Inorg. Chem. **1981**, *20*, 2641-2647

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Metal–Nitroxyl Interactions. 19. Spin-Labeled Derivatives of Copper *meso*-Tetraphenyl-1-(3-acrylic acid)porphyrin

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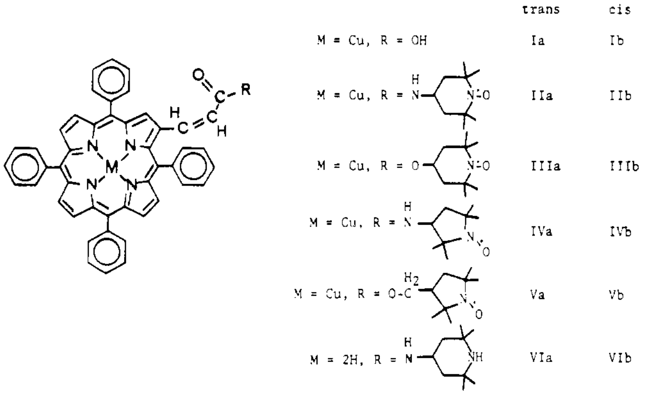
Received September 12, 1980

A series of nitroxyl spin labels have been attached via amide and ester linkages to the cis and trans isomers of copper *meso*-tetraphenyl-1-(3-acrylic acid)porphyrin. Values of the electron–electron coupling, *J*, from 0 to 600 G were observed in the electron paramagnetic resonance (EPR) spectra in fluid solution at room temperature. For the cis isomers the value of *J* is larger in noncoordinating solvents than in coordinating solvents. In coordinating solvents the value of *J* is larger for the trans isomers than for the cis isomers, consistent with the electronic spectra which indicate greater electronic interaction between the substituent and the porphyrin ring in the trans isomers than in the cis isomers. The value of *J* is similar for ester and amide linkages. Differences in the line widths of the EPR spectra are attributed to differences in the rigidity of the bonds between the nitroxyl ring and the porphyrin ring. For one of the trans esters, the formation of nitroxyl–halocarbon complexes was monitored by EPR and NMR.

Introduction

The distances between labeled sites in spin-labeled biomolecules are increasingly frequently calculated by using a purely dipolar model for metal–nitroxyl interaction.[1] This raises the important question of the extent to which spin–spin exchange contributes to metal–nitroxyl interactions. We have recently reported the observation of electron–electron coupling in the EPR spectra of spin-labeled copper complexes in low-viscosity solutions at room temperature.[2–4] Since dipolar interactions would be expected to be small under these experimental conditions, the couplings were attributed to exchange interactions.[2–4] In the present study we have used the cis and trans isomers of the monocarboxycopper porphyrin, I, to prepare the spin-labeled copper complexes II–V. The cis and trans isomers of complexes II–V were designed to determine the impact of four factors on the magnitude of the electron–electron interactions: (1) the difference between the isoelectronic amide and ester linkages, (2) the difference between five- and six-membered nitroxyl rings, (3) the impact of an additional CH_2 group between the copper and the nitroxyl, and (4) the difference between the cis and trans isomers for the three previous effects.



Experimental Section

Infrared spectra were obtained in Nujol mulls on a Perkin-Elmer 337 grating spectrometer. Magnetic susceptibilities were measured on a Bruker Faraday balance with 1-μg sensitivity with use of $HgCo(SCN)_4$ as calibrant.[5] Values of μ_{eff} in Bohr magnetons (μ_B) are reported below with the temperature at which the measurement was made and the diamagnetic correction (χ^{dia})[6] used in the calculation given in parentheses. Magnetic susceptibilities are in cgs-emu throughout the following discussion. The value of 700 × 10^{-6} was used as the diamagnetic correction for H_2TPP.[7] A value of 60 × 10^{-6} was assumed for the temperature-independent paramagnetism of copper.[8] Electronic spectra were obtained in chloroform solution on a Beckman Acta V spectrometer with use of 2.2 × 10^{-5}–4.8 × 10^{-5} M solutions. Data are given below with wavelengths in nanometers and $\log \epsilon$ in parentheses. X-band EPR spectra were obtained on a Varian E-9 spectrometer as previously described.[3] Q-band EPR spectra were obtained with use of a Harvey-Wells magnet and a Varian microwave bridge interfaced to the E-109 console and Varian 620L computer.[9] EPR spectra in the figures are shown with magnetic field increasing to the right. *g*-Values were measured relative to DPPH (2.0036). EPR spectra were run on degassed samples with concentrations of about 10^{-3} M. All coupling constants are given in Gauss except in Table I where values are also given in reciprocal centimeters; 1.0 G equals 0.1 mT and 1.0 cm^{-1} equals 1.99 × 10^{-23} J. EPR and electronic spectra were obtained in dry purified solvents. NMR spectra were run on a Varian HA-100 spectrometer.

Preparation of Compounds. The cis and trans isomers of copper(II) *meso*-tetraphenylporphyrin-1-(2-ethoxycarbonylvinyl)porphyrin (VII) were prepared by the method of Momenteau et al.[10]

Copper(II) *meso*-Tetraphenyl-1-(3-acrylic acid)porphyrin (trans isomer, Ia, and cis isomer, Ib). A solution of 100 mg of the corresponding ethyl ester, VII,[10] in 15 mL of THF and 7.5 mL of 2 N KOH in 80% aqueous ethanol was refluxed for 12 h. The solvent was removed and the residue neutralized with HCl. The product was extracted into $CHCl_3$ and dried over Na_2SO_4. After the volume was reduced to 30 mL, the solution was put on a silica gel column and eluted with $CHCl_3$. Unreacted ester eluted first, followed by product. The product was recrystallized from $CHCl_3$/heptane. The acids appear to decompose when heated for prolonged periods in vacuo.

Trans isomer Ia: yield 64%; IR $\nu_{C=C}$ 1605, $\nu_{C=O}$ 1680 cm^{-1}; VIS 589 (3.84), 549 (4.18), 428 (5.34).

Cis isomer Ib: yield 70%; IR $\nu_{C=C}$ 1600, $\nu_{C=O}$ 1690 cm^{-1}; VIS 578 (3.78), 543 (4.47), 420 (5.71).

Copper(II) *meso*-Tetraphenyl-1-[3-(*N*-(2,2,6,6-tetramethylpiperidinyl-1-oxy))acrylamido]porphyrin (trans isomer, IIa, and cis

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0020-1669/81/1320-2641$01.25/0

Table I. Electron–Electron Coupling Constants at Room Temperature[a]

complex	solvent	J,[b] G	$10^4 J$, cm^{-1}
IIa	$CHCl_3$	19.9	19.0
IIa	1:1 toluene/butylamine	23.7	22.6
IIa	1:1 toluene/THF	24.2	23.1
IIa	1:1 toluene/piperidine	25.3	24.2
IIa	1:1 toluene/pyridine	25.6	24.5
IIa	pyridine	25.6	24.5
IIb	$CHCl_3$	~0[b]	~0
IIb	1:1 toluene/THF	~4[d]	~3.8
IIb	pyridine	3.5[d]	3.5
IIIa	CH_2Cl_2	17.0	16.2
IIIa	9:1 CH_2Cl_2/EtOH	17.0	16.2
IIIa	pyridine	20.5	19.6
IIIa	4:1 toluene/THF	22.0	21.0
IIIa	CS_2	22.5	21.5
IIIa	toluene	23.5	22.5
IIIa	$CHCl_3$	15.5 (60%)	14.8
		26.0 (40%)	24.8
IIIa	1:1 toluene/$CHBr_3$	16.0 (50%)	15.3
		29.2 (50%)	27.9
IIIa	1.2 M $CHCl_3$ in CS_2	15.0 (40%)	14.3
		26.4 (60%)	25.2
IIIa	1.2 M $CHBr_3$ in CS_2	15.7 (55%)	15.0
		28.6 (45%)	27.3
IIIa	1.2 M CHI_3 in CS_2	16.0 (40%)	15.3
		26.6 (60%)	25.4
IIIb	$CHCl_3$	~0[c]	~0
IIIb	CH_2Cl_2	~0[c]	~0
IIIb	4:1 toluene/THF	~3[d]	~2.9
IIIb	1:1 toluene/pyridine	~4[d]	~3.8
IVa	$CHCl_3$	3[d]	2.9
IVa	pyridine	5.2	5.9
IVb	$CHCl_3$	550[e]	525
IVb	$CHCl_3$	600[e,f]	573
IVb	pyridine	~0[c]	~0
Va	$CHCl_3$	<1.0	<1.0
Va	pyridine	<1.0	<1.0
Vb	$CHCl_3$	~0[c]	~0
Vb	CH_2Cl_2	~0[c]	~0
Vb	1:1 toluene/pyridine	~0[c]	~0
Vb	pyridine	~0[c]	~0

[a] Obtained from X-band EPR spectra unless otherwise noted. [b] Based on computer simulation of EPR spectra. Uncertainty ±0.5 G unless otherwise noted. [c] Single broad line observed in the nitroxyl region as in Figures 3a and 4b. Value of J must be ⩽10 G. [d] Three-line pattern in nitroxyl region could not be simulated without assuming a value of J of 3–4 G. Value given has uncertainty of ±1.0 G. [e] Since the outer lines of the spin–spin splitting pattern were not observed, value of J is based only on simulation of the inner lines and uncertainty is ±50 G. [f] Obtained from Q-band spectrum.

isomer, IIb). Oxalyl chloride (1.1 g, 10^{-2} mol) was added to a solution of I (a or b) (0.149 g, 2×10^{-4} mol) in 50 mL of dry benzene. The solution was stirred for 2 h at room temperature. The mixture was taken to dryness under vacuum and kept under vacuum for 2 h. The solid was dissolved in 75 mL of dry THF and 1 mL of dry pyridine. 4-Amino-2,2,6,6-tetramethylpiperidinyl-1-oxy (0.034 g, 2×10^{-4} mol) in 2 mL of dry THF was added dropwise under nitrogen. After 12 h of refluxing, the solvent was removed in vacuo, and the residue was chromatographed on silica gel in $CHCl_3$ solution. The center of the rapidly moving red band was collected.

Trans isomer IIa: recrystallized from $CHCl_3$/heptane; yield 75%; IR $\nu_{\mathrm{C=C}}$ 1600, $\nu_{\mathrm{C=O}}$ 1660, ν_{NH} 3470 cm^{-1} (br); VIS 586 (3.95), 548 (4.39), 426 (5.57); $\mu_{\mathrm{eff}} = 2.58\ \mu_{\mathrm{B}}$ (25 °C, $\chi^{\mathrm{dia}} = -835 \times 10^{-6}$). Anal. Calcd for $C_{56}H_{47}CuN_6O_2$: C, 74.78; H, 5.28; N, 9.34. Found: C, 74.60; H, 5.39; N, 9.25.

Cis isomer IIb: recrystallized from CH_2Cl_2/hexane; yield 78%; IR $\nu_{\mathrm{C=C}}$ 1600, $\nu_{\mathrm{C=O}}$ 1645, ν_{NH} 3400 cm^{-1}; VIS 578 sh (3.89), 542 (4.58), 420 (5.88); $\mu_{\mathrm{eff}} = 2.64\ \mu_{\mathrm{B}}$ (25 °C, $\chi^{\mathrm{dia}} = -835 \times 10^{-6}$). Anal. Calcd for $C_{56}N_{47}CuN_6O_2$: C, 74.78; H, 5.28; N, 9.34. Found: C, 74.51; H, 5.24; N, 9.37.

Copper(II) *meso*-Tetraphenyl-1-[3-(*O*-(2,2,6,6-tetramethylpiperidinyl-1-oxy))acrylic ester]porphyrin (trans isomer, IIIa). The ester IIIa was prepared from the acid chloride of Ia and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy as described above for II (a or b).

Trans isomer IIIa: yield 56%; IR $\nu_{\mathrm{C=C}}$ 1620, $\nu_{\mathrm{C=O}}$ 1720 cm^{-1}; VIS 586 (3.95), 547 (4.27), 428 (5.44); $\mu_{\mathrm{eff}} = 2.65\ \mu_{\mathrm{B}}$ (25 °C, $\chi^{\mathrm{dia}} = -831 \times 10^{-6}$). Anal. Calcd for $C_{56}H_{46}CuN_5O_3$: C, 74.69; H, 5.15; N, 7.78. Found: C, 74.88; H, 5.20; N, 7.85.

When the cis isomer of the porphyrin acid (Ib) was converted to the acid chloride and reacted with 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy as described for the preparation of IIIa, the product obtained had IR, visible, and EPR spectra identical with those of IIIa. Demetalation of the product with $POCl_3$[11] and KOH cleavage of the ester linkage[12] gave a material identical with Ia. Since demetalation and cleavage of the ester linkage do not cause isomerization of analogous complexes, it is apparent that isomerization occurred during the esterification.

Copper(II) *meso*-Tetraphenyl-1-[3-(*O*-(2,2,6,6-tetramethylpiperidinyl-1-oxy))acrylic ester]porphyrin (cis isomer, IIIb). Oxalyl chloride (1.1 g, 10^{-2} mol) was added to a solution of Ib (0.14 g, 2×10^{-4} mol) in 50 mL of benzene to prepare the acid chloride. The solution was stirred for 2 h at room temperature. The mixture was taken to dryness in vacuo. The sodium salt of 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (0.034 g, 2.0×10^{-4} mol) was prepared by refluxing with sodium hydride (0.010 g, 4.0×10^{-4} mol) for 2 h in 25 mL of THF. The porphyrin acid chloride in 25 mL of THF was added slowly to the nitroxyl solution and refined for 7 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel, eluting with $CHCl_3$. The first red band contained a minor side product which was not fully characterized. The dark red second band was collected. The product was recrystallized from CH_2Cl_2/hexane: yield 53%; IR $\nu_{\mathrm{C=C}}$ 1600, $\nu_{\mathrm{C=O}}$ 1715 cm^{-1}; VIS 580 (3.48), 543 (4.16), 419 (5.41). Anal. Calcd for $C_{56}H_{46}CuN_5O_3$: C, 74.69; H, 5.15; N, 7.78. Found: C, 74.58; H, 5.30; N, 7.86.

Copper(II) *meso*-Tetraphenyl-1-[3-(*N*-(2,2,5,5-tetramethylpyrrolidinyl-1-oxy))acrylamido]porphyrin (trans isomer, IVa, and cis isomer, IVb). The complexes were prepared from I (a or b) and 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy as described for II (a or b).

Trans isomer IVa: yield 69%; IR $\nu_{\mathrm{C=C}}$ 1580, $\nu_{\mathrm{C=O}}$ 1640, ν_{NH} 3500 cm^{-1} (br); VIS 586 (3.92), 548 (4.32), 426 (5.51); $\mu_{\mathrm{eff}} = 2.57\ \mu_{\mathrm{B}}$ (25 °C, $\chi^{\mathrm{dia}} = -826 \times 10^{-6}$). Anal. Calcd for $C_{55}H_{46}CuN_6O_2$: O, 74.51; H, 5.23; N, 9.49. Found: C, 74.68; H, 5.07; N, 9.60.

Cis isomer IVb: yield 62%; IR $\nu_{\mathrm{C=C}}$ 1600, $\nu_{\mathrm{C=O}}$ 1645, ν_{NH} 3440 cm^{-1}; VIS 577 sh (3.68), 542 (4.34), 419 (5.64); $\mu_{\mathrm{eff}} = 2.54\ \mu_{\mathrm{B}}$ (25 °C, $\chi^{\mathrm{dia}} = -826 \times 10^{-6}$). Anal. Calcd for $C_{55}H_{45}CuN_6O_2$: C, 74.60; H, 5.12; N, 9.49. Found: C, 74.70; H, 5.22; N, 9.36.

Copper(II) *meso*-Tetraphenyl-1-[3-(*O*-(3-methylene-2,2,5,5-tetramethylpyrrolidinyl-1-oxy))acrylic ester]porphyrin (trans isomer Va). The ester was prepared from the acid chloride of Ia and 3-hydroxymethyl-2,2,5,5-tetramethylpyrrolidinyl-1-oxy as described for II (a or b).

Trans isomer Va: yield 49%; IR $\nu_{\mathrm{C=C}}$ 1620, $\nu_{\mathrm{C=O}}$ 1730 cm^{-1}; VIS 586 (3.92), 548 (4.24), 427 (5.40); $\mu_{\mathrm{eff}} = 2.57\ \mu_{\mathrm{B}}$ (25 °C, $\chi^{\mathrm{dia}} = -834 \times 10^{-6}$). Anal. Calcd for $C_{56}H_{46}CuN_5O_3$: C, 74.69; H, 5.15; N, 7.78. Found: C, 74.71; H, 5.24; N, 7.81.

Attempts to prepare the cis isomer Vb by this method gave only Va. Isomerization occurs in this esterification reaction analogous to the results obtained for IIIb.

Copper(II) *meso*-Tetraphenyl-1-[3-(*O*-(3-methylene-2,2,5,5-tetramethylpyrrolidinyl-1-oxy))acrylic ester]porphyrin (cis isomer Vb). The ester was prepared from Ib and the sodium salt of 3-hydroxymethyl-2,2,5,5-tetramethylpyrrolinyl-1-oxy by using the procedure described for IIIb. The reaction mixture was chromatographed on silica gel eluting with $CHCl_3$. The dark red second band was collected. The product was recrystallized from CH_2Cl_2/hexane: yield 47%; IR $\nu_{\mathrm{C=C}}$ 1590, $\nu_{\mathrm{C=O}}$ 1700 cm^{-1}; VIS 578 (3.55), 543 (4.24), 419 (5.48). Anal. Calcd for $C_{56}H_{46}CuN_5O_3$: C, 74.69; H, 5.15; N, 7.78. Found: C, 74.73; H, 5.34; N, 7.71.

***meso*-Tetraphenyl-1-[3-(*N*-(2,2,6,6-tetramethylpiperidine))acrylamido]porphyrin (trans isomer VIa and cis isomer VIb).** Copper(II) *meso*-tetraphenyl-1-[2-ethoxycarbonylvinyl]porphyrin[10] was demetalated in aqueous $POCl_3$.[11] The ethyl ester was hydrolyzed with KOH

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in pyridine.[12] The acid was condensed with 4-amino-2,2,6,6-tetramethylpiperidine as described for II and chromatographed on activity II alumina in 20:1 $CHCl_3$/MeOH. The first deep red band contained the product.

Trans isomer VIa: yield 18%; IR $\nu_{C=C}$ 1590, $\nu_{C=O}$ 1645, ν_{NH} 3430, 3520 cm^{-1}; NMR ($CDCl_3$ and $CHCl_3$) pyrrole H 8.96, 8.81 (m), phenyl H 8.18 (m), 7.88 (m), and 7.75 (m), olefinic H 7.03 (d) and 6.58 (d) (J = 16 Hz), piperidine CH_3 1.44 (s) and 1.40 (s), NH −2.60; VIS 656 (3.74), 600 (4.03), 562 (4.13), 522 (4.53), 427 (5.69). Anal. Calcd for $C_{56}H_{50}N_6O$: C, 81.70; H, 6.12; N, 10.21. Found (2 samples): C, 76.83, 79.87; H, 6.09, 5.96; N, 9.35, 9.91.

Cis isomer VIb: yield 25%; IR $\nu_{C=C}$ 1590, $\nu_{C=O}$ 1645, ν_{NH} 3350, 3440 cm^{-1}; NMR ($CDCl_3$ and $CHCl_3$) pyrrole H 8.79 (m), phenyl H 8.18 (m), 8.00 (m), and 7.70 (m), olefinic H 6.76 (d) and 5.63 (d) (J = 12 Hz), piperidine CH_3 0.94 (s) and 0.41 (s), NH −2.70; VIS 652 (3.94), 596 (4.07), 555 (4.11), 519 (4.60), 422 (5.87). Anal. Calcd for $C_{56}H_{50}N_6O$: C, 81.70; H, 6.12; N, 10.21. Found (2 samples): C, 77.15, 80.18; H, 5.97, 6.10; N, 9.30, 9.79. The elemental analyses of the amides VIa and VIb were low in carbon and nitrogen by variable amounts despite repeated attempts at purification. The impurity is not the starting porphyrin acid since it is cleanly separated by chromatography and has a higher carbon content than the amides. The IR, NMR, and visible spectra are consistent with the desired product. Since these two compounds were used only for NMR studies of the molecular conformation, the reason for the discrepancy in the bulk elemental analyses was not pursued.

Computer Simulations

The EPR spectra were simulated with the use of the computer program CUNO.[13] The Hamiltonian used is given in eq 1, where g_1 and g_2 are the g values of the metal and nitroxyl

$$\mathcal{H} = g_1\beta H\hat{S}_{1Z} + g_2\beta H\hat{S}_{2Z} + hJ\hat{S}_{1Z}\hat{S}_{2Z} + (hJ/2)(\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}) + hA_M\hat{S}_{1Z}\hat{I}_{1Z} + hA_N\hat{S}_{1Z}\hat{I}_{2Z} + hA_{N'}\hat{S}_{2Z}\hat{I}_{3Z} + (hA_M/2)(\hat{S}_{1+}\hat{I}_{1-} + \hat{S}_{1-}\hat{I}_{1+}) - g_M\beta_M H\hat{I}_{1Z} - g_N\beta_N H\hat{I}_{2Z} - g_{N'}\beta_N H\hat{I}_{3Z} \quad (1)$$

electrons, $\hat{S}_1$ and $\hat{S}_2$ refer to the metal and nitroxyl electron spins, respectively, J is the electron–electron coupling constant in hertz, I_1, I_2, and I_3 refer to the metal nuclear spin, the nuclear spin of the coordinated nitrogens, and the nuclear spin of the nitroxyl nitrogen, respectively; A_M is the metal electron–metal nucleus coupling constant in hertz, A_N is the coupling constant in hertz between the metal electron and the nuclear spins of the coordinated nitrogens, $A_{N'}$ is the coupling constant in hertz between the nitroxyl electron and nuclear spin of the nitroxyl nitrogen, and all other symbols are defined as in ref 9. The first seven terms in the Hamiltonian were treated exactly and the last four were treated as a perturbation to second order for the transition energies and to first order for the transition probabilities. To facilitate visual comparison with the field-swept experimental spectra the values of J, A_M, A_N, and $A_{N'}$ are discussed below in units of gauss with the conversion between hertz and gauss given by eq 2–4. The

$$J\ (\mathrm{G}) = [J\ (\mathrm{Hz})]\frac{h}{2\beta}\left(\frac{1}{g_1} + \frac{1}{g_2}\right) \quad (2)$$

$$A_M\ (\mathrm{G}) = [A_M\ (\mathrm{Hz})]\frac{h}{g_1\beta} \quad (3)$$

$$A_{N'}\ (\mathrm{G}) = [A_{N'}\ (\mathrm{Hz})]\frac{h}{g_2\beta} \quad (4)$$

conversion factor for A_N is the same as for A_M. Only the absolute value of J can be determined from these experiments. The electron–electron coupling results in AB patterns in the EPR spectra. The lines in the spectra are referred to as copper or nitroxyl depending on the nature of the transitions as $J \rightarrow 0$. When J is small relative to the g-value difference between the copper and nitroxyl electrons, each of the copper and nitroxyl lines is split into a doublet. As J becomes larger, the intensity of the outer lines of the AB pattern goes to zero and the positions of the inner copper and inner nitroxyl lines become equal.

In the X-band EPR spectra for all of the spin-labeled copper porphyrins, the nitroxyl lines are superimposed on the broader $m_I = -^3/_2$ copper lines. The $m_I = +^3/_2$ copper lines are severely broadened due to incomplete motional averaging of g and A anisotropy. For most of the complexes reported here, the value of J was <30 G. In these cases J is less than the line widths of the copper lines so the impact of J on the copper lines is only a broadening of the lines. As a result of the overlapping broad lines the copper regions of the spectra are poorly defined. The parameters for CuTPP (g = 2.0944, A_{Cu} = 86.5 G, A_N = 16.0 G in $CHCl_3$, and g = 2.0994, A_{Cu} = 82 G, A_N = 15.5 G in pyridine) were used in simulating the spectra. The spectra were consistent with these parameters within the uncertainty caused by the broad lines.

When J was small, its value was based on the splittings observed in the nitroxyl region of the spectrum. For the room-temperature spectra (except for the cases with specific nitroxyl–halocarbon interactions), the parameters used in simulating the nitroxyl lines were g = 2.0059, A_N = 15.2–16.2 G in the piperidine ring, and A_N = 14.5–15.5 G in the pyrrolidine ring.

For the spectra with larger values of J, the outer lines of the AB pattern were not observed. Therefore the value of J is based on the simulation of the inner copper and nitroxyl lines which are largely superimposed. The appearance of the spectrum depends on the assumed line widths as well as the value of J. Thus the value of J is less certain than for those cases where the outer lines were observed.

Results and Discussion

The spin-labeled copper porphyrins IIa–Va, IIb, and IVb were prepared from the cis and trans acrylic acids Ia and Ib by reaction of the acid chloride with the appropriate amines and alcohols. However, attempts to prepare IIIb and Vb by this method resulted in isomerization to IIIa and Va. The reaction between the acid chloride of Ib and the sodium salts of the appropriate alcohols gave IIIb and Vb with no evidence of isomerization. Since isomerization occurred only when the acid chloride of Ib was in the presence of the alcohols, it appears likely that hydroxyl group attack on the β-carbon of the olefin was responsible for the cis to trans isomerization.

The NMR spectra of the diamagnetic porphyrins VIa and VIb were examined to ascertain the position of the tetramethylpiperidine ring relative to the porphyrin plane. In 4-amino-2,2,6,6-tetramethylpiperidine, the methyl resonances are at 1.12 and 1.20 ppm from Me_4Si.[14] In the trans amide VIa, the methyl resonances are at 1.40 and 1.44 ppm. For the methyl groups to experience such a downfield ring current shift, the piperidine ring must be located beside the porphyrin plane. However, in the cis amide VIb the methyl resonances are at 0.41 and 0.94 ppm. This upfield ring current shift indicates that the piperidine ring is located above the plane of the porphyrin. The ring current shifts of the ethyl protons in the ethyl esters of the free porphyrins derived from Ia and Ib led Momenteau et al. to similar conclusions regarding the geometries of the ethyl esters.[10] It is therefore likely that the spin-labeled esters and amides II–V have geometries which position the nitroxyl ring above the porphyrin plane in the cis isomer and beside the porphyrin plane in the trans isomer. This is consistent with molecular models. On the basis of the models, the copper–nitroxyl distance is about 9 Å in the cis

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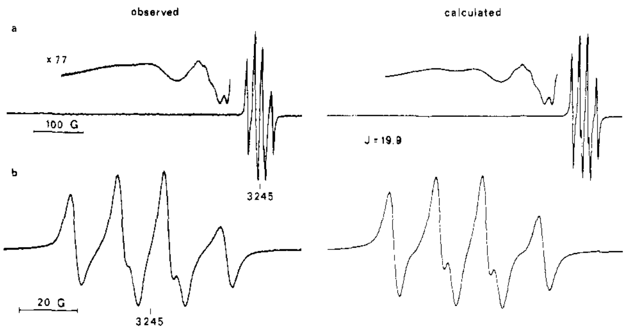

Figure 1. X-Band EPR spectra of the trans amide, IIa, in $CHCl_3$ solution at 20 °C and computer simulations: (a) 600 G scan, 125 G/min scan rate, 2 mW, 0.4 G modulation amplitude, insert of copper region, 30 mW, 4.0 G modulation amplitude; (b) 100 G scan, 12.5 G/min scan rate, 2 mW, 0.4 G modulation amplitude (J is given in gauss).

isomers and about 13 Å in the trans isomers.

The electronic spectra in $CHCl_3$ solution indicate significant differences between the trans and cis isomers. For the trans isomers Ia–Va, the α, β, and Soret bands occur at 586–589, 547–549, and 426–428 nm, respectively. In the cis isomers Ib–Vb, the band positions are 577–580, 542–543, and 419–420 nm, respectively. The band positions for the trans isomers are similar to those observed for the copper complex of 2-formyl-TPP (590, 551, and 430 nm)[10] while the band positions for the cis isomers are closer to those for CuTPP (570, 539, 417 nm).[10] Momenteau et al. have reported similar spectra for esters and amides derived from I (a and b).[10] They observed that saturation of the vinyl group led to compounds with spectra similar to that of CuTPP.[10] Thus the effects on the electronic spectra must be due to electronic interaction between the porphyrin π system and the vinyl group rather than steric effects. Formyl and vinyl substituents have been found to shift the electronic transitions to lower energy in other porphyrins.[15] Gouterman has used the four-orbital model to show that the shifts are consistent with changes in the relative energies of the porphyrin π orbitals.[15] Spectra similar to those of CuTPP indicate weak electronic interactions, while shifts in the transitions to lower energy, as observed in Cu(2-formyl-TPP) indicate greater electronic interaction between the substituent and the porphyrin π orbitals. Thus the electronic spectra indicate that there is less electronic interaction between the substituents and the porphyrin ring in the cis isomers Ib–Vb than in the trans isomers Ia–Va. Electronic transitions also occur at longer wavelengths for the trans isomer of the free porphyrin amide VIa than for the cis isomer VIb. These differences in electronic structure correlate with differences in the electron–electron interaction as discussed below.

The room-temperature magnetic moments for the spin-labeled copper porphyrins fall in the range 2.53–2.65 μ_B. These values are slightly higher than those previously observed for spin-labeled copper complexes[2-4,8] but are consistent with some orbital contribution to the copper magnetic moment and essentially independent spins, i.e., weak interaction ($<kT$) between the copper and nitroxyl electrons.

EPR Spectra of Trans Isomers. The nitroxyl region of the EPR spectrum of the trans amide II in $CHCl_3$ solution exhibits a doublet of triplets characteristic of an AB pattern with an electron–electron coupling constant, J, of 19.9 G (Figure 1). The copper region of the spectrum, although partially obscured by the nitroxyl lines, looks like a somewhat broadened copper porphyrin spectrum since J is smaller than the line widths for most of the lines (Figure 1). So that the effect of axial ligation on the size of J could be determined, spectra of IIa were run in a series of solvents with varying coordinating abilities (Table I). For many copper complexes, increasing axial ligation causes an increase in g value and a decrease in A_{Cu}.[16-18] For CuTPP in various solvents, the g value increases in the order $CHCl_3$ < 1:1 toluene/THF < 1:1 toluene/butylamine < pyridine < 1:1 piperidine/toluene, and A_{Cu} decreases in the same order. The value of J (Table I) increases in the order $CHCl_3$ < 1:1 toluene/butylamine < 1:1 toluene/THF < 1:1 toluene/piperidine < 1:1 toluene/pyridine. Although there are pairwise reversals between the two series, it appears that changes in the energies of the d orbitals resulting from axial ligation may influence the magnitude of the electron–electron interaction. However, the differences in order between the two series indicate that solvent effects other than axial ligation also contribute to the magnitude of J. Specific interaction between $CHCl_3$ and the nitroxyl as discussed below may also contribute to the decreased value of J in that solvent.

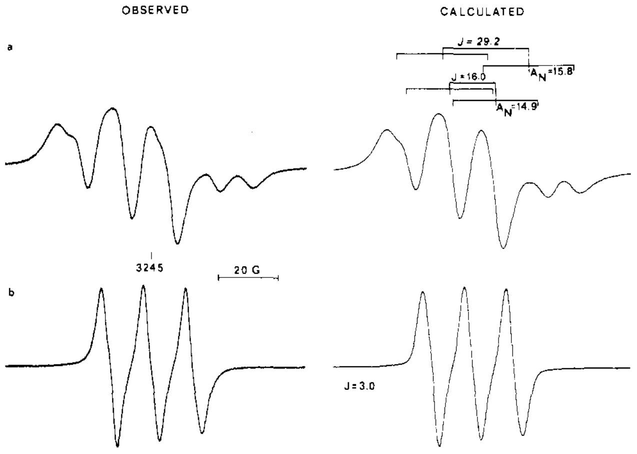

Figure 2. X-Band EPR spectra at 20 °C and computer simulations: (a) 100 G scan of the nitroxyl region for the trans ester, IIIa, in $CHBr_3$ solution, 12.5 G/min scan rate, 5 mW, 1.0 G modulation amplitude; (b) 100 G scan of the nitroxyl region for the trans amide IVa in $CHCl_3$ solution, 12.5 G/min scan rate, 2 mW, 0.32 G modulation amplitude (J and A_N are given in gauss).

In a variety of solvents the EPR spectra of the trans ester IIIa exhibit a doublet of triplets with values of J between 17.0 and 23.5 G. However, in $CHCl_3$ solution two isomers are present with J = 15.5 G (60%) and J = 26.0 G (40%). Identical spectra were obtained in reagent $CHCl_3$ and in $CHCl_3$ from which the ethanol stabilizer had been removed. Furthermore addition of ethanol to a CH_2Cl_2 solution of IIIa did not result in the formation of a second component in the spectrum. Thus interaction with ethanol cannot be the cause of the second species. In 1:1 toluene/$CHBr_3$ solution, two components are also present in the EPR spectrum (Figure 2a) with J = 16.0 G (50%) and J = 29.2 G (50%). In this case the line widths are sufficiently narrow to permit resolution of the lines from the two components both on the low-field and high-field sides of the nitroxyl spectrum. Thus the two components appear to be due to a specific interaction with the halocarbon. So that the interaction could be explored further, EPR spectra of 10^{-3} M IIIa were run in CS_2 containing 1.2 M $CHCl_3$, 1.2 M $CHBr_3$, and 1.2 M CHI_3. In each case two components were observed in the EPR spectra. The component with the larger value of J had a value of the nitrogen hyperfine, A_N, between 15.5 and 15.6 G which is similar to the value of 15.2 G observed in pure CS_2. An increase in A_N

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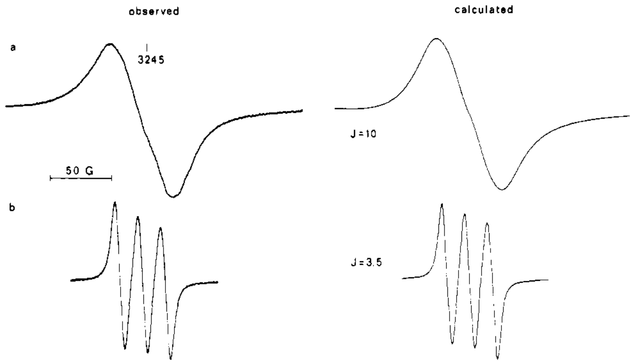

Figure 3. X-Band EPR spectra of the nitroxyl region for the cis amide IIb at 20 °C and computer simulations: (a) $CHCl_3$ solution, 200 G scan, 25 G/min scan rate, 10 mW, 2.0 G modulation amplitude; (b) pyridine solution, 100 G scan, 12.5 G/min scan rate, 5 mW, 1.0 G modulation amplitude (J is given in gauss).

is often observed in more polar solvents so the differences between CS_2 and CS_2/halocarbon solutions could be due to the effect of the halocarbon on the solvent polarity. The components with the smaller value of J had values of A_N of 14.4–14.5 G.

Morishima et al. have examined the ^1H and ^{13}C contact shifts induced in the NMR spectra of halocarbons by nitroxide radicals.[19] They found that the contact shifts caused by di-*tert*-butyl nitroxide (DTBN) increased in the order $CH_2Cl_2 < CHCl_3 < CHBr_3 < CHI_3$ and attributed the interaction to a donor–acceptor interaction between the π orbital containing the nitroxyl unpaired electron and the halogen. Therefore, ^1H NMR spectra of the halocarbons were taken in the presence of IIIa. Concentric NMR tubes were used. The inner tube contained 1.2 M halocarbon in CS_2 and 4% Me_4Si. The outer tube contained ca. 5×10^{-3} M IIIa in the same solvent mixture. It was assumed that there was no specific interaction between the nitroxyl and the Me_4Si so that the chemical shift difference between the two Me_4Si signals ($\Delta\nu(Me_4Si)$) was a measure of the effect of IIIa on the bulk magnetic susceptibility. The ratio of $\Delta\nu$(halocarbon) to $\Delta\nu(Me_4Si)$ would then represent the magnitude of the shift induced by the halocarbon–nitroxyl interactions. These ratios were in the order $CH_2Cl_2 < CHCl_3 < CHBr_3 > CHI_3$, which parallels the magnitudes of the effects observed in the EPR spectra. The fact that CHI_3 binds less strongly than $CHBr_3$ to IIIa but CHI_3 interacts more strongly than $CHBr_3$ with DTBN may reflect greater steric interference in IIIa than in DTBN.

The decreased values for A_N and J and increased g values observed in the EPR spectra of IIIa bound to halocarbons are consistent with Morishima's proposal that spin density is transferred from the nitroxyl to the halocarbon.[19] However, if this interpretation is correct, it is surprising that two components were observed only for IIIa, and not for the many other nitroxyls which we have studied. All of these observations would also be consistent with solvent-dependent conformations of IIIa, which exhibit different values of J.

For the trans amide IVa in $CHCl_3$ solution, the value of J is small relative to the line widths (3.8–4.3 G) and the spectrum looks like a triplet (Figure 2b). However the line shape could not be simulated without including a J of about 3 G. In pyridine solution, the value of J increases to 5.2 G and the doublet of triplets is clearly resolved.

In the EPR spectrum of a $CHCl_3$ solution of the trans ester Va which has a CH_2 group between the nitroxyl ring and the ester linkage, there is a sharp three-line nitroxyl pattern with line widths of 1.5–1.6 G. A similar spectrum was obtained in pyridine solution. The value of J must be <1.0 G for this complex.

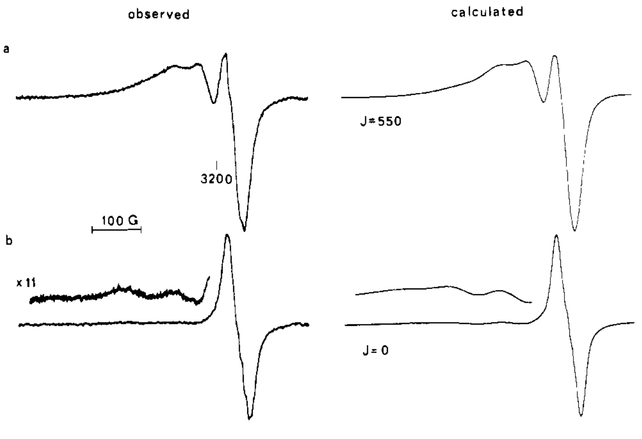

Figure 4. X-Band EPR spectra of the cis amide IVb at 20 °C and computer simulations: (a) $CHCl_3$ solution, 550 G scan, 125 G/min scan rate, 10 mW, 2.0 G modulation amplitude; (b) pyridine solution, 550 G scan, 125 G/min scan rate, 10 mW, 3.2 G modulation amplitude (J is given in gauss).

EPR Spectra of Cis Isomers. For the cis amide IIb in $CHCl_3$ solution, the EPR spectrum of the nitroxyl region shows a single very broad peak which is consistent with a value of $J \leq 10$ G and line widths of 20–25 G (Figure 3a). The simulated spectrum in Figure 3a was obtained with $J = 10$ G and line widths of 20 G. However, similar simulated spectra were obtained with smaller values of J and larger line widths. In 1:1 toluene/THF solution, the nitroxyl region of the EPR spectrum of IIb is a triplet of broad lines which could be simulated with line widths of about 10 G and a J of about 4 G. In pyridine solution the line widths are about 5 G and a J of 3.5 G is required to match the observed spectra (Figure 3b). Increased line widths may arise from uncertainty in the value of J due to fluctuations between conformations with different values of J. Apparently the coordination of THF or pyridine to the copper porphyrin reduces the range of conformations which are accessible to the molecule. The sharper lines in pyridine solution than in 1:1 toluene/THF are consistent with stronger coordination by pyridine than by THF.

The spectra of the cis ester IIIb in $CHCl_3$ and CH_2Cl_2 solution are similar to those obtained for the cis amide IIb in $CHCl_3$ solution (Figure 3a). Since similar spectra were obtained for IIIb in $CHCl_3$ and CH_2Cl_2, interaction of IIIb with $CHCl_3$ as observed for the trans isomer IIIa is not likely to be the cause of the line broadening. In 1:1 toluene/THF and 1:1 toluene/pyridine solution, the nitroxyl region of the EPR spectrum of IIIb is a triplet of broad lines consistent with values of J about 3–4 G. As observed for IIb, coordinating solvents reduce the uncertainty in the value of J for IIIb.

The X-band EPR spectra of the cis amide IVb in $CHCl_3$ solution (Figure 4a) are significantly different from the spectra of the compounds discussed above. The simulated spectrum in Figure 4a was obtained with $J = 550$ G although values of J between 500 and 650 G gave satisfactory agreement with the observed spectrum. The uncertainty in J for this spectrum is large because no outer lines were observed in the spectrum. Broadening of the outer lines can make detection difficult.[4] The spectra of IVb in $CHCl_3$ do not appear to be concentration dependent and are unchanged by the addition of a tenfold excess of the free porphyrin ethyl ester obtained from Ib.[10] Thus the large value of J does not appear to be due to intermolecular interactions. The Q-band EPR spectrum of IVb in $CHCl_3$ solution is a single broad line which could be simulated with values of J between 570 and 630 G. No outer lines were detected in the Q-band spectrum. Since detection of the

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outer lines is easier at Q-band than at X-band,[9] the inability to detect the outer lines even at Q-band indicates that the outer lines must be severely broadened, presumably due to fluctuations in the value of J. When the X-band spectrum of IVb was obtained in pyridine solution, a single broad line was observed in the nitroxyl region (Figure 4b). The simulated spectrum was obtained with $J = 0$ and 20 G line widths for the nitroxyl lines. The copper region looked like a normal copper porphyrin spectrum with broadened lines as had been observed for the other spin-labeled copper porphyrins. Thus the value of J is drastically reduced in the presence of pyridine.

The EPR spectra of the cis ester Vb in $CHCl_3$, CH_2Cl_2, 1:1 toluene/pyridine, and pyridine solution are similar to those shown in Figures 3a and 4b. The line widths are somewhat narrower in the presence of pyridine, but the spectrum does not sharpen to a three line pattern as observed for IIb and IIIb.

Line-Width Effects. Molecular motions which interconvert conformations with different values of J and occur at a rate comparable to the EPR time scale can cause an uncertainty in transition energies which results in line broadening. We have previously noted that nitroxyl line widths in spin-labeled copper complexes increase with increasing temperature.[3,4] These increases are probably due to increased flexibility of the molecules with increasing temperature as well as collisional effects. Changes in dinitroxyl line widths with temperature have also been interpreted in terms of changes in intramolecular motions.[20] The nitroxyl line widths for the trans amides IIa and IVa at room temperature in all the solvents examined fall in the range 2.8–4.1 G whereas the nitroxyl line widths in the trans ester IIIa fall in the range 6.0–9.5 G in various solvents. These results are consistent with a greater flexibility of the ester linkage than of the amide linkage. In the trans ester Va where J is very small, the nitroxyl line widths are small (1.5–1.6 G), indicating that the broadening of the nitroxyl lines for IIa–IVb must be due to intramolecular copper–nitroxyl interactions since collisional effects on Va would be expected to be similar to those for the other three trans isomers.

The EPR spectra of the cis isomers IIb–Vb are more solvent dependent than the spectra of the trans isomers. For IIb (Figure 3) and IIIb, the nitroxyl line widths in pyridine solution are factors of 4 and 2, respectively, sharper than in $CHCl_3$ solution. The nitroxyl line widths for Vb are also sharper in pyridine than in $CHCl_3$. Thus coordination of pyridine to these cis isomers appears to reduce the range of values of J which are accessible by intramolecular motions. For IVb (Figure 4) the spectrum in $CHCl_3$ solution is characteristic of a relatively large value of J while the spectrum in pyridine is typical of the case where J is small but the line widths are large due to uncertainty in the value of J.

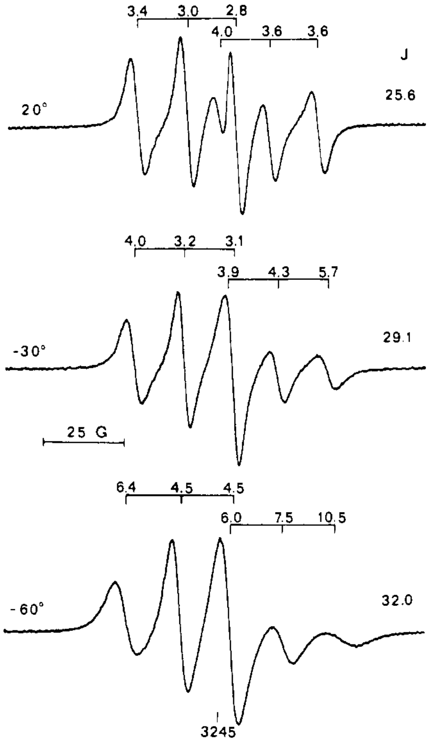

Figure 5. X-Band EPR spectra of the trans amide IIa in 2:1 toluene/pyridine at various temperatures: 135 G scans, 25 G/min scan rate, 2 mW, 0.5 G modulation amplitude. Line widths obtained by computer simulation are indicated above each line. Line widths and J's are given in gauss.

The much larger solvent effects on the spectra of the cis isomers than on the spectra of the trans isomers suggests that coordination of pyridine has a greater impact on copper–nitroxyl interaction in the cis complexes than in the trans complexes. The NMR spectra of the related diamagnetic amides, VIa and VIb, indicated (see above) that the piperidine ring is located beside the porphyrin plane in the trans isomer and above the porphyrin plane in the cis isomer. These geometries would place the carbonyl oxygen beside the porphyrin plane in the trans isomer and directly above the porphyrin plane in the cis isomer. On the basis of molecular models, the carbonyl oxygen in the cis isomer would be pointed toward the copper with a copper–oxygen distance of about 4 Å. Although this distance is longer than a normal copper–oxygen bond length, it suggests the possibility of a weak copper–oxygen interaction which could provide a shorter path for copper electron–nitroxyl electron interaction than through the vinyl group. Coordination of pyridine to the copper would weaken the interaction with the carbonyl oxygen because the oxygen would then be a sixth ligand rather than the fifth ligand. Alternatively, there might be a weak interaction between the carbonyl group and the porphyrin π cloud which could be decreased by a change in conformation due to pyridine coordination. The inability to detect the outer lines in the EPR spectrum of IVb in $CHCl_3$ solution may be due to large variations in the value of J caused by small changes in molecular conformation. The differences in the values of J for IIb–Vb in $CHCl_3$ may reflect slightly different strengths of the copper–oxygen or carbonyl–porphyrin interaction in addition to the differences in porphyrin–nitroxyl linkages and nitroxyl structures.

Another line-width phenomenon is observed when a solution of the trans amide IIa in 2:1 toluene/pyridine is cooled below room temperature (Figure 5). The line widths become highly anisotropic as the temperature is lowered. The pattern of broadening is not the typical pattern for incomplete isotropic averaging of a nitroxyl spectrum where the middle line of the triplet remains sharpest.[21] Instead the line widths in the inner triplet decrease toward high field while the line widths in the outer triplet increase toward high field. This pattern of asymmetric broadening is similar to that observed previously for spin-labeled copper salicylaldimines[3] and spin-labeled pyridine adducts of copper hexafluoroacetylacetonate.[4] Asymmetric line broadening in dinitroxyls at low temperature has been interpreted in terms of incomplete motional averaging of anisotropies including terms which depend on the sign of the electron–electron coupling constant and relative to orientations of the two radicals as well as the g and A anisotropies.[22]

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The asymmetric broadening of the spectra for the spin-labeled copper complexes probably arises from incomplete motional averaging and an analysis of the information which can be obtained from the pattern of line-width changes as a function of temperature is currently under way.

Comparison of Values of *J*. The location of the carbonyl group in the cis isomers permits interaction between the carbonyl oxygen and the copper or the porphyrin π system in noncoordinating solvents which does not occur in the trans isomer. Therefore, to compare the copper–nitroxyl interactions through the cis and trans vinyl groups, it is necessary to examine the spectra in coordinating solvents such as pyridine. In pyridine solution the values of J for all of the compounds examined are less than 30 G, indicating weak electron–electron interactions. For II–IV the values of J in pyridine solution are greater for the trans isomer than for the cis isomer. For V the value of J is ~ 0 for both isomers. As discussed above, the electronic spectra indicate greater electronic interaction between the vinyl substituent and porphyrin ring in the trans isomer than in the cis isomer consistent with greater interaction across the vinyl to porphyrin linkage in the trans geometry than in the cis geometry. The copper–nitroxyl distances in the cis and trans isomers are about 9 and 13 Å, respectively. Thus the greater magnitude of J for the trans isomers than for the cis isomers correlates with greater electronic interaction through the trans vinyl group than through the cis vinyl group and does not correlate with the through-space distances. This is consistent with interpretation of J as an exchange interaction.

For the trans isomers in pyridine solution the value of J decreases in the order IIa > IIIa > IVa > Va. For the cis isomers in pyridine solution, the value of J decreases in the order IIb $\approx$ IIIb > IVb $\approx$ Vb. Thus the changes in linkage and nitroxyl ring size have parallel effects for the cis and trans isomers. For the piperidine nitroxyl the isoelectronic ester and amide linkages in II and III result in similar values for J. The data for IIa and IIIa indicate that J is slightly larger for the amide than for the ester but the differences are small relative to the solvent effects on J. The values of J for IV which contains a pyrrolidine nitroxyl are smaller than for II which contains a piperidine nitroxyl. The additional CH_2 group between the ester and the nitroxyl ring in V reduces J to about 0 for both the cis and trans isomers.

Comparison with Prior Results. The small values of J observed in these spin-labeled porphyrins in coordinating solvents are similar to those observed in spin-labeled copper salicylaldimines where several saturated linkages intervene between the copper and the nitroxyl[3] and indicates that electronic interaction between the vinyl group and the porphyrin ring is small. Steric congestion probably forces the vinyl group to remain nearly perpendicular to the porphyrin plane. The decrease in J when an additional CH_2 is placed between the copper and the nitroxyl is similar to that which was observed for the spin-labeled pyridine adducts of copper bis(hexafluoroacetylacetonate).[4] However, the observation of a larger value of J for the piperidine nitroxyl (IIa and IIb) than for the pyrrolidine derivatives (IVa and IVb) is the reverse of the pattern observed for spin-labeled derivatives of copper bis(hexafluoroacetylacetonate)[4] and implied in other less quantitative results in the literature.

The EPR spectra of IIIa in halogenated solvents constitute an unusual case. For none of the other complexes was it possible to observe the distinct EPR spectra for the nitroxyl in the presence of halocarbon. IIIa appears to be a fortuitous case where the equilibrium constant is sufficiently large and the lifetime of the species is sufficiently long to permit observation of the two species. However, to whatever extent similar interaction occurs it may explain why the value of J is smaller in $CHCl_3$ than in other solvents. Such equilibria may be important contributions to EPR line widths in various solutions.

The discussion presented in this paper concerning intramolecular motions, weak orbital interactions, and solvent effects requires further studies for full confirmation. However, the results obtained to date indicate that metal–nitroxyl interactions may be a powerful probe of these broad uncharted areas of chemistry.

Acknowledgment. We thank M. Momenteau for a preprint of ref 10. Elemental analyses were performed by Spang Microanalytical Laboratory. This work was supported in part by the National Institutes of Health (Grant No. 21156). The Q-band spectrometer was funded in part by the National Science Foundation (Grant No. CHE78-16195). Helpful discussions with Professor J. M. Hornback regarding the synthesis of the cis esters are acknowledged.

Registry No. Ia, 77698-95-4; Ia, acid chloride, 77629-56-2; Ib, 77629-57-3; Ib, acid chloride, 77698-48-7; IIa, 76451-29-1; IIb, 76497-30-8; IIIa, 77629-58-4; IIIb, 77698-49-8; IVa, 77629-59-5; IVb, 77698-50-1; Va, 77629-60-8; Vb, 77698-51-2; VIa, 77629-61-9; VIb, 77698-52-3; VIIa, 71774-36-2; VIIb, 71763-50-3; 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy, 14691-88-4; 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy, 2226-96-2; 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy, sodium salt, 77629-20-0; 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, 34272-83-8; 3-hydroxymethyl-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, 27298-75-5; 3-hydroxymethyl-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, sodium salt, 77629-21-1; 4-amino-2,2,6,6-tetramethylpiperidine, 36768-62-4.