmed to room temperature and refluxed gently for 24 h. After addition of a few drops of water, the mixture was filtered. The ether solution was dried over Na_2SO_4. Removal of the ether under vacuum yielded a yellow liquid and solid unreacted amide. The solid was removed by filtration, and the yellow solution was vacuum distilled at 55 °C (0.1 mm, short path). The distillate solidified to a pale yellow solid on standing.

The following procedure is typical of the method used to prepare the ligands. Purification and characterization data are given below for the remaining ligands.

4-[(2,2,5,5-Tetramethyl-3-pyrrolidinyl-1-oxy)iminomethyl]pyridine (IV). To a solution of 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy (0.50 g, 3.2×10^{-3} mol) in 15 mL of absolute ethanol was added 0.34 g (3.2×10^{-3} mol) of pyridine-4-carboxaldehyde. After the solution refluxed for 2 h, the solvent was removed under reduced pressure, yielding a yellow solid. The compound was recrystallized from hexane, giving yellow needles: yield 0.66 g (85%); mp 94.5–95.5 °C; IR $\nu_{C=N}$ 1640 cm^{-1}; EPR (CCl_4) $g = 2.0059$, $A_N = 14.1$ G; $\mu_{eff} = 1.68$ μ_B (24.5 °C, $\chi^{dia} = -142.7 \times 10^{-6}$). Anal. Calcd for $C_{14}H_{20}N_3O$: C, 68.26; H, 8.18; N, 17.06. Found: C, 68.36; H, 7.91; N, 16.90.

3-[(2,2,5,5-Tetramethyl-3-pyrrolidinyl-1-oxy)iminomethyl]pyridine (V): recrystallized from hexane; yield 73%; mp 100–101.5 °C; IR $\nu_{C=N}$ 1645 cm^{-1}; EPR (CCl_4) $g = 2.0059$, $A_N = 14.1$ G; $\mu_{eff} = 1.69$ μ_B (23 °C, $\chi^{dia} = -142.7 \times 10^{-6}$). Anal. Calcd for $C_{14}H_{20}N_3O$: C, 68.26; H, 8.18; N, 17.06. Found: C, 68.34; H, 8.05; N, 17.04.

2-[(2,2,5,5-Tetramethyl-3-pyrrolidinyl-1-oxy)iminomethyl]pyridine (VI): recrystallized from hexane; yield 73%; mp 57.5–59.5 °C; IR $\nu_{C=N}$ 1645 cm^{-1}; EPR (CCl_4) $g = 2.0059$, $A_N = 14.1$ G; $\mu_{eff} = 1.66$ μ_B (24.5 °C, $\chi^{dia} = -142.7 \times 10^{-6}$). Anal. Calcd for $C_{14}H_{20}N_3O$: C, 68.26; H, 8.18; N, 17.06. Found: C, 68.19; H, 8.33; N, 16.96.

4-[(2,2,5,5-Tetramethyl-3-pyrrolidinyl-1-oxy)methylimino-methyl]pyridine (VII): synthesized from nitroxyl VIII; recrystallized from hexane; yield 78%; mp 67–69 °C; IR $\nu_{C=N}$ 1645 cm^{-1}; EPR (CCl_4) $g = 2.0059$, $A_N = 14.1$ G; $\mu_{eff} = 1.65$ μ_B (25.5 °C, $\chi^{dia} = -154.6 \times 10^{-6}$). Anal. Calcd for $C_{15}H_{22}N_3O$: C, 69.20; H, 8.52; N, 16.14. Found: C, 69.45; H, 8.67; N, 15.95.

2-[(2,2,5,5-Tetramethyl-3-pyrrolidinyl-1-oxy)iminomethyl]-pyridine–Copper Bis(hexafluoroacetylacetonate) Adduct (IX). Anhydrous $Cu(hfac)_2$, weighed under N_2, was dissolved in dry CCl_4. One equivalent of VI in dry CCl_4 was added. The color changed immediately from deep purple to yellow green. After part of the solvent was removed under vacuum a green solid formed. The precipitate was filtered in air and recrystallized from CH_2Cl_2/hexane: yield 96%; IR $\nu_{C=N}$ 1660 cm^{-1}; $\mu_{eff} = 2.40$ μ_B (24.5 °C, $\chi^{dia} = -289.7 \times 10^{-6}$); vis (1:1 mixture in CCl_4 at 20 °C) λ_{max} 800 nm (ϵ_{max} 40.3). Anal. Calcd for $C_{24}H_{23}CuF_{12}N_3O_4$: C, 39.82; H, 3.06; N, 5.80. Found: C, 39.55; H, 3.01; N, 5.72.

Computer Simulations. The EPR spectra were simulated by using the computer program CUNO which has been described previously.[4,12] The g values and hyperfine coupling constants for the nitroxyl ligands (IV–VII) were used in simulating the spectra of the $Cu(hfac)_2$ adducts. The g value of the copper electron, the copper hyperfine coupling constant, the value of J, and the line widths were adjusted to obtain the best fit to the observed spectra of the adduct.

Equilibrium Constants. The equilibrium constants for binding of the spin-labeled pyridines to $Cu(hfac)_2$ were obtained by analysis of the EPR spectra and the absorption at 775 nm when $Cu(hfac)_2$ was titrated with ligand. The mass balance and equilibrium constant equations (see below) were solved to obtain a fifth-order equation in the concentration of free ligand. An interactive computer program was written by using an IMSL[13] subroutine to find the roots of the equation. The physically reasonable root was chosen by operator inspection and then used in the program to calculate the concentrations of all other species in the solution and to calculate the visible absorbance. Equilibrium constants and molar extinction coefficients were varied to obtain the best fit to the combined EPR and visible spectral data as discussed below. The uncertainties given for the values in Table I indicate the extent to which each parameter could be varied with compensating adjustments in other parameters while maintaining good agreement between calculated and observed absorbances (average discrepancy <0.003 A) and agreement within experimental uncertainty (uncertainty varies with concentration) between the calculated concentrations and the concentrations obtained from the EPR spectra.

Results and Discussion

Solution Equilibria. The equilibria involving ligands IV–VII were studied by titrating $Cu(hfac)_2$ with ligand in CCl_4 at 20 °C and monitoring the changes in the visible spectra. The ligand:metal ratio was varied from 0.25:1.0 to 5.0:1.0. For all of the ligands, the absorbance at 775 nm reached a maximum at a ligand:metal ratio about 0.75:1.0 and then decreased at higher ligand:metal ratios. For ligands IV, V, and VII the absorbance continued decreasing up to a metal:ligand ratio >5.0:1.0. For the bidentate ligand VI the absorbance at 775 nm remained essentially constant at ligand:metal ratios ≥1.0:1.0. There were no isosbestic points in the titration spectra. Clearly, more than two species are present in the equilibrium mixture.

Ligands IV–VII contain three potential donor sites: pyridine

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Table I. Equilibrium Constants and Extinction Coefficients[a] at 20 °C

ligand	K_1^{py}, M^{-1}	$10^{-2}K_2^{py}$, M^{-1}	K_1^{NO}, M^{-1}	K_{dimer}^{NO}, M^{-1}	ϵ_{py}, $M^{-1}\,cm^{-1}$	$\epsilon_{(py)_2}$, $M^{-1}\,cm^{-1}$	ϵ_{NO}, $M^{-1}\,cm^{-1}$	ϵ_{dimer}, $M^{-1}\,cm^{-1}$
X			$(1.7 \pm 0.4) \times 10^3$				222 ± 15	
IV	$(6 \pm 2) \times 10^5$	4.0 ± 1	*b*	$(7.0 \pm 2) \times 10^2$	87 ± 1	26 ± 2	176 ± 15^c	263 ± 15
V	$(6 \pm 2) \times 10^5$	3.5 ± 1	*b*	$(8.0 \pm 2) \times 10^2$	86 ± 1	27 ± 2	185 ± 15^c	271 ± 15
VI	$\geqslant 1 \times 10^{7\,d}$		*b*	$(1.3 \pm 0.3) \times 10^3$	39 ± 1		156 ± 15^c	195 ± 15
VII	$(6 \pm 2) \times 10^5$	4.5 ± 1	*b*	$(1.2 \pm 0.4) \times 10^3$	82 ± 1	27 ± 2	223 ± 15^c	305 ± 15

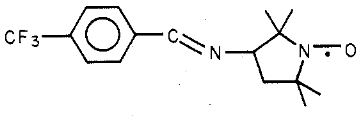
[a] In CCl_4. See text for definition of *K*'s and ϵ's. $\epsilon_{Cu} = 17 \pm 0.5$ $M^{-1}\,cm^{-1}$. [b] Calculation is insensitive to K_1^{NO} so K_1^{NO} was set equal to value for ligand X. [c] Calculation is insensitive to value of ϵ^{NO} due to low concentration of that species. The value is based on the assumption that $\epsilon_{dimer} = \epsilon_{py} + \epsilon_{NO}$. [d] Since K_1^{py} is so large, only a lower limit on the value could be obtained.

Table II. EPR Spectra of Complexes with Nitroxyl Ligands

			Cu parameters			nitroxyl parameters[j]	% soln compn			
							copper species[f]			
complex	*J*,[a] G	*J*, cm^{-1}	g_{iso}[a,b]	A_{Cu},[a,c] G	A_N,[a,d] G	A_N,[e] G	1:1 adduct	$Cu(hfac)_2$	dimer	free nitroxyl[g]
$Cu(hfac)_2\cdot IV$	620	6.02×10^{-2}	2.153	56.0	11.0	14.0	86.2	1.4	8.6	2.25
$Cu(hfac)_2\cdot V$	490	4.75×10^{-2}	2.153	51.0	11.0	14.0	86.1	1.2	8.9	3.70
$Cu(hfac)_2\cdot VI$	>2000	$>1.94 \times 10^{-1}$	2.157	42.0	12.0	14.0	100.0	0	0	1.0
$Cu(hfac)_2\cdot VII$	100[h]	9.68×10^{-3}	2.148	49.0	11.0	14.0	82.2	1.2	11.2	3.0
	110[i]	1.06×10^{-2}	2.148	51.0	11.0	14.0	32.9	1.2	11.2	2.0
	28	2.71×10^{-3}	2.150	56.0	11.0	13.0	49.3			

[a] Obtained by computer simulation of EPR spectra of a 1:1 mixture of $Cu(hfac)_2$ and ligand in CCl_4 at 20 °C. [b] Uncertainty ±0.001. [c] Value for ^{63}Cu; uncertainty ±1.0 G. [d] Simulations were insensitive to changes in this value. [e] Uncertainty ±0.2 G. [f] Percent of total copper concentration present in each species based on equilibrium constants from Table I and used in simulations. $Cu(hfac)_2(py{\sim}NO)_2$ is 3.8–5.4% of the total Cu; this species was not included in the simulations. [g] The concentration of free nitroxyl (relative to total copper) is the value adjusted to fit the observed spectra and differs slightly from the value based on the equilibrium constants. [h] Parameters for simulation with one isomer. [i] Parameters for simulation as mixture of two isomers. [j] $g_{iso} = 2.0059$.

N, azomethine N, and nitroxyl O. To obtain information on the coordinating ability of the pyrrolidine nitroxyl oxygen, we studied model ligand X. X was prepared by condensation of



X

p-(trifluoromethyl)benzaldehyde with 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy. Analysis of the visible spectrum obtained when 5.21×10^{-3} M $Cu(hfac)_2$ in CCl_4 was titrated with X gave a nitroxyl-binding constant of $(1.7 \pm 0.2) \times 10^3$ (Table I). There was no indication of the formation of a six-coordinate complex. This value of the equilibrium constant is very similar to values obtained previously for coordination of other nitroxyl radicals to $Cu(hfac)_2$.[5,14] Pyridine is known to coordinate strongly to $Cu(hfac)_2$ forming both mono and bis adducts.[5,15,16] The coordination of the azomethine N has been found to be negligible for ligands similar to IV, V, and VII.[5] Therefore the equilibria involving ligands IV–VII were analyzed in terms of eq 1–5 with $py{\sim}NO$ representing a

$$\mathrm{Cu(hfac)_2 + py{\sim}NO \overset{K_1^{py}}{\rightleftharpoons} Cu(hfac)_2(py{\sim}NO)} \quad (1)$$

$$\mathrm{Cu(hfac)_2 + py{\sim}NO \overset{K_1^{NO}}{\rightleftharpoons} Cu(hfac)_2(NO{\sim}py)} \quad (2)$$

$$\mathrm{Cu(hfac)_2(py{\sim}NO) + py{\sim}NO \overset{K_2^{py}}{\rightleftharpoons} Cu(hfac)_2(py{\sim}NO)_2} \quad (3)$$

$$\mathrm{Cu(hfac)_2(py{\sim}NO) + Cu(hfac)_2 \overset{K^{NO}_{dimer}}{\rightleftharpoons} Cu(hfac)_2(py{\sim}NO)Cu(hfac)_2} \quad (4)$$

$$\mathrm{Cu(hfac)_2(NO{\sim}py) + Cu(hfac)_2 \overset{K^{py}_{dimer}}{\rightleftharpoons} Cu(hfac)_2(py{\sim}NO)Cu(hfac)_2} \quad (5)$$

ligand with both pyridine and nitroxyl moieties.[6] Since K_2^{py} is small and there is no indication of any formation of a six-coordinate complex of $Cu(hfac)_2$ with ligand X, it was assumed that $Cu(hfac)_2(NO{\sim}py)_2$ and $Cu(hfac)_2(py{\sim}NO)(NO{\sim}py)$ would make negligible contributions to the equilibrium mixture. The two equilibrium constants for dimer formation are not independent variables but are related by $K^{py}_{dimer} = K^{NO}_{dimer}K_1^{py}/K_1^{NO}$.

Values of the equilibrium constants were obtained by fitting the data from both the EPR and visible spectra. For systems previously reported in which copper was bound directly to the nitroxyl oxygen, the complex was observed to be strongly antiferromagnetically coupled and there was no observable EPR spectrum at room temperature.[14,17] For the present system it was assumed that a similar antiferromagnetic coupling occurred when copper was bound to the nitroxyl oxygen. Since the concentration of $Cu(hfac)_2(NO{\sim}py)$ was negligible, the difference between the expected integrated intensity of the EPR spectrum at a particular ligand:metal ratio and the observed integrated intensity was used to monitor the dimer concentration. For each ligand, the equilibrium constants and molar extinction coefficients were varied iteratively to obtain the best agreement with both the visible spectra and the EPR data. The molar extinction coefficient for $Cu(hfac)_2$, ϵ_{Cu}, was obtained directly from the visible spectrum before adding ligand. The calculations were insensitive to the value of K_1^{NO} and the molar extinction coefficient for $Cu(hfac)_2(NO{\sim}py)$, ϵ_{NO}, because of the low concentration of this species in the equilibrium mixture. Therefore K_1^{NO} was set equal to the value obtained for the model ligand X, and ϵ_{NO} was assumed to be equal to $\epsilon_{dimer} - \epsilon_{py}$; i.e., it was assumed that the absorbance of the dimer was due to two independent copper centers. With these assumptions the values in Table I were obtained. In all cases the calculated absorbances and concentrations (from EPR) were in good agreement with the

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experimental values. The values of the equilibrium constants in Table I are similar to those reported for closely related compounds.[5,14-16]

The changes in the visible absorption can thus be explained as follows. At low ligand concentrations there is a significant dimer concentration, and since $\epsilon_{NO} > \epsilon_{py} > \epsilon_{Cu}$, the visible absorption increases rapidly with increasing ligand concentration. At higher ligand concentrations the dimer concentration decreases because the nitroxyl oxygen is displaced by the stronger donor pyridine and the absorption decreases because $\epsilon_{py} < \epsilon_{NO}$. At metal:ligand ratios near 1:1, the 1:1 adduct is the primary species in solution. No further changes in the visible spectrum occur for the bidentate ligand, VI, as ligand is added in excess of a 1:1 ratio. However for the other ligands (monodentates) as excess ligand is added, the concentration of the six-coordinate bis(pyridine) adduct increases and the absorbance drops further because $\epsilon_{(py)_2} < \epsilon_{py}$.

The calculated compositions of solutions containing a 1:1 ratio of ligand:metal are given in Table II. These species were taken into consideration in simulating the EPR spectra.

EPR Spectra. Electron–electron coupling in copper complexes of ligands which contain a nitroxyl radical results in an ABMXY$_n$ spin system where A and B represent the tightly coupled copper electron spin and nitroxyl electron spin, M represents the spin $^3/_2$ copper nucleus, X represents the spin 1 nitroxyl nitrogen nucleus, and Y$_n$ represents the nitrogen nuclei in the copper coordination sphere.[12] The AB coupling results in transitions which are commonly referred to as "inner" and "outer" lines.[12] Although each transition is a combination, the lines are referred to as "copper" or "nitroxyl" depending on the character of the transition as $J \rightarrow 0$.[12]

The EPR spectra of Cu(hfac)$_2$·IV in CCl$_4$ solution at room temperature are shown in Figure 1. The positions of the outer lines defined the value of the electron–electron coupling constant, J, as 620 G (Table II). The equilibrium calculations indicated the presence of dimer, Cu(hfac)$_2$(py$\sim$NO)Cu(hfac)$_2$, in the 1:1 equilibrium mixture. It was assumed that the EPR spectrum of the dimer would be a superposition of the spectra of Cu(hfac)$_2$py and Cu(hfac)$_2$NO, but since the spins in Cu(hfac)$_2$NO are strongly antiferromagnetically coupled,[14,17] that portion of the dimer would make no contribution to the EPR spectra. The simulated spectra included contributions from Cu(hfac)$_2$ and dimer as calculated from the equilibrium constants in Table I. The parameters used in the simulations are given in Table II.

Figure 2 gives the EPR spectra of Cu(hfac)$_2$·V in CCl$_4$ at room temperature. The value of J for this complex was found to be 490 G. The parameters for the simulated spectra are included in Table II. For Cu(hfac)$_2$·IV and Cu(hfac)$_2$·V the values of J in toluene solution were within 10 G of those observed in CCl$_4$ solution.

The EPR spectrum of the six-coordinate complex Cu(hfac)$_2$·VI (Figure 3) is characteristic of the case where J is large relative to the energy difference $|(g_2 - g_1)\beta H|$ between the coupled spins. The inner copper and nitroxyl lines are superimposed at a g value which is the average of the values expected for copper and nitroxyl spins in the absence of coupling. The outer lines were not detected. Simulations indicated that J must be greater than 2000 G to obtain as narrow a line as was observed. The simulated spectrum in Figure 3 was calculated by using J = 5000 G (Table II). We have previously observed outer lines for a complex with J = 2650 G,[2] but if the line widths of the outer lines were greater in the present case, it would be more difficult to detect the outer lines.

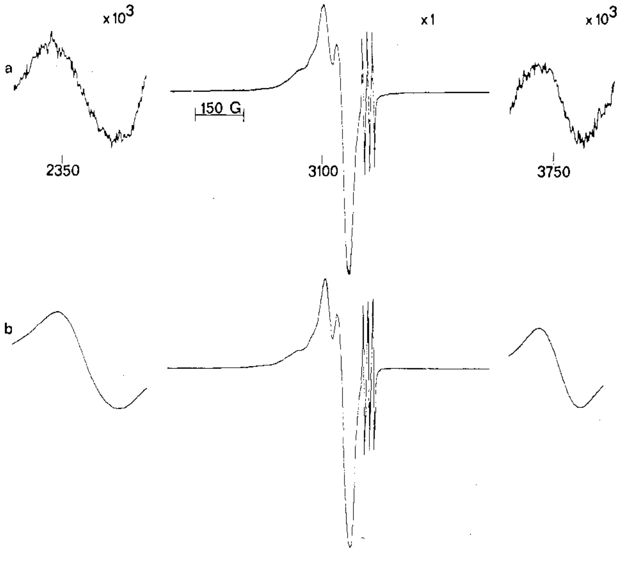

Figure 1. X-Band EPR spectra of Cu(hfac)$_2$·IV in CCl$_4$ solution at 20 °C and computer simulations: (a) observed spectra, 2000-G scan, 250-G/min scan rate (Parameters for center lines were 1.25-G modulation amplitude, 5 mW. Product of gain, modulation amplitude, and square root of power level was 10^3 times greater for outer lines than for inner lines.); (b) computer simulations as described in text and Table II.

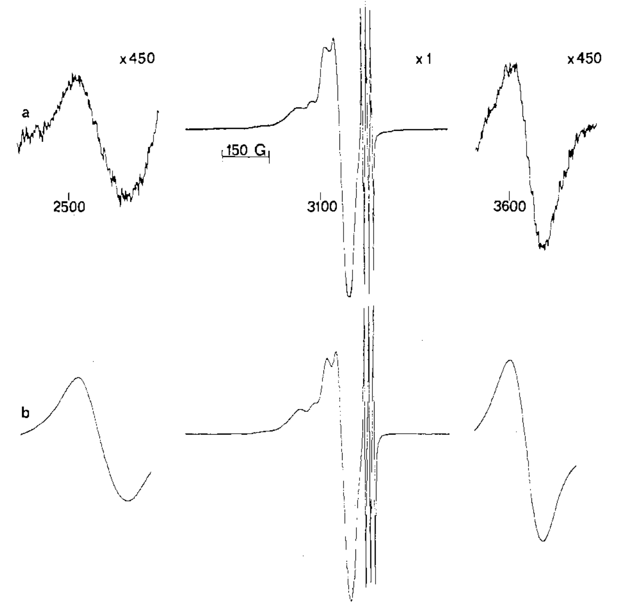

Figure 2. X-Band EPR spectra of Cu(hfac)$_2$·V in CCl$_4$ solution at 20 °C and computer simulations: (a) observed spectra, 2000-G scan, 250-G/min scan rate (Parameters for center lines were 1.6-G modulation amplitude, 5 mW. Product of gain, modulation amplitude, and square root of power level were 460 times greater for outer lines than for center lines.); (b) computer simulations as described in text and Table II.

The EPR spectra of Cu(hfac)$_2$·VII (Figure 4a) were poorly resolved in both CCl$_4$ and toluene solution at room temperature. Spectra at lower temperatures were also poorly resolved. The most distinctive feature of the spectra is the extreme broadening of the "outer nitroxyl" lines such that the region to high field of the free nitroxyl lines (region 1) looks like a gradually sloping line. The broadness of the lines may arise from a greater flexibility of VII relative to the other ligands examined which allows the ligand to move between conformations with different values of J. Figure 4b is the best simulation obtained by assuming the presence of a single isomer with J = 100 G. Although the major peaks in the spectrum are adequately reproduced in the simulation, the

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(17) Zelonka, R. A.; Baird, M. C. *Chem. Commun.* **1970**, 1148. Zelonka, R. A.; Baird, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 6066–70.

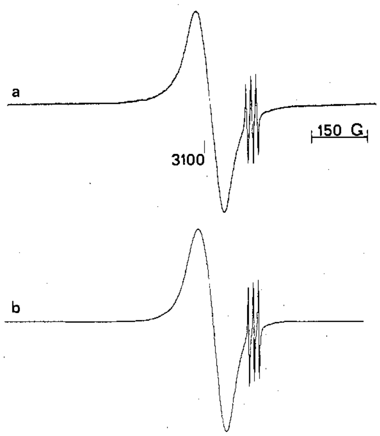

Figure 3. X-Band EPR spectra of Cu(hfac)$_2$·VI in CCl$_4$ solution at 20 °C and computer simulation: (a) observed spectra, 1000-G scan, 125-G/min scan rate, 5 mW, 1.25-G modulation amplitude; (b) computer simulation as described in text and Table II.

agreement between observed and calculated spectra is not as good as has been obtained for other copper–nitroxyl complexes. Some improvement was obtained by assuming that the complex exists as a mixture of two isomers with J_1 = 110 G (35–50%) and J_2 = 25–50 G (65–50%). As shown in Figure 4c, the simulations using two isomers gave a more curved line in region 1 and a less negative feature in region 2 than did the simulation with one isomer (Figure 4b). The simulations of the copper lines (region 3) are strongly dependent on g values, A_{Cu}, and line widths for both isomers and were not fully optimized. Due to the broadness of the lines in the spectrum, the composition of the solution is poorly defined, and the possibility of multiple isomers with differing values of J cannot be ruled out. Nevertheless it is clear that one component has a J value of 105 ± 15 G and that if there are other major species present, the value of J for these isomers must be less than 100 G. However, minor components with broad lines would not be detected. Thus the presence of the additional CH$_2$ group between the nitroxyl and the copper in Cu(hfac)$_2$·VII results in at least a factor of 5 decrease in the magnitude of the electron–electron coupling when compared with Cu(hfac)$_2$·IV. McConnell's calculations of exchange interactions in biradicals indicated that the addition of a CH$_2$ group to a polymethylene chain connecting two radicals would cause about an order of magnitude decrease in the interaction and a change in sign.[18] The signs of the copper–nitroxyl coupling constants are not known, but the difference in the magnitude of the J's in Cu(hfac)$_2$·IV and Cu(hfac)$_2$·VII is similar to that predicted by McConnell.[18]

The existence of two isomers of Cu(hfac)$_2$·II and the possibility of isomers of Cu(hfac)$_2$·VII necessitates caution in comparing values of J for the Cu(hfac)$_2$ complexes of ligands I–VII. If the complexes adopt different geometries then arguments based only on differences in the ligands may be misleading. However, with this caveat, certain patterns are apparent.

Comparison of the Cu(hfac)$_2$ adducts of ligands IV–VI indicates that J varies with the position of attachment to the pyridine ring in the order 3-substituted < 4-substituted < 2-substituted. Thus J is not solely dependent on the distance or number of bonds between the metal and nitroxyl. Details of the intervening molecular orbitals must also be important.

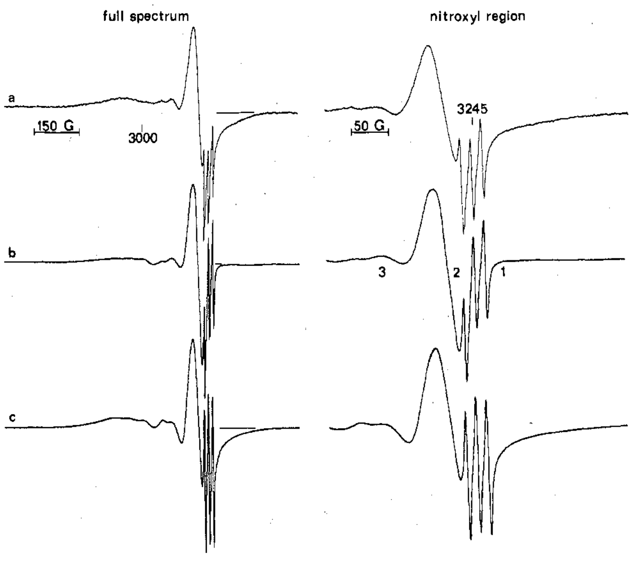

Figure 4. X-Band EPR spectra of Cu(hfac)$_2$·VII in CCl$_4$ solution at 20 °C and computer simulations: (a) observed spectra (full spectrum, 1000-G scan, 125-G/min scan rate, 5 mW, 0.5-G modulation amplitude; nitroxyl region, 400-G scan, 50-G/scan rate, 5 mW, 0.5-G modulation amplitude); (b) computer simulation with one isomer; (c) computer simulation with two isomers. A portion of the baseline is indicated for each of the full spectra. Simulation parameters are discussed in text and given in Table II.

Ligands IV and V differ from I and II only in the size of the nitroxyl ring. J is 5–10 times as large for the adducts of the ligands containing the 5-membered nitroxyl rings (IV and V) as for the adducts of the ligands containing the six-membered nitroxyl rings (I and II). A similar comparison is not possible for ligands III and VI since only a lower limit on J could be obtained for the adducts of these ligands.

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Registry No. IV, 72444-16-7; V, 72444-17-8; VI, 72444-18-9; VII, 72444-19-0; VIII, 54606-49-4; IX, 72442-86-5; X, 72444-20-3; 3-carboxamide-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, 4399-80-8; pyridine-4-carboxaldehyde, 872-85-5; pyridine-3-carboxaldehyde, 500-22-1; pyridine-2-carboxaldehyde, 1121-60-4; *p*-(trifluoromethyl)benzaldehyde, 455-19-6; Cu(hfac)$_2$, 14781-45-4; Cu(hfac)$_2$·X, 72442-85-4; Cu, 7440-50-8; 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, 34272-83-8.

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