indicates that the magnitude of J correlates with the extent of metal electron delocalization.

In systems of this complexity, one-parameter fits are not to be expected and many additional complexes will have to be examined before a quantitative description of exchange interactions emerges.

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Registry No. I, 64020-57-1; II, 78249-04-4; III, 78249-05-5; IV, 42953-54-8; V, 64012-89-1; VI, 64012-92-6; VII, 78248-88-1; 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy, 14691-88-4; 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy, 2226-96-2; 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, 34272-83-8.

Contribution from the Departments of Chemistry, University of Denver, Denver, Colorado 80208, and University of Colorado at Denver, Denver, Colorado 80202

Metal–Nitroxyl Interactions. 22. Copper–Nitroxyl Spin–Spin Interaction as a Probe of Weak Orbital Overlaps in Derivatives of Copper Tetraphenylporphyrin

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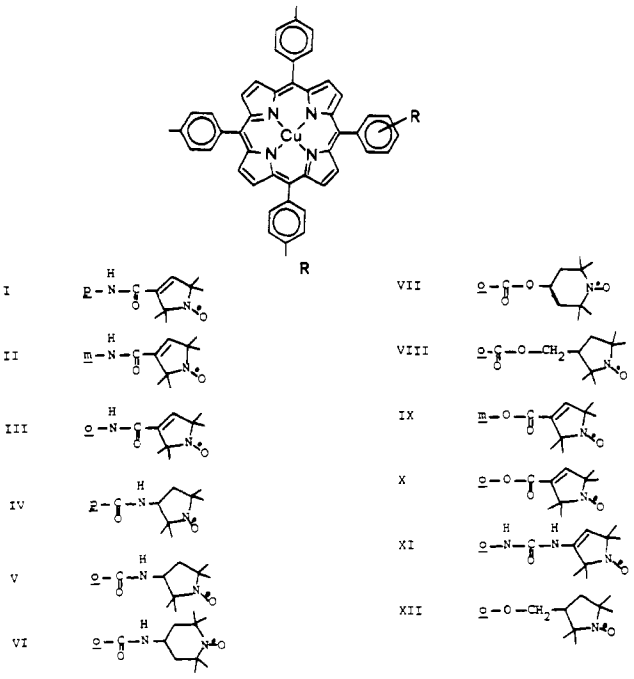
Derivatives of copper tetraphenylporphyrin have been prepared with nitroxyl groups attached via amide, ester, ether, or urea linkages to the ortho, meta, or para position of one phenyl ring. The magnitude of the copper–nitroxyl spin–spin coupling constant, J, was determined from the EPR spectra in low-viscosity solvents at room temperature. When the position of the phenyl ring substituent is varied, J decreases in the order ortho substituted $\gg$ para substituted $\geq$ meta substituted. The larger value of J for a substituent at the para position than at the meta position suggests that the spin–spin interaction occurs via the π orbitals of the phenyl ring. The much larger values of J for substituents at the ortho position than at the meta or para positions suggest an additional pathway for spin–spin interaction. The proximity of the ortho substituents to the porphyrin ring may result in overlap of orbitals on the substituents with the porphyrin π orbitals. In some of the complexes, there may also be a weak interaction between keto groups on the ortho substituents and the copper atom.

Introduction

We have recently reported the observation of high-resolution electron spin–electron spin splitting in the EPR spectra of spin-labeled copper(II) and silver(II) complexes in solution at room temperature.[1-5] Under these conditions the splittings are due to electron–electron-exchange interactions. The magnitude of the spin–spin coupling constant, J, was found to be sensitive to details of the molecular stereochemistry and electron delocalization.[4,5] Values of J between $\sim$2 and $\sim$3000 G ($\sim 2 \times 10^{-4}$ to $\sim$0.3 cm^{-1}) can be determined from the EPR spectra of spin-labeled copper complexes.[1] Thus interactions which are too weak to be readily probed by other techniques can readily be studied in spin-labeled metal complexes.

Several studies by other groups (see below) have found that unpaired spin density is larger at the ortho positions of the phenyl rings in paramagnetic metallotetraphenylporphyrins than at the meta and para positions. These results have led to proposals of specific orbital interactions between the ortho substituents and the porphyrin π system. In order to use metal–nitroxyl interactions to probe the spin-delocalization into the phenyl ring and to examine possible mechanisms for interaction of ortho substituents with the porphyrin ring, we have prepared a series of phenyl-substituted derivatives of copper tetraphenyl porphyrin which are spin-labeled at the ortho, meta, or para position of one phenyl ring, I–XII. This series permits comparison of amide linkages at the ortho, meta, and para positions, and a comparison of three amide, two ester, an ether, and a urea linkage at the ortho position. EPR spectra were taken in the presence and absence of coordinating solvents and as a function of temperature to provide information concerning the mechanism of spin–spin interaction.



Experimental Section

Physical Measurements. All spectra were obtained in dried purified solvents. Infrared spectra were obtained in Nujol mulls on a Perkin-Elmer 337 grating spectrometer. Visible spectra were obtained

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

compd	solvent (temp, °C)	J,[b] G	10^4J, cm^{-1}
I	$CHCl_3$	2.2	2.1
I	19:1 toluene/THF	2.2	2.1
I	pyridine	2.7	2.6
III	toluene (22)	125[c]	119
III	toluene (80)	350	334
III	$CHCl_3$	275	263
III	1:1 toluene/pyridine	~0	~0
III	pyridine	~0	~0
V	toluene (22)	1000[c]	955
V	toluene (80)	2000	1910
V	$CHCl_3$	800	764
V	1:1 toluene/pyridine	350	334
V	pyridine	100	96
V	butylamine	200	191
VI	toluene (22)	575[c]	549
VI	toluene (80)	650	620
VI	$CHCl_3$	600	573
VI	1:1 toluene/pyridine	200	191
VI	pyridine	25	24
VI	1:1 toluene/lutidine	400	382
VI	1:1 toluene/piperidine	400	382
VII	toluene (22)	525	500
VII	toluene (80)	800	763
VII	$CHCl_3$	750	716
VII	1:1 toluene/pyridine	175	167
VIII	toluene (22, 80)	300	276
VIII	$CHCl_3$	325	310
VIII	1:1 toluene/pyridine	200	191
X	benzene or toluene (22)	30 (65%),[c] 1300 (35%)[c]	29, 1240
X	toluene (80)	145 (90%), 1300 (10%)	138, 1240
X	$CHCl_3$	200 (65%), 1300 (35%)	191, 1240
X	pyridine	175 (75%), 1300 (25%)	167, 1242
XI	toluene	32 (25%),[c] 800 (50%),[c] 3500 (25%)[c]	31, 770, 3450
XI	$CHCl_3$	33 (35%), ≥800 (65%)	32, ≥770
XI	pyridine	42,[d] ≥800[d]	40, ≥770
XII	toluene (22, 80)	850[c]	812
XII	$CHCl_3$	1100	1050
XII	1:1 toluene/pyridine	800	764
XXIII	$CHCl_3$	2.8	2.7
XXIII	3:1 toluene/THF (20)	2.5	2.4
XXIII	3:1 toluene/THF (−60)	3.3	3.1
XXIII	pyridine	1.8	1.7

[a] Obtained from X-band spectra at room temperature unless otherwise noted. [b] Based on computer simulation of the EPR spectra. Uncertainty is ±10%. [c] Obtained from X-band and Q-band spectra. [d] Proportions of isomers cannot be determined due to severe broadening of the copper lines.

in chloroform solution on a Beckman Acta V spectrometer. Data are given below with wavelengths in nanometers and log ϵ in parentheses. Magnetic susceptibilities were measured at room temperature on a Bruker Faraday balance with 1-μg sensitivity with $HgCo(SCN)_4$ as calibrant.[6] Values of μ_{eff} in Bohr magnetons are given below with the temperature at which the measurement was made and the diamagnetic correction[7] (χ^{dia}) used in the calculation given in parentheses. A value of -700×10^{-6} was used as the diamagnetic correction for tetraphenylporphyrin[8] and a temperature-independent paramagnetism (TIP) of 60×10^{-6} was assumed for Cu(II). Samples for magnetic susceptibility measurements were used without grinding.[9] X-Band EPR spectra were obtained on a Varian E-9 spectrometer interfaced to a Varian 620L computer. Q-Band EPR spectra were obtained with a Harvey-Wells magnet and a Varian microwave bridge interfaced to the E-9 console and Varian 620L computer.[10] EPR spectra are shown in the figures with magnetic field increasing to the right. Values of the electron spin–electron spin coupling constant, J, are given in gauss and reciprocal centimeters in Table I. However, to facilitate comparison with the experimental field-swept spectra, values of J in the following discussion are given in gauss. ^1H NMR spectra were obtained on a Varian HA-100 spectrometer or a JEOL FX-90Q spectrometer in $CHCl_3$ solution. Chemical shifts are in parts per million from Me_4Si. Elemental analyses were performed by Spang Microanalytical Laboratory.

Preparation of Compounds. Porphyrins. The following porphyrins were prepared by literature methods: 5-(2-hydroxyphenyl)-10,15,20-tritolylporphyrin,[11] 5-(3-hydroxyphenyl)-10,15,20-tritolylporphyrin,[11] 5-(2-aminophenyl)-10,15,20-tritolylporphyrin,[12] and 5-(4-carboxyphenyl)-10,15,20-tritolylporphyrin.[13]

5-(4-Aminophenyl)-10,15,20-tritolylporphyrin. A 0.71-g (10^{-3} mol) sample of 5-(4-acetamidophenyl)-10,15,20-tritolylporphyrin[11] was refluxed for 4 h in 50 mL of 1:1 ethanol/concentrated aqueous HCl. After being cooled, the solution was added to 50 mL of saturated sodium acetate solution and extracted with 100 mL of $CHCl_3$. The $CHCl_3$ solution was washed twice with 20 mL of H_2O and dried over sodium sulfate. Shiny purple crystals were obtained by reducing the volume to 10 mL and adding 10 mL of methanol; yield 0.63 g (89%). IR: ν_{NH} 3330, 3385, 3475 cm^{-1}. VIS: 651 (3.53), 595 (3.41), 555 (3.74), 520 (3.95), 421 (5.32). NMR: −2.7 (br, porphyrin N-H), 2.68 (s, CH_3), 7.01, 7.53 (m, *m*-H), 7.98, 8.09 (m, *m*-H), 8.83 (s, pyrrole-H), 8.87 (AB pattern with J = 5 Hz, pyrrole H). Anal. Calcd for $C_{47}H_{37}N_5$: C, 84.03; H, 5.55; N, 10.42. Found: C, 83.22; H, 5.46; N, 10.15.

5-(3-Aminophenyl)-10,15,20-tritolylporphyrin. The mixed porphyrin was prepared from 18 g of tolualdehyde, 7.5 g of 3-nitrobenzaldehyde, and 13.4 g of pyrrole.[11] The nitroporphyrin was not readily separated from tetratolylporphyrin so the nitro group was reduced to an amino group by the method of Collman et al.[14] before separating the mixture. A 6.0-g sample of the mixture of porphyrins was dissolved in 200 mL of concentrated aqueous HCl, and 12 g of $SnCl_2$ was slowly added at room temperature. After 25 min of heating the mixture at 60–70 °C, the solution was cooled and neutralized with NH_4OH. To this was added 600 mL of $CHCl_3$, and the solution was stirred for 1 h. The $CHCl_3$ layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined $CHCl_3$ solutions were washed with NH_4Cl solution and water and dried over sodium sulfate. The volume of the $CHCl_3$ solution was reduced to 300 mL. After addition of 150 mL of heptane and 100 mL of ethanol, the mixture of porphyrins crystallized. The mixture was chromatographed on silica gel in $CHCl_3$. The second purple band contained the product. It was recrystallized from $CHCl_3$/MeOH; yield 12%, based on pyrrole. IR: ν_{NH} 3430, 3480, 3570 cm^{-1}. VIS: 650 (3.59), 592 (3.72), 554 (3.95), 518 (4.28), 421 (5.67). NMR: −2.6 (br, porphyrin N-H), 2.68 (s, CH_3), 7.01, 7.42, 7.52 (m, *m*-H, *p*-H), 7.62, 8.08 (m, *o*-H), 8.88 (m, pyrrole H). Anal. Calcd for $C_{47}H_{37}N_5$: C, 84.03; H, 5.55; N, 10.42. Found: C, 83.27; H, 5.58; N, 10.01.

Although the two aminoporphyrins appeared to give single bands by chromatography, the carbon analyses were consistently low. Since acceptable analyses were obtained for their copper complexes (see below), the reason for the low-carbon analyses of the free porphyrins was not pursued.

5-(2-Carboxyphenyl)-10,15,20-tritolylporphyrin. The porphyrin was prepared by the same procedure as the para carboxy analogue.[13] The mixture of porphyrins was chromatographed on silica gel in $CHCl_3$. Tetratolylporphyrin was eluted with $CHCl_3$. A solution of 19:1 $CHCl_3$/ethanol eluted a second purple band which contained the desired product. It was recrystallized from $CHCl_3$/methanol; yield 4% based on pyrrole. IR: $\nu_{C=O}$ 1675, ν_{NH} 3420 cm^{-1}. VIS: 651

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(3.59), 593 (3.54), 554 (3.76), 518 (4.07), 421 (5.47). NMR: −2.5 (br, porphyrin N-H), 2.67 (s, CH_3), 7.58, 7.66, 8.48 (m, *m*-H, *p*-H), 8.05, 8.73 (m, *o*-H), 8.81 (m, pyrrole H). Anal. Calcd for $C_{48}H_{36}N_2O_2$: C, 82.26; H, 5.18; N, 7.99. Found: C, 82.19; H, 5.27; N, 8.10.

Copper Porphyrins. The following complexes were prepared by refluxing a pyridine solution of porphyrin and 1.25 equiv of cupric acetate until the visible spectrum indicated complete conversion to the copper porphyrin. The products were purified by chromatography on alumina in $CHCl_3$ and recrystallized from $CHCl_3$/heptane.

Copper 5-(4-Aminophenyl)-10,15,20-tritolylporphyrin (XIII): yield 91%; IR ν_{NH} 3300, 3350 cm^{-1} (br); VIS 541 (4.52), 418 (5.88); EPR ($CHCl_3$) g = 2.0948, A_{Cu} = 87.0 G, A_N = 16.0 G. Anal. Calcd for $C_{47}H_{35}CuN_5$: C, 76.98; H, 4.81; N, 9.55. Found: C, 76.87; H, 4.92; N, 9.61.

Copper 5-(3-Aminophenyl)-10,15,20-tritolylporphyrin (XIV): yield 89%; IR ν_{NH} 3480, 3580 cm^{-1}; VIS 541 (4.43), 417 (5.75); EPR ($CHCl_3$) g = 2.0941, A_{Cu} = 86.5 G, A_N = 16.0 G. Anal. Calcd for $C_{47}H_{35}CuN_5$: C, 76.98; H, 4.81; N, 9.55. Found: C, 76.85; H, 4.84; N, 9.69.

Copper 5-(2-Aminophenyl)-10,15,20-tritolylporphyrin (XV): yield 82%; IR ν_{NH} 3490, 3590 cm^{-1}; VIS 541 (4.32), 417 (5.64); EPR ($CHCl_3$) g = 2.0945, A_{Cu} = 86.5 G, A_N = 16.0 G. Anal. Calcd for $C_{47}H_{35}CuN_5$. C, 76.98; H, 4.81; N, 9.55. Found: C, 77.00; H, 4.89; N, 9.61.

Copper 5-(2-Hydroxyphenyl)-10,15,20-tritolylporphyrin (XVI): yield 90%; IR ν_{OH} 3620 cm^{-1}; VIS 541 (4.52), 417 (5.89); EPR ($CHCl_3$) g = 2.0940, A_{Cu} = 86.3 G, A_N = 16.0 G; μ_{eff} = 1.87 μ_B (27 °C, $\chi^{dia} = -746 \times 10^{-6}$). Anal. Calcd for $C_{47}H_{34}CuN_4O$: C, 76.87; H, 4.67; N, 7.63. Found: C, 76.57; H, 4.57; N, 7.74.

The following complexes were prepared by adding 1.25 equiv of $CuCl_2$ in portions over a 20-min period to a refluxing DMF solution of 1.0 equiv of porphyrin. Reflux was continued until the visible spectrum showed no free porphyrin bands (about 15 min). The copper complexes were purified by chromatography on silica gel in $CHCl_3$ solution and recrystallized from $CHCl_3$/heptane.

Copper 5-(3-Hydroxyphenyl)-10,15,20-tritolylporphyrin (XVII): yield 89%; IR ν_{OH} 3500 cm^{-1} (br); VIS 541 (4.37), 417 (5.75); EPR ($CHCl_3$) g = 2.0940, A_{Cu} = 86.3 G, A_N = 16.0 G; μ_{eff} = 1.84 μ_B (27 °C, $\chi^{dia} = -746 \times 10^{-6}$). Anal. Calcd for $C_{47}H_{34}CuN_4O$: C, 76.87; H, 4.67; N, 7.63. Found: 76.80; H, 4.75; N, 7.56.

Copper 5-(4-Carboxyphenyl)-10,15,20-tritolylporphyrin (XVIII): yield 85%; IR ν_{CO} 1680 cm^{-1}; VIS 540 (4.42), 418 (5.74); EPR ($CHCl_3$) g = 2.0944, A_{Cu} = 86.5 G, A_N = 16.0 G. Anal. Calcd for $C_{48}H_{34}CuN_4O_2$: C, 75.62; H, 4.50; N, 7.35. Found: C, 75.45; H, 4.58; N, 7.41.

Copper 5-(2-Carboxyphenyl)-10,15,20-tritolylporphyrin (XIX): yield 85%; IR ν_{CO} 1685 cm^{-1}; VIS 541 (4.50), 418 (5.86); EPR ($CHCl_3$) g = 2.0941, A_{Cu} = 86.5 G, A_N = 16.0 G; μ_{eff} = 1.79 μ_B (26 °C, $\chi^{dia} = -760 \times 10^{-6}$). Anal. Calcd for $C_{48}H_{34}CuN_4O_2$: C, 75.62; H, 4.50; N, 7.35. Found: C, 75.55; H, 4.67; N, 7.23.

Copper 5-(3-Chloro-4-aminophenyl)-10,15,20-tritolylporphyrin (XX). $CuCl_2$ was reacted with 5-(4-aminophenyl)-10,15,20-tritolyporphyrin in DMF solution as described above. Chromatography of the crude product on silica gel in $CHCl_3$ solution gave two fractions with visible and EPR spectra characteristic of copper porphyrins. The smaller slower moving component was identical with XIII. The major component was identified as XX by demetalation and characterization of the free porphyrin XXI. VIS: 541 (4.52), 418 (5.88). IR: ν_{NH} 3300 cm^{-1}. EPR ($CHCl_3$): g = 2.0945, A_{Cu} = 87.0 G, A_N = 16.0 G.

5-(3-Chloro-4-aminophenyl)-10,15,20-tritolylporphyrin (XXI). The copper porphyrin XX was demetalated with $POCl_3$.[4] The crude material was chromatographed on silica gel in $CHCl_3$ solution and recrystallized from $CHCl_3$/MeOH; yield 77%. IR: ν_{NH} 3430, 3500, 3600 cm^{-1}. VIS: 650 (3.75), 5.94 (3.74), 557 (4.04), 519 (4.24), 422 (5.65). NMR: −2.7 (b, 2 H, NH), 2.70 (s, 9 *m*-H, CH_3), 7.54 (d, J = 8 Hz, 6 H, *m*-H, tolyl ring), 7.09 (d, J = 8 Hz, 1 H, *m*-H, unique ring), 8.09 (d, J = 8 Hz, 6 H, *o*-H, tolyl ring), 7.89 (d of d, J = 8 Hz, 2 Hz, 1 H, *o*-H, unique ring (signal for other ortho proton was not detected)), 8.84 (s, 4 H, pyrrole H), 8.87 (br, 4 H, pyrrole H). Mass spectrum: M^+/e 705.26 with isotope distribution characteristic of chlorine. Anal. Calcd for $C_{47}H_{36}N_5Cl$: C, 79.93; H, 5.14; N, 9.92; Cl, 5.02. Found: C, 79.78; H, 5.21; N, 9.73; Cl, 5.12.

Spin-Labeled Copper Porphyrins. Copper 5-(4-(((2,2,5,5-Tetramethyl-1-oxypyrrolin-3-yl)carbonyl)amino)phenyl)-10,15,20-tritolylporphyrin (I). To a cold solution of 0.184 g (1.0 mmol) of 2,2,5,5-tetramethyl-1-oxypyrrolinyl-3-carboxylic acid and 0.16 mL (2.0 mmol) of pyridine in 20 mL of dry benzene under N_2 atmosphere was added dropwise 0.24 g (2.0 mmol) of thionyl chloride in 5 mL of benzene during a 10-min interval. After 2 h of stirring at room temperature, the mixture was filtered and the solvent removed in vacuo. The solid residue was added to a solution of 72 mg (0.1 mmol) of XIII and 0.16 mL (2.0 mmol) of pyridine in dry THF and refluxed for 3 h. The solvent was removed in vacuo and the product was chromatographed on alumina-III with benzene as eluant. The second band contained the product which was recrystallized from $CHCl_3$/heptane; yield 17%. IR: ν_{CO} 1650, ν_{NH} 3250 cm^{-1}. VIS: 541 (4.37), 418 (5.74). Anal. Calcd for $C_{56}H_{47}CuN_6O_2$: C, 74.77; H, 5.27; N, 9.34. Found: C, 74.84; H, 5.35; N, 9.47.

Copper 5-(3-(((2,2,5,5-Tetramethyl-1-oxypyrrolin-3-yl)carbonyl)amino)phenyl)-10,15,20-tritolylporphyrin (II). The complex was prepared by the same procedure as I using copper porphyrin XIV; yield 30%. IR: ν_{CO} 1680, ν_{NH} 3450 cm^{-1}. VIS: 541 (4.27), 417 (5.64). Anal. Calcd for $C_{56}H_{47}CuN_6O_2$: C, 74.77; H, 5.27; N, 9.34. Found: C, 74.63; H, 5.35; N, 9.50.

Copper 5-(2-(((2,2,5,5-Tetramethyl-1-oxypyrrolin-3-yl)carbonyl)amino)phenyl)-10,15,20-tritolylporphyrin (III). The complex was prepared by the same procedure as I using copper porphyrin XV; yield 60%. IR: ν_{CO} 1680, ν_{NH} 3540 cm^{-1}. VIS: 541 (4.37), 417 (5.73). Anal. Calcd for $C_{56}H_{47}CuN_6O_2$: C, 74.77; H, 5.27; N, 9.34. Found: C, 74.79; H, 5.36; N, 9.53.

Copper 5-(4-(((2,2,5,5-Tetramethyl-1-oxypyrrolidin-3-yl)amino)carbonyl)phenyl)-10,15,20-tritolylporphyrin (IV). To a solution of 0.132 g (0.2 mmol) of XVIII in 50 mL of dry benzene was added 1.13 g (10 mmol) of oxalyl chloride. After 2 h of stirring at room temperature, the benzene was removed in vacuo. The residue was dried for 2 h in vacuo and then dissolved in 75 mL of dry THF. To this were added 1 mL of dry pyridine and 31 mg (0.2 mmol) of 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy. After 3 h of refluxing, the solvent was removed in vacuo. The product was chromatographed on silica gel in $CHCl_3$ solution. The first red band was collected; yield 64%. IR: ν_{CO} 1655, ν_{NH} 3340 cm^{-1}. VIS: 540 (4.25), 417 (5.61). μ_{eff} = 2.60 μ_B (26 °C, $\chi^{dia} = -843 \times 10^{-6}$). Anal. Calcd for $C_{56}H_{49}CuN_6O_2$: C 74.60; H, 5.48; N, 9.32. Found: C, 74.70; H, 5.49; N, 9.40.

Copper 5-(2-(((2,2,5,5-Tetramethyl-1-oxypyrrolidin-3-yl)amino)carbonyl)phenyl)tritolylporphyrin (V). The complex was prepared by the same procedure as IV using copper porphyrin XIX; yield 67%. IR: ν_{CO} 1660, ν_{NH} 3540 (br) cm^{-1}. VIS: 541 (4.13), 418 (5.50). μ_{eff} = 2.65 μ_B (26 °C, $\chi^{dia} = -843 \times 10^{-6}$). Anal. Calcd for $C_{56}H_{49}CuN_6O_2$: C, 74.60; H, 5.48; N, 9.32. Found: C, 74.50; H, 5.63; N, 9.37.

Copper 5-(2-(((2,2,6,6-Tetramethyl-1-oxypiperidin-4-yl)amino)carbonyl)phenyl)-10,15,20-tritolylporphyrin (VI). The complex was prepared by the same procedure as IV using copper porphyrin XIX and 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy; yield 60%. IR: ν_{CO} 1660, ν_{NH} 3520 cm^{-1}. VIS: 541 (4.61), 418 (5.99). μ_{eff} = 2.62 μ_B (26 °C, $\chi^{dia} = -855 \times 10^{-6}$). Anal. Calcd for $C_{57}H_{51}CuN_6O_2$: C, 74.77; H, 5.61; N, 9.18. Found: C, 74.58; H, 5.88; N, 9.14.

Copper 5-(2-(((2,2,6,6-Tetramethyl-1-oxypiperidin-4-yl)oxy)carbonyl)phenyl)-10,15,20-tritolylporphyrin (VII). The complex was prepared from the acid chloride of XIX and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy by the method described for IV. After removal of the solvent from the reaction mixture, the residue was dissolved in $CHCl_3$ and chromatographed on silica gel. The faster moving red band contained an unidentified side product, the second red band contained VII. The product was recrystallized from $CHCl_3$/heptane; yield 44%. IR: ν_{CO} 1710 cm^{-1}. VIS: 541 (4.31), 418 (5.68). Anal. Calcd for $C_{57}H_{50}CuN_5O_3$: C, 74.69; H, 5.50; N, 7.64. Found: C, 74.72; H, 5.68; N, 7.66.

Copper 5-(2-((((2,2,5,5-Tetramethyl-1-oxypyrrolidin-3-yl)methylene)oxy)carbonyl)phenyl)-10,15,20-tritolylporphyrin (VIII). The product was obtained from the acid chloride of XIX and 3-(hydroxymethyl)-2,2,5,5-tetramethylpyrrolidinyl-1-oxy by the method described for IV. When the reaction mixture was chromatographed on silica gel, the first red band contained an unidentified side product and the second red band contained VIII; yield 39%. IR: ν_{CO} 1730 cm^{-1}. VIS: 540 (4.27), 418 (5.64). Anal. Calcd for $C_{57}H_{50}CuN_5O_3$: C, 74.69; H, 5.50; N, 7.64. Found: C, 74.48; H, 5.36; N, 7.70.

Copper 5-(3-(((2,2,5,5-Tetramethyl-1-oxypyrrolin-3-yl)carbonyl)oxy)phenyl)-10,15,20-tritolylporphyrin (IX). The complex was prepared by the same procedure as I from copper complex XVII and 2,2,5,5-tetramethyl-1-oxypyrrolinyl-3-carboxylic acid; yield 48%. IR: ν_{CO} 1730 cm^{-1}. VIS: 541 (4.39), 418 (5.77). μ_{eff} = 2.59 μ_B (27 °C, $\chi^{dia} = -848 \times 10^{-6}$). Anal. Calcd for $C_{56}H_{46}CuN_5O_3$: C, 74.69; H, 5.15; N, 7.78. Found: C, 74.65; H, 5.16; N, 7.65.

Copper 5-(2-(((2,2,5,5-Tetramethyl-1-oxypyrrolin-3-yl)carbonyl)oxy)phenyl)-10,15,20-tritolylporphyrin (X). The complex was prepared by the same procedure as I from copper complex XVI and 2,2,5,5-tetramethyl-1-oxypyrrolinyl-3-carboxylic acid; yield 22%. IR: ν_{CO} 1750 cm^{-1}. VIS: 540 (4.34), 417 (5.71). Anal. Calcd for $C_{56}H_{46}CuN_5O_3$: C, 74.69; H, 5.15; N, 7.78. Found: C, 74.63; H, 5.12; N, 7.87.

Copper 5-(2-((((2,2,5,5-Tetramethyl-1-oxypyrrolin-3-yl)amino)carbonyl)amino)phenyl)-10,15,20-tritolylporphyrin (XI). To a solution of 0.15 g (0.2 mmol) of XV in 50 mL of dry THF was added 36 mg (0.2 mmol) of 3-isocyanato-2,2,5,5,-tetramethylpyrrolinyl-1-oxy.[15] After 3 h of refluxing, the solvent was removed under vacuum. The product was chromatographed on silica gel in $CHCl_3$ and recrystallized from CH_2Cl_2/hexane; yield 60%. IR: ν_{CO} 1670 (br), ν_{NH} 3470 cm^{-1}. VIS: 541 (4.15), 417 (5.49). μ_{eff} = 2.59 μ_B (26 °C, $\chi^{dia} = -842 \times 10^{-6}$). Anal. Calcd for $C_{56}H_{48}CuN_7O_2$: C, 73.54; H, 5.29; N, 10.72. Found: C, 73.40; H, 5.44; N, 10.74.

Copper 5-(2-(((2,2,5,5-Tetramethyl-1-oxypyrrolidin-3-yl)methylene)oxy)phenyl)-10,15,20-tritolylporphyrin (XII). To a solution of 175 mg (0.25 mmol) of 5-(2-hydroxyphenyl)-10,15,20-tritolylporphyrin in 15 mL of DMF was added 120 mg of crushed KOH pellets. To this was added dropwise 75 mg (0.25 mmol) of 3-(bromomethyl)-2,2,5,5-tetramethylpyrrolidinyl-1-oxy[16] in 5 mL of DMF during 1 h. After 30 h of stirring at room temperature, 70 mL of water was added and the reaction mixture was extracted with $CHCl_3$ (4 × 25 mL). The combined extract was washed with water. The product was chromatographed on alumina in $CHCl_3$ and recrystallized from $CHCl_3$/hexane; yield 45%. IR: (ether) 1036 cm^{-1}. The copper complex was prepared by the method reported for XVII–XX; yield 50%. IR: (ether) 1000 cm^{-1}. VIS: 539 (4.35), 418 (5.69). Anal. Calcd for $C_{56}H_{50}CuN_5O_2$: C, 75.70; H, 5.67; N, 7.88. Found: C, 75.69; H, 5.58; N, 7.85.

Computer Simulations

The EPR spectra were simulated with use of the computer program CUNO.[17] The Hamiltonian used in the calculation is given in eq 1, where g_1 and g_2 are the g values of the metal

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

and nitroxyl 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 nuclear 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 the nuclear spin of the nitroxyl nitrogen, and all other symbols are defined as in ref 17. 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. So that visual comparison with the field-swept experimental spectra could be facilitated, 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.

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

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

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

The conversion factor for A_N is the same as for A_M. Only the absolute value of J can be determined from these experiments.

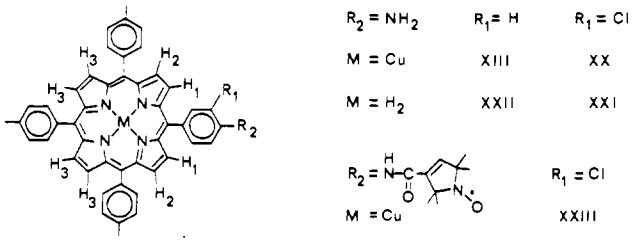
The electron–electron coupling results in AB quartet patterns in the EPR spectra. The lines in the spectra are referred to as copper or nitroxyl depending on the nature of the transitions as J approaches 0. When J is small relative to the g-value difference between the copper and nitroxyl electrons, 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 0 and the positions of the inner copper and inner nitroxyl lines become equal.

The parameters for CuTPP (g = 2.0944, A_{Cu} = 86.5 G, and A_N = 16.0 G in toluene and g = 2.0994, A_{Cu} = 82.0 G, and A_N = 15.5 G in pyridine) were used as starting parameters in simulating the EPR spectra of the spin-labeled copper porphyrins. The nitroxyl input parameters were g = 2.0059 and A_N = 15.5–16.2 G for the piperidine rings and A_N = 14.3–14.9 G for the pyrroline and pyrrolidine rings. Little or no adjustment of these parameters was required to match the observed spectra. For most of the spectra where J was greater than about 100 G, the outer lines of the AB pattern were not observed. In these cases the value of J is based on the simulation of the inner copper and nitroxyl lines which are largely superimposed at X-band and partially superimposed at Q-band. The appearance of the simulated spectrum depends on the assumed line widths as well as the value of J. Thus the values of J for these compounds are less certain than for the cases where the outer lines were observed.

Results and Discussion

The spin-labeled copper porphyrins were prepared by standard methods. In all cases, except for the one discussed below, the expected products were obtained in good yield and chromatographic purification indicated a single major product.

Attempts to prepare the copper porphyrin XIII by reaction



of $CuCl_2$ with the amino porphyrin XXII in refluxing DMF resulted in two products which were separated by chromatography in $CHCl_3$ solution on alumina. The second and smaller fraction moved on TLC plates (alumina or silica gel) the same as the single product obtained from XXII and copper acetate in pyridine solution. Demetalation of these products with $POCl_3$[4] regenerated the starting porphyrin, XXII. Thus the second fraction from the DMF reaction and the product of the pyridine reaction were identified as the copper porphyrin XIII. Other characterization data were consistent with this assignment. Demetalation of the major product from the DMF reaction (XX) gave free porphyrin XXI. A high-res-

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olution mass spectrum of XXI indicated that it differed from porphyrin XXII by the replacement of one hydrogen by a chlorine. Elemental analyses also were consistent with the presence of a chlorine. The position of the substitution was determined by a comparison of the ^1H NMR spectra of porphyrins XXI and XXII. The pyrrole protons H_1–H_3 in these unsymmetrically substituted porphyrins are nonequivalent if the electron-donating properties of the substituents on the unique phenyl ring are different from the electron-donating properties of the methyl groups on the tolyl rings.[11,13] In the NMR spectrum of the starting porphyrin XXII, there is a singlet at 8.83 ppm for H_3 and an AB pattern centered at 8.87 ppm for H_1 and H_2 with $\Delta\nu$ = 0.07 ppm and J = 7 Hz. In the NMR spectrum of XXI, the chemical shift difference between H_1 and H_2 is sufficiently small that the AB pattern looks like a single broadened line. The signal for H_3 is unchanged from that in XXII. Substitution of a chlorine on the unique phenyl ring would partially offset the electron-donating effect of the amino group, thereby making the net electron density in the unique ring similar to that in the tolyl rings. This would result in similar chemical shifts for H_1 and H_2. The amino group in XXII shifts the signals for the ortho and meta protons on the unique phenyl ring (7.76, 7.05 ppm) upfield from the signals due to the ortho and meta protons on the tolyl rings (8.10, 7.54 ppm). In XXI, resolved signals were observed for one ortho proton and one meta proton. The splitting of the ortho signal (J = 8, 2 Hz) indicates that there is a proton on the other ortho position of the ring although the signal must be obscured by one of the more intense signals. Thus the chlorine is on the meta position, adjacent to the amino group. The observed chemical shifts for the ortho and meta protons on the unique ring (7.89, 7.09 ppm) are closer to those for the ortho and meta protons on the tolyl ring (8.10, 7.55 ppm) than was observed for XXII, consistent with chlorine substitution on the unique ring in XXI. Either the $CuCl_2$ or the HCl produced by the metalation reaction could be the source of the chloride. In either case it is surprising to find chloride attack on the electron-density-rich amino-substituted ring. However, protonation of the amino group could reduce the electron density in the ring and facilitate the attack. If, in addition, there is significant H^+Cl^- ion pair formation, interaction of the H^+ with the amino group could position the Cl^- near the meta carbon which might facilitate the attack. In the absence of mechanistic data, this suggestion must be regarded as speculative. Nevertheless, the observation of chloride attack indicates that caution must be exercised in preparing complexes of amino-substituted porphyrins.

Complexes Spin-Labeled at the Meta or Para Position. The EPR spectra of the meta and para spin-labeled copper porphyrins II, IV, and IX in $CHCl_3$ solution at room temperature are superpositions of a sharp three-line nitroxyl pattern and a four-line copper spectrum, indicating that the electron–electron coupling constant in these complexes is $<\sim 1$ G. The room-temperature EPR spectra of the para-spin-labeled complex I in $CHCl_3$ or 19:1 toluene/THF solution at room temperature show a doublet of triplets in the nitroxyl region consistent with J = 2.2 G. In pyridine solution the value of J for I increases to 2.7 G. The larger value of J for I than for II indicates that the exchange interaction for the same nitroxyl ring and nitroxyl–porphyrin linkage is greater when the nitroxyl is attached at the para position than at the meta position. This suggests that the spin–spin interaction is via the π orbitals of the phenyl ring.

When the temperature is decreased, the value of J for I in 19:1 toluene/THF solution increases, and the line widths for the nitroxyl signals become unequal (Figure 1). The line widths for the inner lines of the AB pattern increase to higher field while the line widths for the outer lines decrease to higher field. This pattern of asymmetric broadening is the opposite of that observed for a spin-labeled pyridine adduct of copper bis(hexafluoroacetylacetonate)[2] and for a copper porphyrin spin-labeled at the pyrrole position.[5] For the latter two cases, the line widths for the inner triplet decreased to higher field and the line widths for the outer triplet increased to higher field. The asymmetric line broadening of the spectra for the spin-labeled copper complexes probably arises from incomplete motional averaging of terms which depend on the sign of J and the relative orientations of the copper and nitroxyl as well as g and A anisotropy.[5] 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.

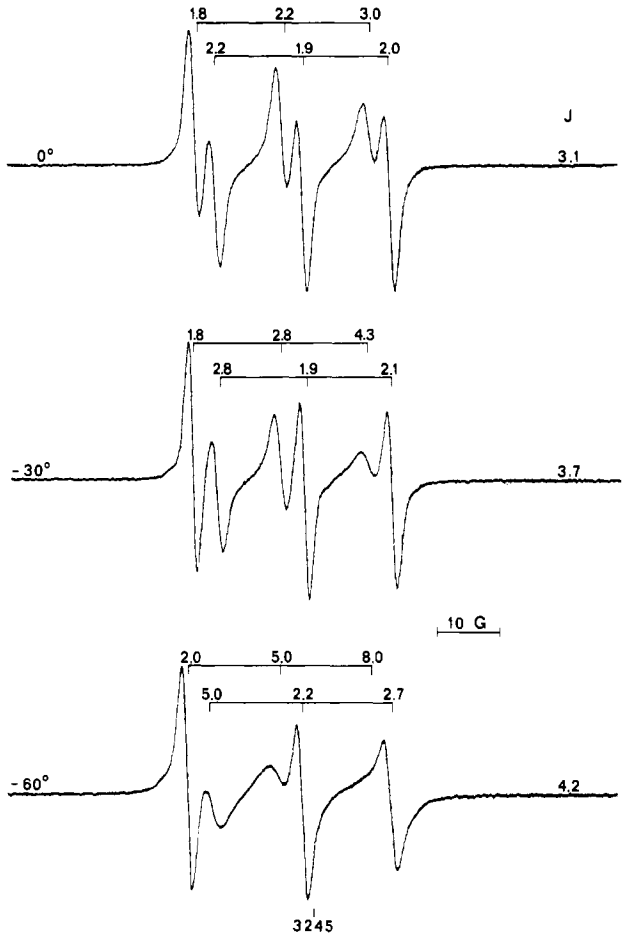

Figure 1. X-Band (9.11-GHz) EPR spectra of the para-spin-labeled copper porphyrin I in 19:1 toluene/THF solution as a function of temperature. Experimental spectra were obtained with 100 G scan width, 1 mW power, and 0.05 G modulation amplitude. Peak-to-peak line widths obtained by computer simulation are indicated above each line. J is given in gauss.

The meta-chlorinated copper complex XX was spin-labeled to give XXIII. The EPR spectra of XXIII were similar to those of I which does not have the chlorine in the meta position of the phenyl ring but the values of J are slightly different. In $CHCl_3$ solution the value of J for XXIII (2.8 G) is greater than that for I (2.2 G), but in pyridine solution the value of J for XXIII (1.9 G) is smaller than that for I (2.7 G). When a toluene/THF solution of XXIII was cooled from 20 to −60 °C, the value of J increased from 2.5 G to 3.3 G which is a smaller change than was observed for I (2.2 G at 20 °C and 4.2 G at −60 °C). The line-width changes for XXIII as a function of temperature were similar to those observed for I (cf. Figure 1). The changes in J for I and XXIII as a function of temperature and solvent may reflect variations in the conformation of the amide linkage relative to the phenyl ring. Larger values of J would be expected when the amide linkage

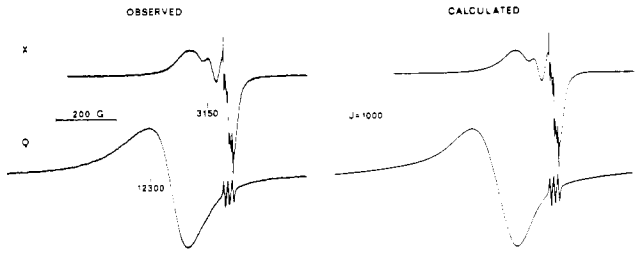

Figure 2. EPR spectra of the ortho-spin-labeled copper porphyrin V in toluene solution at room temperature. The X-band (9.11 GHz) spectrum is an 800 G scan obtained with 20 mW power and 0.63 G modulation amplitude. The Q-band (35.25 GHz) spectrum is a 1000 G scan obtained with 1.5 mW power and 2.5 G modulation amplitude. J is given in gauss. The simulated spectra include the contribution from "free" nitroxyl with a concentration 0.1% of the concentration of V.

is more nearly coplanar with the phenyl ring.[18] The bulky meta chlorine may prevent the amide group in XXIII from achieving conformations which are as favorable for spin–spin interaction as are available to I at low temperature. However, the solvent dependence of J cautions against a simple interpretation.

Complexes Spin-Labeled at the Ortho Position. When the nitroxyl group is attached to the ortho position of the phenyl ring, the EPR spectra are substantially different from the spectra of the complexes in which the nitroxyl group is attached to the meta or para position. The EPR spectra of the ortho-spin-labeled copper porphyrin V in toluene solution at X-band and Q-band frequencies are shown in Figure 2. The outer lines of the AB pattern were not observed at either frequency. The sharp three-line pattern present in both spectra is due to nitroxyl which is not interacting with copper (subsequently denoted as "free" nitroxyl) which may be due to a small amount of impurity or decomposition. At X-band, the spectrum approaches the four-line pattern with a copper hyperfine splitting of $^1/_2A_{Cu}$ which occurs when J is much larger than A_{Cu} (86 G) and much larger than the g-value difference between the copper and nitroxyl electrons. At Q-band, a broad partially averaged signal occurs at a g-value intermediate between the g values for the copper and nitroxyl electrons. Both the X-band and Q-band spectra could be computer simulated with J = 1000 G as shown in Figure 2. Since the appearance of the simulated spectrum is dependent on the assumed line widths as well as J, there is an uncertainty in the value of J of about ±75 G. As the temperature is increased between 20 and 80 °C, the value of J in toluene solution increases. At 80 °C the X-band spectrum is a well-resolved four-line pattern characteristic of $J \approx 2000$ G. At room temperature the value of J for V in $CHCl_3$ solution is similar to that in toluene solution. However, in the presence of coordinating solvents such as pyridine or butylamine, the value of J is greatly reduced (cf. Table I).

The behavior of the ortho-spin-labeled copper porphyrin VI is similar to that of V. The two complexes differ only in the size of the nitroxyl ring. The value of J for VI in $CHCl_3$ or toluene solution at room temperature is about 575 G. In toluene solution the value of J increases to about 650 G at 80 °C. To determine whether the large value of J for VI was due to intermolecular copper-nitroxyl interactions in porphyrin dimers, we took EPR spectra of VI in $CHCl_3$ solution in the presence of a tenfold excess of the diamagnetic ortho amino porphyrin. To whatever extent dimerization occurs, the large excess of free porphyrin would be expected to cause most of the copper porphyrins to interact with a diamagnetic porphyrin

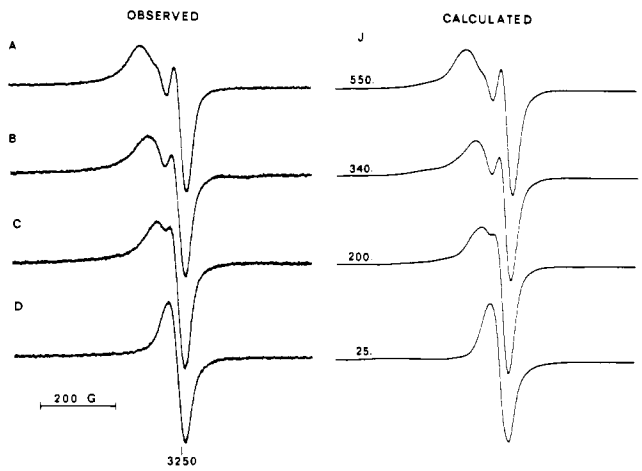

Figure 3. X-Band (9.11-GHz) EPR spectra of the ortho-spin-labeled copper porphyrin VI (10^{-3} M) at room temperature: (a) toluene solution, 800 G scan, 90 mW power, and 1.6 G modulation amplitude; (b) toluene solution containing 2000:1 ratio of pyridine/VI, 800 G scan, 20 mW power, and 2 G modulation amplitude; (c) toluene solution containing 10000:1 ratio of pyridine/VI, 800 G scan, 50 mW power, and 1.6 G modulation amplitude; (d) pyridine solution, ~ 20000:1 ratio of pyridine/VI, 800 G scan, 15 mW power, and 2 G modulation amplitude.

instead of another copper porphyrin. Since the excess porphyrin caused no change in the EPR spectrum, it seems unlikely that the copper–nitroxyl interaction in VI is intermolecular. Further, dimerization would be expected to decrease with increasing temperature. Thus if the copper–nitroxyl interaction were intermolecular, J would be expected to decrease with increasing temperature which is the opposite of the observed temperature dependence.

In pyridine solution the value of J for VI is reduced to about 25 G. To examine the effect of pyridine on the value of J, we took EPR spectra for 10^{-3} M VI in toluene solution containing varying amounts of pyridine. No appreciable change was observed in the EPR spectra upon addition of 10, 50, or 100 equiv of pyridine. However, addition of larger amounts of pyridine led to a gradual decrease in J (Figure 3). To determine whether the change in J was due to coordination of pyridine to the copper porphyrin or a general solvent effect, it was necessary to have an estimate of the pyridine binding constant. The shifts of the bands in the visible spectra of copper tetraphenylporphyrin (CuTPP) due to pyridine coordination are too small to permit a determination of the binding constant.[19] However, coordination of pyridine to CuTPP causes a decrease in the value of the copper hyperfine coupling constant from 86.5 to 82 G. The changes in A_{Cu} as a function of pyridine concentration indicate a value of about 1 for the pyridine binding constant. Since the polarity of the various solvent mixtures differ considerably, the results permit only a rough estimate of the binding constant. However, a value of about 1 seems reasonable since the binding constant for piperidine to copper mesoporphyrin IX dimethyl ester is 21 in THF solution.[20] A plot of the values of A_{Cu} observed for CuTPP vs. J for VI at the same mole ratio of pyridine to porphyrin in toluene solution gave a linear correlation. Thus the changes in J for VI correlate with coordination of pyridine to copper.

In the spin-labeled copper porphyrin VII, the nitroxyl group is attached to the ortho position of the phenyl ring by an ester linkage which is isoelectronic with the amide linkage in VI. The values of J for VII are similar to those for VI. Analogous

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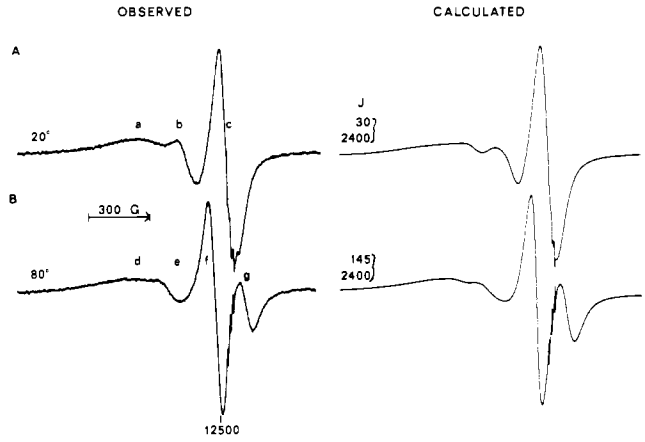

Figure 4. Q-Band (35.25-GHz) EPR spectra of the ortho-spin-labeled copper porphyrin X in toluene solution. Experimental spectra were obtained with 1500 G scan width, 15 mW power, and 2 G modulation amplitude: (a) 22 °C; (b) 80 °C. Assignments of peaks are discussed in text. J is given in gauss. The simulated spectra include the contribution from "free" nitroxyl with a concentration 0.9% of the concentration of X.

to the behavior of VI, the values of J for VII in toluene solution increase with increasing temperature and in the presence of pyridine the value of J is greatly reduced. The similarity between the ester and amide linkages is consistent with results obtained for another series of spin-labeled copper porphyrins.[5] In the ortho-spin-labeled copper porphyrin VIII, there is a CH_2 group between the ester linkage and the nitroxyl ring. For ester VIII the value of J in toluene solution is smaller than that for the ester VII. Previous results have also shown that an additional CH_2 group generally reduces the value of J.[3,5] In the presence of pyridine, the value of J for VIII is substantially reduced. Thus all of the complexes derived from the ortho carboxy porphyrin (V–VIII) have values of J which are much smaller in 1:1 toluene/pyridine and in pyridine solutions than in noncoordinating solvents such as toluene or chloroform.

In the spin-labeled copper complex III, the nitroxyl group is attached to the ortho position of the phenyl ring by an amide linkage as in V and VI, but in III the amide was obtained from the amino porphyrin whereas in V and VI the carboxy porphyrin was used. The values of J for III in $CHCl_3$ and toluene solutions are 125 and 275 G, respectively, which are substantially smaller than those for the amide VI. For the analogous linkages at the para position, J was larger for I than for IV. If the mechanism of spin–spin interaction were the same at the ortho position as at the para position it would be expected that the relative order of the values of J would be the same for the two linkages at the ortho position and at the para position and that J would be greater for III than for V. The reversal of this order suggests that different factors control the magnitude of J at the ortho and para positions.

In the spin-labeled copper complex XII, the nitroxyl group is attached to the phenyl ring by an ether linkage. The values of J for XII in $CHCl_3$ and toluene solutions are 850 and 1100 G, respectively. These values are similar to the ones observed for the complexes with ester and amide linkages. However, unlike the behavior of previously discussed complexes, the values of J for XII are not appreciably changed by the presence of pyridine or by changes in temperature. Possible explanations for these differences are discussed below.

At both X-band and Q-band, the EPR spectra of the spin-labeled copper complex X indicate the presence of two components with different values of J. The Q-band EPR spectrum of X in toluene solution at room temperature is given in Figure 4a. The simulated spectrum was obtained with J = 30 G (65%) and J = 1300 G (35%). The copper lines in the spectra are severely broadened due to incomplete motional averaging which results in lineshapes that are neither Lorentzian nor Gaussian. This causes a discrepancy between the observed and calculated line shapes. Due to the overlap of the spectra and the inability to detect the outer lines of the AB pattern for the component with the larger value of J, there is an uncertainty of about ±30% in the values of J. The features of the spectra which are labeled in Figure 4a are assigned as follows: a , inner and outer copper lines for J = 30 G; b, inner copper and inner nitroxyl lines for J = 1300 G; c, inner and outer nitroxyl lines for J = 30 G. The sharp three-line pattern at about 12550 G is due to free nitroxyl with a concentration approximately 1% of the concentration of X. As the temperature was increased from 20 to 80 °C, the value of J for one component increased from 30 to 145 G and its population increased from about 65% to about 90%. The value of J for the second component did not appear to be temperature dependent, but the small populations at high temperature and the overlap of the lines made an accurate determination of J difficult. The features of the spectra at 80 °C (Figure 4b) are assigned as follows: d, inner and outer copper lines for J = 145 G; e, inner copper and inner nitroxyl lines for J = 2400 G; f, inner nitroxyl lines for J = 145 G; g, outer nitroxyl lines for J = 145 G. The temperature-dependent changes in the EPR spectra were fully reversible. The changing populations of the two components as a function of temperature would be consistent with the presence of two conformations of X which differ slightly in energy. To check for the possibility of separable components or impurities, we ran thin-layer chromatograms of X on alumina, silica gel, and Whatman C_{18} reverse-phase plates. In a wide range of solvents X moved as a single spot. It therefore seems likely that the two values of J arise from different conformations of X.

The nitroxyl region of the X-band EPR spectrum of XI in toluene solution at room temperature is a doublet of triplets consistent with J = 32 G. The rest of the spectrum is broad and poorly resolved but could not be computer simulated by using only J = 32 G. A second component with $J \geq 800$ (~65%) was required to match the observed spectra. Similar spectra were obtained in $CHCl_3$ and pyridine solution. The Q-band EPR spectra of XI in toluene solution at 22 °C (Figure 5a) also indicate the presence of more than one component. The computer simulation shown in Figure 5b was obtained for a mixture of three components: J = 32 G (25%), J = 800 G (50%), and J = 3500 G (25%). Parts c–e of Figure 5 show the computer-calculated contributions for the three components individually. The weak lines marked by the arrows in Figure 5a are consistent with a few percent of an additional component with J = 175 G which was not included in the computer simulations. When the temperature was increased from 20 to 80 °C, the smallest value of J increased from 32 to 50 G and the population of this component decreased from ~25% to ~15%. Due to the large amount of overlap in the spectra, it was difficult to determine the effect of temperature on the other values of J. However, the values do not appear to change greatly with temperature. Thin-layer chromatography of XI on silica gel, alumina, and Whatman C_{18} reverse phase plates in a variety of solvents gave a single spot. If the four components observed in the EPR spectra were due to chemically different species, some chromatographic separation would be expected under the range of conditions examined. The inability to physically separate the components observed in the EPR spectra suggests that the urea linkage can adopt a range of conformations which interconvert slowly on the EPR time scale and that the magnitude of the spin–spin interaction depends on the molecular conformation.

Possible Mechanisms of Spin–Spin Interaction. Several features of the spectra described above suggest that the

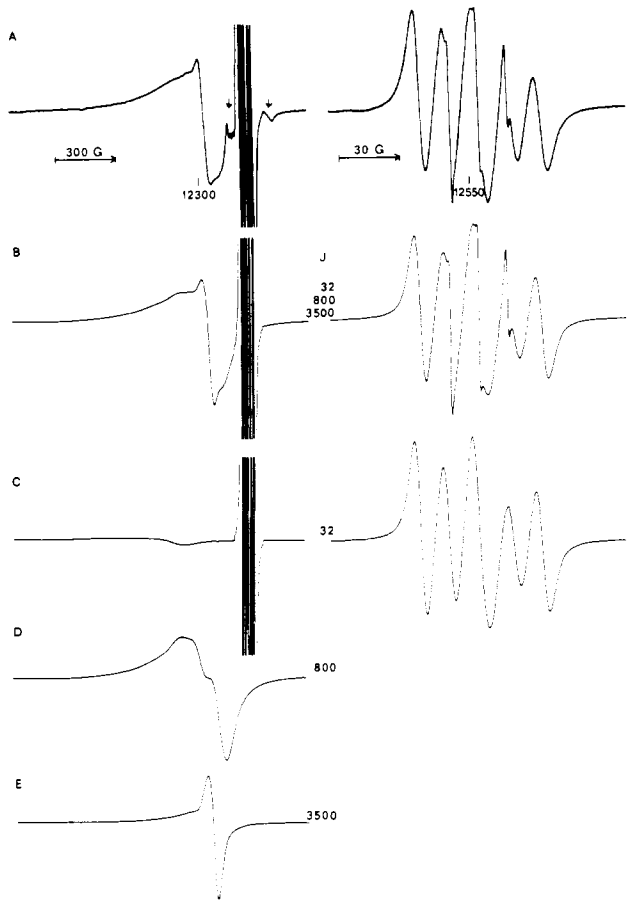

Figure 5. (a) Q-Band (35.25-GHz) EPR spectra of the ortho-spin-labeled copper porphyrin XI in toluene solution at room temperature. The full spectrum was obtained with 1500 G scan width, 158 mW power, and 2 G modulation amplitude. The expansion of the nitroxyl region was obtained with 150 G scan width, 15 mW power, and 0.5 G modulation amplitude. The arrows indicate the contribution from a component with $J \approx 170$ G which was not included in the computer simulations. (b) Simulated spectrum including contributions for J = 32 G (25%), J = 800 G (50%) J = 3500 G (25%) and "free" nitroxyl (0.6%). (c) Contribution to simulated spectrum for J = 32 G. (d) Contribution to simulated spectrum for J = 800 G. (e) Contribution to simulated spectrum for J = 3500 G.

mechanism of spin–spin interaction for the ortho-spin-labeled porphyrins is different from that for the meta- or para-spin-labeled porphyrins. (1) The larger value of J for the para-spin-labeled porphyrin I than for the analogous meta-spin-labeled porphyrin II suggests that the spin–spin interaction at these positions is dominated by interaction through the π orbitals of the phenyl ring. However, if this were the primary mechanism of interaction for the ortho-substituted porphyrins, the magnitude of J for the ortho-spin-labeled complexes would be expected to be similar to the values of J for the meta- and para-substituted complexes. The observed values of J are much larger for the ortho-substituted complexes than for analogous meta- or para-substituted complexes. (2) For the para-substituted complex I and for other spin-labeled copper complexes,[5,18] the values of J in pyridine solution are slightly greater than the values of J in toluene or $CHCl_3$ solution. However, for most of the ortho-substituted complexes, the values of J in pyridine solution are much less than the values of J in toluene or $CHCl_3$ solution. (3) For the para-substituted complexes, J is greater for the amide (I) derived from the amino porphyrin than for the amide (IV) derived from the carboxylic acid porphyrin. The pattern is reversed at the ortho position such that J for the amide (V) derived from the carboxylic acid porphyrin is greater than J for the amide (III) derived from the amino porphyrin. Furthermore ENDOR spectra of CuTPP have shown that the unpaired spin density on the phenyl ortho protons is less than that on the pyrrole protons.[21] Attachment of a spin label by an ester or amide linkage to the pyrrole position of a copper porphyrin results in values of J between 75 and 200 G.[18] On the basis of ENDOR results, a smaller value of J would be expected for attachment at the ortho position of the phenyl ring than at the pyrrole position unless a more effective mechanism of spin–spin interaction were available for the ortho-substituted porphyrins than for the pyrrole-substituted porphyrins.

Mispelter et al. have observed that the unpaired spin density at the ortho carbons in FeTPPCl is much larger than at the meta or para carbons.[22] They proposed that the larger spin density on the ortho carbon could be due to mixing of the meso carbon π orbitals with the σ-bonding orbitals of the ortho carbons.[22] Fajer et al. have also interpreted the large spin density on the ortho protons of the phenyl rings in the porphyrin cation radicals $ZnTPP^{+\cdot}$ and $MgTPP^{+\cdot}$ as arising from interaction of the π orbitals on the meso carbon with the σ orbitals of the perpendicular phenyl ring.[23,24] We have previously observed that the hyperfine coupling constant, A_N, between the copper unpaired electron and the porphyrin nitrogens can be used as an approximate indicator of the extent of unpaired electron delocalization into the porphyrin ring.[4] When pyridine coordinates to CuTPP, the value of A_N decreases from 16.0 to 15.5 G which suggests only a small change in the electron spin density in the porphyrin ring. Also, coordination of pyridine causes such small shifts in the visible spectra of CuTPP that the binding constant could not be determined from the visible spectra.[19] Thus it seems unlikely that shifts in the π-orbital energies due to pyridine coordination are sufficiently large to drastically effect the extent of the porphyrin π-phenyl σ mixing. Coordination of pyridine may cause some changes in the conformation of the porphyrin ring. However, the bulky ortho substituents are likely to force an appproximately perpendicular conformation of the phenyl ring. Thus it seems unlikely that conformational changes in the porphyrin ring greatly disrupt the porphyrin π–phenyl σ interaction in these cases. Although such an interaction may contribute to the large values of J for the ortho-substituted complexes, it does not appear to provide a plausible explanation for the large changes in the value of J which occur when pyridine coordinates to most of the ortho-spin-labeled copper porphyrins.

In a series of zinc tetraphenylporphyrin derivatives with amide groups attached to the ortho position of one phenyl ring, Walker and Benson have noted that there appears to be an orbital interaction between the amide group and the porphyrin π system.[25] When the amide linkage was part of a side arm to a coordinating pyridyl group, an X-ray crystallographic study showed that the amide nitrogen was 2.9 Å from the meso carbon and the carbonyl group was perpendicular to the phenyl ring.[26] The distances between the porphyrin ring atoms and the amide nitrogen or oxygen are longer than ordinary bond lengths but are not inconsistent with the weak interactions discussed in this paper. The exact orientation of the carbonyl group in this case is probably strongly influenced by the coordination of the pyridyl group to the zinc. In the spin-labeled complexes (V–VIII) derived from the ortho carboxylic acid

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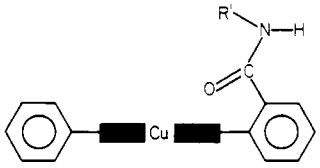
porphyrin, the carbonyl group of the amide or ester linkage is in close proximity to the porphyrin π system as indicated by the side-on sketch of V–VIII given in XXIV. This



XXIV

proximity could provide an effective orbital overlap pathway for spin–spin interaction. When the carbonyl group is one atom away from the phenyl carbon, as in III, it would be less favorably oriented for overlap with the π system which might explain the smaller value of J for III than for V. The degree of overlap between the carbonyl group and the porphyrin orbitals would be sensitive to the conformation of the ester or amide groups. If coordination of pyridine to the copper forced changes in the conformation of the ring substituents due perhaps to some out of plane movement of the copper, the value of J might be greatly reduced. In the ether XII there is no carbonyl group but the value of J is still large. In this case there may be overlap of an ether oxygen lone pair with the porphyrin π orbitals. Since the ether oxygen in XII is in such close proximity to the π system, the extent of overlap may be less sensitive to small conformational changes of the porphyrin which might explain the observation that J for XII is not strongly dependent on temperature or on pyridine coordination. A similar interaction between the ester oxygen in X and the porphyrin plane might account for the large value of J for one conformer of X. Molecular models of the amide III indicate that steric interaction of the amide proton with the pyrrole proton and the meta proton on the phenyl ring makes it difficult for the amide linkage to adopt a conformation which could permit interaction of the nitrogen lone pair with the porphyrin π system. This steric interaction could explain why the value of J is smaller for the amide III than for one conformation of the ester X. In another porphyrin system we have observed that differences in steric interference correlated with a smaller value of J through an amide linkage than through an analogous ester linkage.[18] Thus all of the data on the ortho-substituted complexes appear to be consistent with overlap of orbitals on the substituent with the porphyrin π system. However, the evidence available cannot rule out other possibilities.

Molecular models of the esters and amides V–VIII indicate that relatively unstrained conformations are accessible which position the carbonyl oxygen about 4.5 Å away from the copper. Although this distance is much longer than a normal copper–oxygen bond length, there might be a weak copper–oxygen interaction. Coordination of pyridine to the copper might decrease the copper–oxygen interaction since a 5-coordinate copper porphyrin pyridinate would have less affinity for an additional ligand than would a 4-coordinate copper porphyrin. This could account for the large decrease in J for V–VIII which occurs when pyridine is coordinated. In III the carbonyl oxygen would be further from the copper than in V which could account for the smaller value of J for III than for V. Since an amide oxygen would be expected to be more basic than an ester oxygen, the copper–oxygen interaction would be expected to be stronger in VI than VII.[27] However, the values of J are similar for VI and VII. The absence of a keto group in XII indicates that however important a copper–oxygen interaction might be in some of the other complexes it cannot be the only mechanism for spin-delocalization onto the ortho substituents.

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Registry No. I, 78280-04-3; II, 78280-05-4; III, 78280-06-5; IV, 78280-07-6; V, 78280-08-7; VI, 76451-31-5; VII, 78280-09-8; VIII, 78280-10-1; IX, 78280-11-2; X, 78280-12-3; XI, 78280-13-4; XII, 78280-14-5; XIII, 78280-15-6; XIV, 78280-16-7; XV, 78280-17-8; XVI, 73169-97-8; XVII, 73169-96-7; XVIII, 78280-18-9; XIX, 73469-15-5; XIX acid chloride, 78280-19-0; XX, 78280-20-3; XXI, 78265-40-4; XXII, 73170-32-8; XXIII, 78280-21-4; 5-(3-aminophenyl)-10,15,20-tritolylporphyrin, 78265-41-5; 5-(2-carboxyphenyl)-10,15,20-tritolylporphyrin, 78265-42-6; 5-(4-acetamidophenyl)-10,15,20-tritolylporphyrin, 57412-12-1; 2,2,5,5-tetramethyl-1-oxypyrrolinyl-3-carboxylic acid, 2154-67-8; 3-amino-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, 34272-83-8; 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy, 14691-88-4; 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy, 2226-96-2; 3-(hydroxymethyl)-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, 27298-75-5; 3-isocyanato-2,2,5,5-tetramethylpyrrolinyl-1-oxy, 78265-43-7; 5-(2-hydroxyphenyl)-10,15,20-tritolylporphyrin, 57412-07-4; 3-(bromomethyl)-2,2,5,5-tetramethylpyrrolidinyl-1-oxy, 78265-44-8.

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