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Metal-Nitroxyl Interactions. 51. Collapse of Iron-Nitroxyl Electron-Electron Spin-Spin Splitting due to the Increase in the Electron Spin Relaxation Rate for High-Spin Iron(III) When Temperature Is Increased

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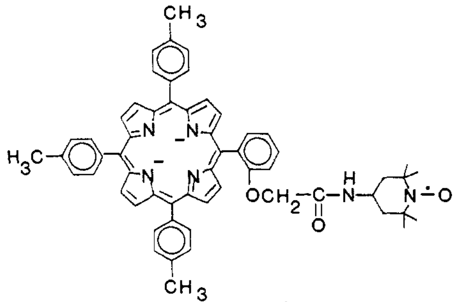
Abstract: The EPR spectra of five-coordinate, high-spin iron(III) complexes of a spin-labeled tetraphenylporphyrin were examined at temperatures between 8 and 120 K. The axial ligands were F^-, Cl^-, and Br^-. At 8 K the resolved electron-electron spin-spin splittings of the nitroxyl signal and iron $g = 6$ signal were similar for the three halides. As the temperature was increased, the iron signals broadened, and the splitting of the nitroxyl signal collapsed due to the increasing rate of relaxation of the iron unpaired electrons. The temperatures at which the splitting of the nitroxyl signals was collapsed increased in the order axial ligand = $Br^- < Cl^- < F^-$. This order is consistent with the expectation that the metal relaxation rate increases with increased zero-field splitting and with temperature.

Electron-electron spin-spin coupling between slowly relaxing inequivalent unpaired electrons results in AB splitting of the EPR signals. These splittings have been examined for nitroxyl spin-labeled complexes of Cu(II),[1,2] Ag(II),[3,4] VO(IV),[2,4,5] low-spin Co(II),[6] and Cr(III).[7] As the relaxation rate for the metal unpaired electron increases, the relaxation "decouples" the metal spin from the nitroxyl spin. A model has been proposed to interpret the EPR spectrum of a nitroxyl radical interacting with a rapidly relaxing paramagnetic metal to obtain the distance between the two paramagnetic centers.[8] One parameter in that model is the metal relaxation rate (T_1^{-1}).



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Despite the interest in the effect of metal T_1 on the line shape of an interacting paramagnetic center there does not appear to be any example in the literature in which it has been possible to examine the spectra of a slowly relaxing paramagnetic species that is coupled to a more rapidly relaxing paramagnetic center over a temperature range in which the electron spin relaxation rate changes from slow relative to the mutual coupling to fast. We now report spectra of Fe(P)X, where P is spin-labeled porphyrin I and X = F, Cl, Br, in which the spin-spin splitting is resolved at 8 K and collapses as the temperature is raised due to increasing rates of relaxation of the high-spin iron(III).

Experimental Section

X-band EPR spectra at temperatures above about 90 K were obtained on a Varian E9 interfaced to an IBM CS9000 computer. The Varian V-6040 temperature controller was used. Spectra at 4-90 K were obtained on an X-band EPR spectrometer constructed largely from commercial Varian components. An Air Products Helitran cold end and temperature controller were used. Temperatures were monitored with a thermocouple positioned at the base of the sample. Spectra were obtained with 100 kHz modulation at microwave powers and modulation amplitudes that did not cause distortion of the line shape.

Fe(P)Cl, P = I, was prepared as reported in ref 9.

Preparation of Solutions for EPR Studies. A 1.0 mM solution (1.0 mL) of Fe(P)Cl in toluene solution was shaken with 0.5-1.0 mL of 0.05 M NaOH for 2 min to form Fe(P)OH.[10,11] The green solution of Fe(P)OH was shaken with 1 mL of 2% HX to form Fe(P)X. For X = Cl or Br the product was red-brown. For X = F the product was green. The visible spectra confirmed that the product was Fe(P)F and not Fe(P)F_2^-.[12]

Computer Simulations. At ca. 8 K the iron in Fe(P)Br is predominantly in the $m_s = \pm{}^1/_2$ state due to the large zero-field splitting. Approximate simulations of the EPR spectra were obtained for two interacting $S = {}^1/_2$ centers. A program (METNO) that employs Belford's fourth-order frequency shift perturbation method was used.[13,14] The Hamiltonian included the Zeeman interactions for iron(III) and nitroxyl, dipolar interaction between the two paramagnetic centers, and an isotropic exchange interaction ($-JS_1 \cdot S_2$).[7] A negative sign of J indicates an antiferromagnetic interaction. The nitroxyl nitrogen hyperfine coupling was not included in the calculations since the line widths of the nitroxyl signals were substantially greater than the nitroxyl hyperfine splitting. The orientation of the axes for the anisotropic nitroxyl g values can be specified in the calculation, but the g anisotropy is so small relative to the line widths that the orientation of the nitroxyl axes had no observable impact on the spectra calculated in this study. The nitroxyl g values were as follows: $g_x = 2.0089$, $g_y = 2.0062$, $g_z = 2.0027$.[1] The iron g values were $g_x = 6.0$, $g_y = 6.0$, and $g_z = 2.0$.[15]

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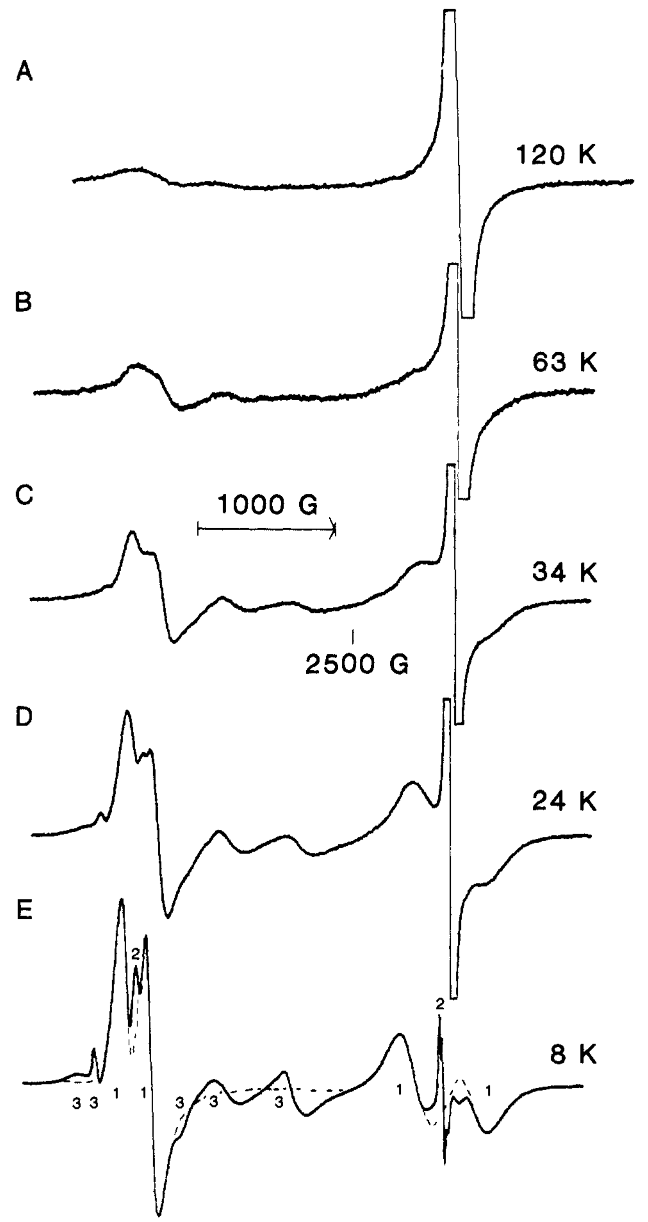

Figure 1. 4000-G scans of the X-band (9.1 GHz) EPR spectra of a 1 mM solution of Fe(P)Br as a function of temperature. Spectra were obtained with 2.0–2.5 G modulation amplitude and 4–10 mW microwave power. The dotted line in part E indicates regions in which the simulated spectrum for component 1 does not overlay the experimental spectrum.

Results and Discussion

In an EPR study of the low-spin iron(III) complexes of a series of spin-labeled porphyrins, including porphyrin I, it was observed that the complexes adopted two or more conformations that differed in the magnitude of the iron–nitroxyl spin–spin interaction.[9] Evidence for several conformations of Cu(II) and Ag(II) complexes of ortho spin-labeled porphyrins has also been obtained.[3,16] Therefore, it was anticipated that multiple conformations might also be observed for the high-spin iron(III) complexes of porphyrin I.

The EPR spectrum of Fe(P)Br in a toluene glass at 8 K is shown in Figure 1E. The spectrum consists of several overlapping components due to conformations of the complex with substantially different magnitudes of iron–nitroxyl spin–spin interaction. The signals labeled 1 are the primary focus of this paper. The weak signals labeled 2 are due to small amounts of high-spin Fe(III) and nitroxyl impurities and/or a small amount of a conformation with very weak iron–nitroxyl interaction. The signals labeled 3 are due to one or more conformations with substantially stronger iron–nitroxyl interaction than was observed for 1. The analysis of the signals denoted by 3 will be discussed later.[17] The following discussion concerns the spectrum labeled 1.

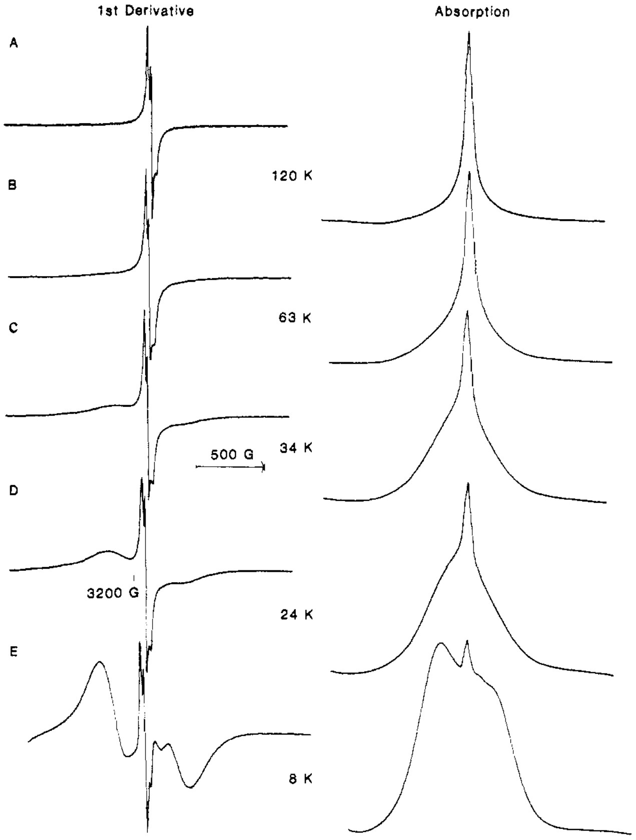

Figure 2. 2000-G scans of the nitroxyl regions of the spectra shown in Figure 1. The first derivative and absorption presentations of the spectra are compared.

The splitting of the iron $g = 6$ signal due to interaction with the nitroxyl unpaired electron was about 170 G (1400 MHz) and showed no additional splitting due to anisotropy of the spin–spin interaction in the xy (porphyrin) plane. The small anisotropy could indicate that the dominant contribution to the spin–spin interaction was exchange or that the nitroxyl was located close to the iron z axis. The splitting of the nitroxyl signal was about 500 G (1400 MHz). The low-field component was more intense than the high-field component as expected for an "inner" line of an AB pattern in which the exchange contribution was greater than the dipolar contribution. The relative intensities of the two components of the nitroxyl signals could not be reproduced with $r <$ about 7 Å. The simulated spectrum was obtained with an interspin distance, $r = 8$ Å, $J = -0.034$ cm^{-1}, and a 25° angle between the iron z axis and the interspin vector. Comparable agreement with the experimental spectrum was also obtained for simulated spectra with other orientations of the interspin vector and compensating changes in the values of r and J, including $r = 8$ Å, $J = 0.045$ cm^{-1}, and the interspin vector along the iron z axis. These angles and interspin distances are consistent with strain-free conformations of CPK molecular models. The iron $g_{\parallel}$ signal is superimposed on the nitroxyl signal and was not resolved. The inability to determine the orientation dependence of the spin–spin interaction precluded a precise determination of the dipolar contribution to the interaction. Nevertheless it is evident that there was a significant exchange contribution.

As the temperature was increased, the iron $g = 6$ signal broadened due to the increasing rate of electron spin relaxation, and the nitroxyl splitting collapsed into a single peak (Figure

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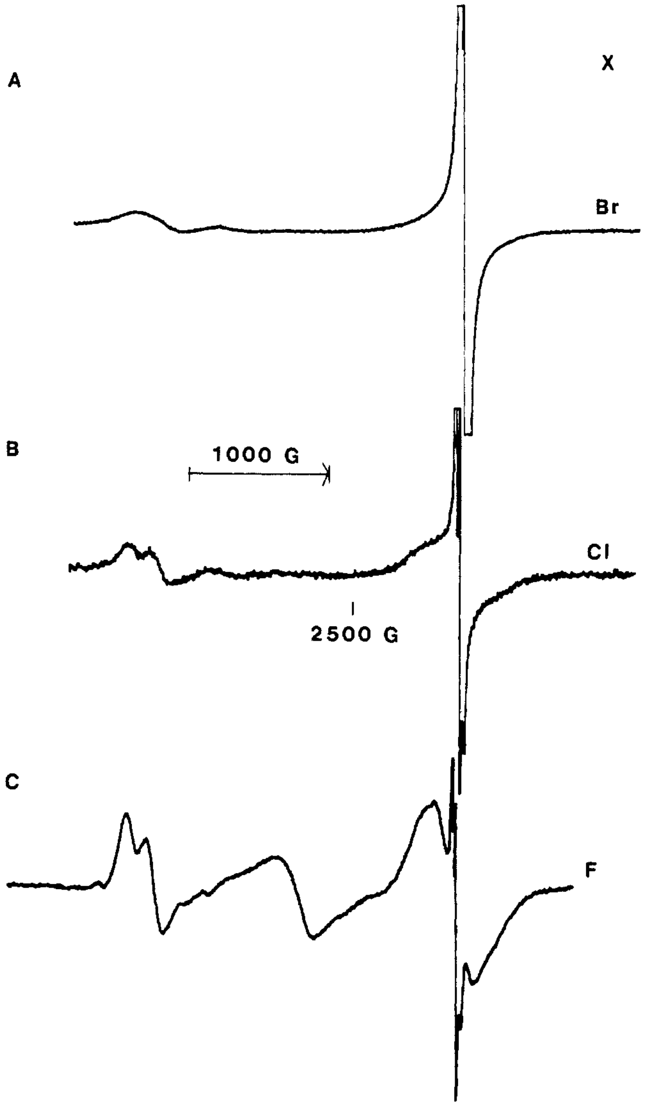

Figure 3. 4000-G scan of the X-band EPR spectra of 1 mM solutions of Fe(P)X in toluene at 95 K: (A) X = Br, spectrum obtained with 2.5-G modulation amplitude and 10-mW microwave power; (B) X = Cl, spectrum obtained with 2-G modulation amplitude and 2 mW-microwave power; (C) X = F, spectrum obtained with 4-G modulation amplitude and 20-mW microwave power.

1A–D). EPR spectra are customarily displayed as the first derivatives of the absorption spectra. However, this presentation tends to accentuate the sharp features of the spectra and minimize the impact of broader signals. Figure 2 shows the nitroxyl regions of the spectra as a function of temperature in the typical first derivative display and the absorption spectra (first integral of the experimental data). The broader portions of the spectra are more clearly seen in the latter than in the former. The absorption presentation also highlights the similarity between these spectra and the more familiar dynamic NMR solution spectra. However, there is an important difference between these spectra and dynamic NMR spectra for two-site exchange. Since there is an anisotropic contribution to the electron–electron spin–spin interaction, the splitting is a function of the orientation of the molecule in the magnetic field. In a frozen solution sample there is a range of splittings. The smaller splittings collapse to an averaged signal at slower rates of the iron relaxation than do the larger splittings. Thus there is a distribution of line shapes in the spectra at intermediate values of T_1^{-1} rather than the single line shape observed for two-site dynamic NMR spectra.

As a first estimate of the iron relaxation rate, it was assumed that the collapse of the average nitroxyl splitting (500 G) could be approximated as a two-site exchange. The line shape of the nitroxyl signal at 34 K (Figures 1 and 2) was similar to that expected at coalescence. A T_1 value of 3.2×10^{-10} s/rad was estimated for the iron at 34 K from the expression $T_1 = 2\sqrt{2}/\Delta\omega$ where $\Delta\omega$ is the nitroxyl splitting in Hz.[18] If T_2 is approximately equal to T_1, this relaxation rate gives a 70-G peak-to-peak line width for the iron signal. At 34 K the peak-to-peak line width of the iron $g = 6$ signal was about 90 G. Unresolved Br hyperfine coupling to the iron signal also contributes to the observed line width.[19] The agreement between the observed and calculated line widths supports the proposal that the collapse of the splitting of the nitroxyl signal was due to the increase in the iron relaxation rate. More accurate estimates of the iron relaxation rate require a more precise analysis of the line shape of the nitroxyl signal.

Variation of Axial Ligand

The EPR spectra of Fe(P)X, X = F, Cl, at 8 K also showed splittings of the nitroxyl signals of about 500 G and splittings of the iron $g = 6$ signal of about 170 G which indicated that the electron–electron spin–spin interaction was similar for the three complexes.

The value of T_1 for high-spin iron(III) porphyrins is inversely proportional to the zero-field splitting (ZFS).[20] Literature values for the ZFS parameter D are Fe(TPP)Cl, 6.0,[21] 6.5,[22] and 7.0 cm^{-1},[23] and Fe (TPP)Br, 12.5 cm^{-1}.[24,25] Since the value of D for Fe(protoporphyin IX)F is 5.6 cm^{-1} [26] and ZFS for iron tetraphenylporphyrins tend to be smaller than for natural porphyrins,[21,23] the value of D for Fe(P)F is probably between 3.0 and 5.0 cm^{-1}. Even with these uncertainties, the values of D clearly increase in the order X = $F^- < Cl^- < Br^-$. Therefore, at constant temperature the values of T_1 for Fe(P)X would be expected to decrease in the order X = F > Cl > Br. All of the T_1 values are expected to decrease with increasing temperature.

The EPR spectra for Fe(P)X, X = F, Cl, Br, at about 95 K are shown in Figure 3. At this temperature the splitting of the nitroxyl signal is largely collapsed in the spectrum of Fe(P)Br. In the spectrum of Fe(P)Cl the nitroxyl signal is approximately at coalescence and the peak-to-peak line width of the iron signal is similar to that for Fe(P)Br at 34 K. Thus the iron relaxation rate for X = Cl at 95 K is similar to that for X = Br at 34 K. In the spectrum of Fe(P)F, the splitting of the nitroxyl signal is still clearly resolved at 95 K. Therefore, the relaxation rate for X = F is substantially slower than for X = Cl or Br. The extent of collapse of the nitroxyl splitting at 95 K indicates that the iron relaxation rate (T_1^{-1}) increases in the order X = F < Cl < Br as expected on the basis of the differences in zero-field splitting.

The detailed analysis of the line shapes of these signals as a function of temperature will provide the first opportunity to carefully examine the effects of T_1 on the line shapes of a nitroxyl EPR signal interacting with a rapidly relaxing paramagnetic metal.

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