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# Metal–Nitroxyl Interactions. 45. Increase in Nitroxyl Relaxation Rates in Fluid Solution due to Intramolecular Interaction with Iron(III) and Manganese(III)

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Nitroxyl relaxation rates, $T_1^{-1}$ and $T_2^{-1}$, were determined by computer simulation of continuous-wave EPR power saturation curves and saturated spectra for spin-labeled porphyrins and spin-labeled iron(III) and manganese(III) porphyrins in fluid solution at room temperature. The impact of the metal on the nitroxyl relaxation rates decreased as the distance between the metal and the nitroxyl increased and decreased in the order high-spin Fe(III) > high-spin Mn(III) > low-spin Fe(III). These trends are consistent with dipolar contributions to the interaction. The greater interaction for one of the high-spin Fe(III) porphyrins than for the other metalloporphyrins suggests that exchange contributions may also be significant.

## Introduction

In spin-labeled complexes of transition metals with $S = {}^1/_2$ and slow electron spin relaxation rates such as Cu(II), Ag(II), and $\mathrm{V^{IV}O}$, electron–electron spin–spin interaction causes splitting of the allowed transitions in the EPR spectra[1,2] and gives intensity to the half-field transition. The distance between the two unpaired electrons can be obtained from the ratio of the intensity of the half-field transition to the intensity of the allowed transitions.[3] In some cases the interspin distance can also be obtained by simulation of the allowed transitions in rigid lattice spectra.[4] For transition metals with rapid electron spin relaxation rates, the EPR spectra of the metals are not readily observed and splitting of the EPR signal of a nitroxyl radical due to interaction with the metal is collapsed by the metal relaxation. Therefore, different methods of determining interspin distances are required for rapidly relaxing transition metals than for slowly relaxing transition metals. One approach to the problem is to study changes in the relaxation rate of the nitroxyl unpaired electron due to the interaction with the transition metal. To obtain distance information, it is necessary to separate the exchange and dipolar contributions to the interaction. As a first step we wish to determine the relative importance of the two contributions in molecules of known structure.

Although considerable work has been done on changes in the line width of the nitroxyl EPR signal due to collision interactions with transition metals.[1,5,6] much less is known about intramolecular effects on line widths and relaxation rates in fluid solution. Preliminary results obtained for two spin-labeled high-spin iron(III) porphyrins indicated that the nitroxyl relaxation rates were increased significantly by interaction with the metal.[7] We have therefore examined the nitroxyl relaxation rates for high-spin manganese(III) and high-spin and low-spin iron(III) complexes of porphyrins P-trans-SL and P-cis-SL andd the high-spin manganese(III) complex of porphyrin P-para-SL (see Chart I). These three porphyrins provide a range of metal–nitroxyl distances and linkages to permit a comparison of the dipolar and exchange contributions to the interaction.

## Experimental Section

Infrared spectra were obtained in Nujol mulls on a Perkin-Elmer 337 or 283B spectrometer. Visible spectra were obtained in chloroform solution on a Beckman Acta V spectrometer. Spectra are reported below with wavelengths in nm and log $\epsilon$ in parentheses following the wavelength. Elemental analyses were performed by Spang Microanalytical Laboratory. EPR spectra were run on a Varian E-9 spectrometer with a field/frequency lock and with an E231 cavity containing a quartz variable-temperature Dewar insert. Spectra were obtained with 100-kHz modulation and modulation amplitudes less than one-tenth of the line width of the sharpest lines. The values of $T_1$ obtained for these compounds were sufficiently short that $\omega_m T_1 < 1$ ($\omega_m$ is the modulation frequency) was satisfied at 100 kHz and the relaxation rates were independent of modulation frequency (270 Hz–100 kHz). The loaded $Q$ for the cavity ($Q_L$) was measured as previously reported.[8] For toluene solutions in 4-mm quartz tubes the values of $Q_L$ were 3490–3590. When 0.1 M 1-methylimidazole (1-Me-im) was added to the toluene solutions to form the six-coordinate low-spin Fe(III) complexes, the values of $Q_L$ were 2190–2330. The microwave magnetic field, $H_1$, in the cavity was calibrated with a $9.5 \times 10^{-4}$ M solution of Fremy's salt (peroxylamine disulfonate) in air-saturated 0.05 M potassium carbonate solution.[7,9-11] With the Dewar insert in the cavity we obtained $H_1 = 2.67 \times 10^{-2}(Q_L P)^{1/2}$, where $P$ is the microwave power read from the Varian bridge.[7] Spectra of the spin-labeled porphyrins and metalloporphyrins were obtained on toluene solutions that were degassed by multiple freeze–pump–thaw cycles on a vacuum line (ca. 1 mtorr). The 10-G sweep of the field/frequency lock unit was used to obtain spectra of the nitrogen $m_I = 0$ line at 16–20 microwave power levels between 0.1 and 200 mW. The amplitude of the signal was measured at the magnetic fields corresponding to the maxima and minima in the unsaturated first-derivative spectra. The maximum amplitude of the signal was set equal to 100. Other values were scaled accordingly and plotted as a function of the square root of the microwave power read from the bridge. These plots are subsequently referred to as power saturation curves. Replicate measurements of the power saturation curves indicated that the degassing procedure was reproducible. The shapes of the power saturation curves and the line shapes of the unsaturated and saturated spectra were simulated with the computer program SIMSAT.[7] For each of the porphyrins the values of the proton hyperfine coupling constants that gave the best agreement with the spectra for M = 2 H were used in the simulations of the spectra of the corresponding metal complexes. The proton hyperfine coupling constants (in gauss) used in the simulations were as follows: M(P-cis-SL), (6 H), 0.455, (6 H) 0.02, (2 H) 0.293, (2 H) 0.480, and (1 H) 0.08; M(P-trans-SL), (6 H) 0.455, (6 H) 0.02, (2 H) 0.290, (2 H) 0.490, and (1 H) 0.08; M(P-para-SL), (6 H) 0.450, (6 H) 0.02, (2 H) 0.293, (2 H), 0.480, and (1 H) 0.08.

**Preparation of Compounds.** All starting materials were commercially available unless otherwise noted. $H_2$(P-cis-COOEt),[12] $H_2$(P-trans-COOEt),[12] $H_2$(P-para-COOEt),[13] $H_2$(P-cis-SL),[14] $H_2$(P-trans-SL),[14] $H_2$(P-para-SL),[14] Fe(P-trans-SL)Cl,[7] and Fe(P-cis-SL)Cl[7] were prepared by literature methods.

**Manganese(III) 5-(4-Carboxyphenyl)-10,15,20-tritolylporphyrin Chloride Hydrate (I).** 5-(4-Carboxyphenyl)-10,15,20-tritolylporphyrin[13] was reacted with manganese acetate by the method of Adler;[15] yield 0.63

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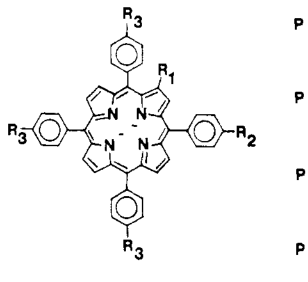
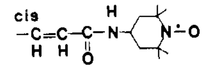
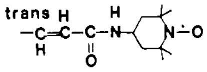
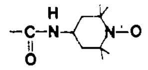
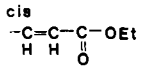
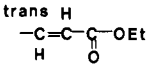
Chart I



| abbrev. | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| P-cis-SL |  | H | H |
| P-trans-SL |  | H | H |
| P-para-SL | H |  | $CH_3$ |
| P-cis-COOEt |  cis $-\underset{H}{C}{=}\underset{H}{C}{-}\underset{\overset{\|}{O}}{C}{-}OEt$ | H | H |
| P-trans-COOEt |  trans $-\underset{H}{C}{=}\overset{H}{C}{-}\underset{\overset{\|}{O}}{C}{-}OEt$ | H | H |
| P-para-COOEt | H | COOEt | $CH_3$ |

g, 80%. IR: 3600 (OH), 1720 (CO) cm$^{-1}$. Vis: 621 (4.11), 585 (4.06), 530 (3.90), 480 (5.06), 378 (4.84).

**Manganese(III) 5-(4-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)phenyl)-10,15,20-tritolylporphyrin Chloride Hydrate, Mn(P-para-SL)Cl.** To a solution of I (79 mg, 0.10 mmol) in benzene (100 mL) was added excess oxalyl chloride (1.9 g, 10 mmol). The mixture was stirred for 3 h at room temperature. The solvent was removed under vacuum, and the residue was dissolved in 50 mL of THF. 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy (34 mg, 0.20 mmol) and 0.5 mL of pyridine were added, and the solution was refluxed for 3 h. The solvent was removed under vacuum, and the residue was dissolved in chloroform. The solution was put on a silica gel column. Impurities were eluted with chloroform, and the product was eluted with chloroform:methanol (98:2). The product was recrystallized from dichloromethane/hexane; yield 57 mg, 60%. IR: 3300 (NH), 1650 (CO) cm$^{-1}$. Vis: 621 (4.09), 586 (4.03), 532 (3.86), 480 (5.06), 381 (4.84). Anal. Calcd for $C_{57}H_{53}N_6O_3MnCl{\cdot}0.10CH_2Cl_2$: C, 70.78; H, 5.53; N, 8.67; Cl, 4.38. Found: C, 70.60; H, 5.57; N, 8.48; C, 4.10.

**Manganese(III) 2-(2-Carboxyethenyl)-5,10,15,20-tetraphenylporphyrin Chloride, Cis Isomer (II).** 2-(2-Carboxyethenyl)-5,10,15,20-tetraphenylporphyrin, cis isomer,[12] was reacted with manganese acetate by the method of Adler;[15] yield 62%. IR: 3600 (OH), 1700 (CO) cm$^{-1}$. Vis: 621 (4.03), 586 (4.04), 530 (3.85), 483 (5.02), 380 (4.77).

**Manganese(III) 2-(2-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)ethenyl)-5,10,15,20-tetraphenylporphyrin Chloride, Cis Isomer, Mn(P-cis-SL)Cl.** The complex was prepared from II and 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy by a procedure analogous to that described for the preparation of Mn(P-para-SL)Cl and recrystallized from dichloromethane/hexane; yield 50%. IR: 3400 (NH), 1660 (CO) cm$^{-1}$. Vis: 621 (3.96), 586 (4.00), 530 (3.84), 483 (4.98), 380 (4.73). Anal. Calcd for $C_{56}H_{47}N_6O_2MnCl$: C, 72.60; H, 5.11; N, 9.07; Cl, 3.83. Found: C, 72.36; H, 5.22; N, 8.94; Cl, 4.14.

**Manganese(III) 2-(2-Ethoxyethenyl)-5,10,15,20-tetraphenylporphyrin Chloride, Trans Isomer (III).** The complex was prepared from 2-(2-ethoxyethenyl)-5,10,15,20-tetraphenylporphyrin, trans isomer,[12] and manganese acetate by the method of Adler[15] and recrystallized from dichloromethane/hexane; yield 70%. IR: 1720 (CO) cm$^{-1}$. Vis: 624 (3.95), 590 (3.97), 530 (3.78), 483 (4.95), 379 (4.70). Anal. Calcd for $C_{49}H_{34}N_4O_2MnCl{\cdot}0.33CH_2Cl_2$: C, 71.43; H, 4.21; N, 6.75; Cl, 7.12. Found: C, 71.37; H, 4.21; N, 6.87; Cl, 7.08.

**Manganese(III) 2-(2-Carboxyethenyl)-5,10,15,20-tetraphenylporphyrin Chloride, Trans Isomer(IV).** To a solution of III (0.40 g, 5.0 mmol) in 100 mL of pyridine was added 2 N methanolic KOH (50 mL). The mixture was stirred for 30 h at room temperature. The solution was neutralized with 200 mL of 2 N HCl and extracted with chloroform. The chloroform solution was dried over sodium sulfate. The solvent was removed, and the residue was recrystallized from dichloromethane/hexane; yield 0.24 g, 70%. IR: 3600 (OH), 1690 (CO) cm$^{-1}$. Vis: 624 (3.99), 591 (4.01), 525 (3.84), 486 (4.84), 383 (4.62).

**Manganese(III) 2-(2-(((2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)amino)carbonyl)ethenyl)-5,10,15,20-tetraphenylporphyrin Chloride, Trans Isomer, Mn(P-trans-SL)Cl.** The complex was prepared from IV and 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy by a procedure similar to that described for the preparation of Mn(P-para-SL)Cl and recrystallized from chloroform/heptane; yield 56%. IR: 3400 (NH), 1660 (CO) cm$^{-1}$. Vis: 624 (4.05), 591 (4.10), 530 (3.95), 486 (4.79), 383 (4.81). Anal. Calcd for $C_{56}H_{49}N_6O_3MnCl{\cdot}0.08CHCl_3$: C, 70.64; H, 5.19; N, 8.81; Cl, 4.56. Found: C, 70.54; H, 4.94; N, 8.85; Cl, 4.57.

## Results and Discussion

Although nitroxyl radicals are relatively stable under a range of conditions, they are destroyed by redox reactions with some Fe(II) and Mn(II) compounds. Therefore, the spin-labeled iron(III) and manganese(III) porphyrins were prepared by the usual reaction of diamagnetic porphyrins with Fe(II) or Mn(II) and air oxidation,[15] prior to attachment of the spin label. The Fe(III) and Mn(III) porphyrins were isolated with chloride as the axial ligand. Some of the Mn(III) porphyrins crystallized with water in the sixth coordination site as has been observed previously.[16] Chlorinated solvents were retained in the crystal lattice of some of the metalloporphyrins even after prolonged drying under vacuum as has been observed for other spin-labeled porphyrins.[17,18] 1-Methylimidazole (1-Me-im, 0.1 M) was added to the solutions of the spin-labeled iron porphyrin chlorides to form the corresponding low-spin $(1\text{-Me-im})_2$ adducts. Visible spectra indicated that, under these conditions, conversion to the six-coordinate species was >95% complete. The 1-methyl derivative was used to minimize hydrogen bonding by the imidazole.

Aggregation of porphyrins in fluid solution is a widely recognized phenomenon. Interaction between two nitroxyl radicals on aggregated porphyrins or between a nitroxyl on one porphyrin and the metal of a second porphyrin could increase the nitroxyl relaxation rates. The concentration of the spin-labeled porphyrins was kept below 0.5 mM to decrease aggregation. In addition, a 10-fold excess of the porphyrin $H_2$(P-cis-COOEt), $H_2$(P-trans-COOEt), or $H_2$(P-para-COOEt) was added to the solutions of the corresponding spin-labeled porphyrins and metalloporphyrins. With the large ratio of diamagnetic porphyrin to spin-labeled porphyrin, the probability of aggregation of two or more spin-labeled porphyrins is small. We observed previously that addition of a 5-fold excess of diamagnetic porphyrin caused a decrease in nitroxyl relaxation rate for some spin-labeled porphyrins but greater excess had no additional impact.[7]

The EPR spectra of the three spin-labeled porphyrins showed well-resolved proton hyperfine splitting (Figure 1A). The proton hyperfine coupling constants obtained by ENDOR and paramagnetic NMR for several piperidinyl radicals, including one with an amide at the 4-position, showed little dependence of the coupling constants on the 4-substituent.[19-23] The values used in the sim-

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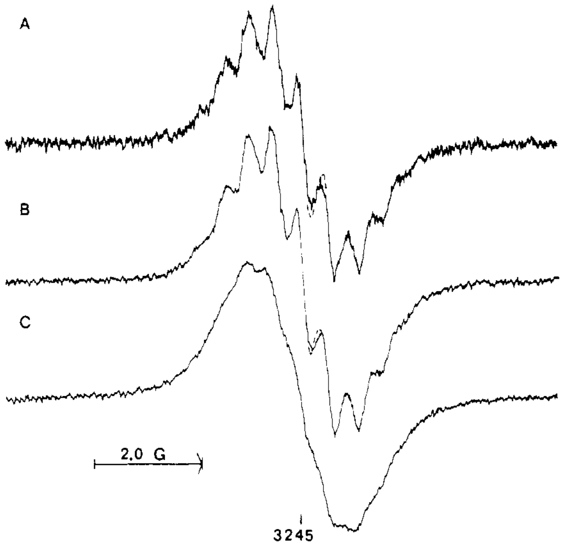

**Figure 1.** Scans (10 G) of the X-band (9.109 GHz) EPR spectra of the nitrogen $m_I = 0$ line of $1.0 \times 10^{-4}$ M M(P-trans-SL) in toluene solution in the presence of $1.0 \times 10^{-3}$ M $H_2$(P-trans-COOEt) at room temperature: (A) M = 2 H, microwave power 0.2 mW, and modulation amplitude 0.02 G; (B) M = MnCl, microwave power 0.5 mW, and modulation amplitude 0.02 G; (C) M = FeCl, microwave power 1.0 mW, and modulation amplitude 0.02 G. The dotted lines indicate regions in which the simulated spectra did not overlay the experimental data. The simulated spectra were obtained with the proton hyperfine coupling constants given in the text and the following values of $T_2$ ($\mu$s): (A) 0.30; (B) 0.27; (C) 0.17.

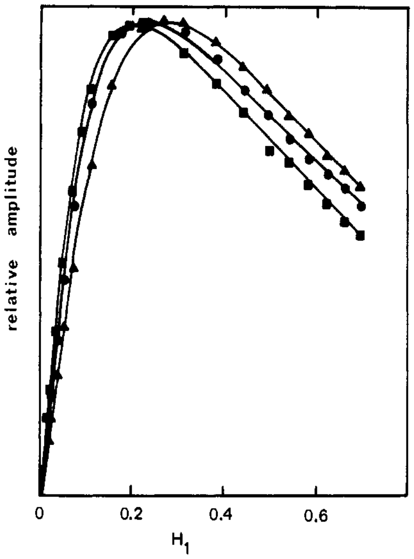

**Figure 2.** Power saturation curves obtained at room temperature for $1.0 \times 10^{-4}$ M toluene solution of M(P-trans-SL) in the presence of $1.0 \times 10^{-3}$ M $H_2$(P-trans-COOEt): (■) M = 2 H (A); (●) M = MnCl (B); (▲) M = FeCl (C). The solid lines are the simulated curves obtained with the proton hyperfine coupling constants given in the text and the values of $T_1$ ($\mu$s) = 0.60 (A), 0.50 (B), and 0.45 (C) and $T_2$ ($\mu$s) = 0.30 (A), 0.27 (B), and 0.17 (C).

**Table I.** Values of $T_1^{-1}$ for M(P-X-SL)[a]

| | X | | |
|---|---|---|---|
| M | cis | trans | para |
| $H_2$ | 1.4 | 1.5 | 1.7 |
| Fe(1-Me-im)$_2$ | 1.6 | 1.8 | |
| | (0.2) | (0.3) | |
| MnCl | 1.9 | 1.8 | 1.5 |
| | (0.5) | (0.3) | (0.2) |
| FeCl | 2.1 | 2.0 | |
| | (0.7) | (0.5) | |

[a] In MHz for toluene solutions at room temperature. Values are extrapolated to infinite dilution. The values of $\Delta$ are given in parentheses. Uncertainties are ±0.1 MHz for $T_1^{-1}$ and ±0.2 MHz for $\Delta$.

**Table II.** Values of $T_2^{-1}$ for M(P-X-SL)[a]

| | X | | |
|---|---|---|---|
| M | cis | trans | para |
| $H_2$ | 2.5 | 3.0 | 3.0 |
| Fe(1-Me-im)$_2$ | 3.0 | 3.3 | |
| | (0.5) | (0.3) | |
| MnCl | 4.0 | 3.6 | 3.6 |
| | (1.5) | (0.6) | (0.6) |
| FeCl | 5.5 | 5.4 | |
| | (3.0) | (2.4) | |

[a] In MHz for toluene solutions at room temperature. Values are extrapolated to infinite dilution. The values of $\Delta$ are given in parentheses. Uncertainties are ±0.1 MHz for $T_2^{-1}$ and ±0.2 MHz for $\Delta$.

ulations of the spectra of the spin-labeled porphyrins (see Experimental Section) fell within the range of literature values.[7] Uncertainty in proton hyperfine coupling constants can be a major source of error in measurements of electron spin relaxation rates by continuous-wave (CW) EPR. This is less of a problem for the piperidinyl radicals used in this study than for other radicals because the values of the coupling constants are known accurately. In addition, by simulation of the full shape of the power saturation curves and the line shapes of the saturated spectra the values of $T_1$ and $T_2$ can be obtained more accurately than is possible by other CW methods.[7] We have shown previously that the values of $T_1$ and $T_2$ obtained for nitroxyl radicals by this method were consistent with literature values of the relaxation times.[7] Furthermore, since the same coupling constants were used for each spin-labeled porphyrin and its metal complexes, small systematic errors caused by uncertainties in the coupling constants tend to cancel out when the difference ($\Delta$) between the nitroxyl relaxation rates for the spin-labeled metalloporphyrin and the spin-labeled porphyrin is calculated.

The proton hyperfine splitting was less well resolved in the EPR spectra of the spin-labeled metalloporphyrins (Figure 1B,C) than in the spectra of the spin-labeled porphyrins (Figure 1A), which indicated that interaction between the nitroxyl unpaired electron and the unpaired electrons on the transition metals caused an increase in the electron spin relaxation rate of the nitroxyl unpaired electron. EPR spectra and power saturation curves for the porphyrins and metalloporphyrins were obtained at four concentrations, 0.05, 0.10, 0.20, and 0.40 mM. Typical power saturation curves are shown in Figure 2 for M(P-trans-SL) at $1 \times 10^{-4}$ M. The values of $T_1^{-1}$ and $T_2^{-1}$ for the nitroxyl were obtained as previously described.[7] Even at these concentrations there is some contribution to the nitroxyl relaxation due to collisions between paramagnetic centers. Contributions to the relaxation rates are expected to be additive, and the contribution to the relaxation rate due to collisions with other paramagnetic centers is expected to be linearly dependent on concentration. Thus linear extrapolation of the values of $T_1^{-1}$ and $T_2^{-1}$ to infinite dilution should give relaxation rates without contributions from collisions. The relaxation rates were more strongly concentration dependent for the spin-labeled metalloporphyrins than for the spin-labeled porphyrins. This is consistent with the expectation that collision interactions with transition metals with rapid electron spin relaxation rates would have a greater impact on the nitroxyl electron spin relaxation rate than collision interactions with another nitroxyl radical. The extrapolation to infinite dilution should be a more accurate method to correct for collision interactions than comparison of values obtained for mixtures of metalloporphyrins and spin-labeled porphyrins.[7]

The values obtained for $T_1^{-1}$ and $T_2^{-1}$ at infinite dilution for the nitroxyl unpaired electron on the spin-labeled porphyrins and spin-labeled metalloporphyrins are summarized in Tables I and

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II, respectively. For each of the spin-labeled metalloporphyrins the difference, Δ, between the relaxation rate for the spin-labeled metalloporphyrin and that for the corresponding spin-labeled porphyrin is also included in the tables. Since there is an uncertainty of about ±0.2 MHz in the values of Δ, the individual values must be regarded as quite uncertain. However, the trends in the data have a greater significance than the individual values. The first conclusion that can be drawn is that the metal in the spin-labeled metalloporphyrins caused an increase in the nitroxyl relaxation rate.

The three spin-labeled porphyrins were selected to permit a comparison of the relative importance of dipolar and exchange contributions to the values of Δ. The EPR spectra of the Cu(II), Ag(II), and $V^{IV}O$ complexes of P-cis-SL and P-trans-SL have been studied in fluid solution, in frozen solution, and as dopants into $Zn(TPP)(THF)_2$. The analysis of the rigid-lattice spectra gave metal–nitroxyl distances of 9–11 Å for the complexes of P-cis-SL and 12–14 Å for the complexes of P-trans-SL.[4,24–26] Agreement between the values of the exchange coupling constant, $J$, obtained in fluid solution and in the rigid lattice indicated that the conformations of the metal–nitroxyl linkage were similar in the two media. Molecular models indicate that the metal–nitroxyl distance in the complexes of P-para-SL is 15–16 Å. Since dipolar interactions are determined by the distance between the two paramagnetic centers, the dipolar interaction is expected to decrease in the order P-cis-SL > P-trans-SL > P-para-SL. Dipolar interactions also decrease with decreasing numbers of unpaired electrons so the effect of the metal ions is expected to decrease in the order high-spin Fe(III) ($S = {}^5/_2$) > high-spin Mn(III) ($S = 2$) > low-spin Fe(III) ($S = {}^1/_2$).

Intramolecular exchange interactions depend upon the bonding between the two paramagnetic centers. The EPR spectra of the Cu(II), Ag(II), and $V^{IV}O$ complexes of P-cis-SL and P-trans-SL indicated that the magnitude of the intramolecular exchange interaction between the metal and the nitroxyl was dependent on the unpaired spin density on the pyrrole carbon.[14] Paramagnetic NMR spectra of high-spin Mn(III), high-spin Fe(III), and low-spin Fe(III) complexes show that the unpaired electron spin density on the pyrrole carbon is several times larger for high-spin Fe(III) porphyrins than for low-spin Fe(III) porphyrins or high-spin Mn(III) porphyrins.[27] Therefore, the exchange contribution to the metal–nitroxyl interaction in M(P-trans-SL) and M(P-cis-SL) is expected to be substantially greater for high-spin Fe(III) than for either high-spin Mn(III) or low-spin Fe(III). The spectra of the Cu(II), Ag(II), and $V^{IV}O$ complexes of P-cis-SL and P-trans-SL also indicated that exchange interaction was greater for the trans isomer than for the cis isomer.[12,26] Since the paramagnetic NMR shifts are very small for the para position of the phenyl rings,[27] the exchange contribution for M(P-para-SL) is likely to be small. Therefore, the exchange interaction is expected to decrease in the order P-trans-SL > P-cis-SL > P-para-SL.

Changes in the metal electron spin relaxation time may also effect the interaction between the metal and the nitroxyl. NMR line widths in paramagnetic samples are dependent on the metal $T_1$ such that a longer value of $T_1$ gives a broader line.[28] The line widths for the pyrrole protons in the NMR spectra of metalloporphyrins[27] indicate that the values of the metal $T_1$'s decrease in the order high-spin Mn(III) > high-spin Fe(III) > low-spin Fe(III).

When the metal–nitroxyl linkage was held constant, the values of Δ for both $T_1^{-1}$ and $T_2^{-1}$ for the nitroxyl unpaired electron in the spin-labeled metalloporphyrins decreased in the order M = FeCl ($S = {}^5/_2$) > MnCl ($S = 2$) > $Fe(1\text{-}Me\text{-}im)_2$ ($S = {}^1/_2$). This dependence of the interaction on the number of unpaired electrons on the metal is consistent with a dipolar interaction between the two paramagnetic centers. When the metal spin is held constant, there is generally a trend cis > trans > para, which is the order expected for dipolar interaction. Thus these two trends suggest that dipolar interaction is a major factor in determining the effect of the metal on the nitroxyl relaxation rates in these compounds.

The dependence of the values of Δ on the metal (high-spin Fe(III) > Mn(III) > low-spin Fe(III)) is not the same as the relative values of $T_1$ for the metals (high-spin Mn(III) > high-spin Fe(III) ≥ low-spin Fe(III)). Thus the value of the metal $T_1$ does not appear to be the most important factor in determining the effect of the metal on the nitroxyl relaxation rate.

The values of Δ for $T_2^{-1}$ for the high-spin complexes Fe(P-cis-SL)Cl and Fe(P-trans-SL)Cl were substantially larger than for the other complexes, and the value of Fe(P-trans-SL)Cl was almost as large as the value of Fe(P-cis-SL)Cl. On the basis of dipolar interaction alone, the values for high-spin Fe(III) are not expected to be that much larger than for the high-spin Mn(III) complexes and the value for the cis isomer is expected to be substantially larger than for the trans isomer. The arguments above indicated that the exchange interaction was expected to be larger for the high-spin Fe(III) than for the other metals and would be greater for the trans isomer than for the cis isomer. Therefore, the larger than expected values of Δ for the high-spin Fe(III) complexes suggest that an exchange contribution may be present, particularly for Fe(P-trans-SL)Cl.

## Conclusions

The data for these complexes with interspin distances between 9 and 16 Å and weak exchange interactions indicate that dipolar interactions are a significant factor in determining the effect of the metal on the nitroxyl electron spin relaxation. However, the data cannot be explained solely by the trends expected for dipolar interaction and therefore exchange contributions are probably significant. Further studies of a variety of complexes will be needed to understand the roles of the two contributions.

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