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Models of the Cytochromes *b*. 8. Two-Dimensional Nuclear Overhauser and Exchange Spectroscopy Studies of Paramagnetic "Cavity" Type (Tetraphenylporphinato)iron(III) Complexes of Planar Ligands[1]

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Abstract: The paramagnetic bis-2-methylimidazole complex of (tetramesitylporphinato)iron(III) chloride, with short T_1 and T_2 relaxation times, was investigated in CD_2Cl_2 by NOESY (nuclear Overhauser and exchange spectroscopy) experiments as a function of temperature (−29, −54, −74 °C). The two-dimensional (2-D) maps obtained at −29 and −54 °C revealed cross peaks due to both chemical exchange and the nuclear Overhauser effect (NOE), while the map obtained at −74 °C showed only NOE cross peaks. The NOE cross correlations are consistent with the 2-MeImH ligands being positioned over or near the meso carbon atoms, rather than over the porphyrin nitrogens, as previously suggested by Nakamura and Groves (*Tetrahedron* **1988**, *44*, 3225). The nonbonded interactions between the methyl groups of the 2-methylimidazole (2-MeImH) ligands and the mesityl groups of the porphyrin phenyl rings for this orientation of the axial ligands produce a strongly ruffled porphyrin core having two oblong "cavities" at right angles to each other, one above and one below the plane of the porphyrin ring, which hold the "hindered" axial ligands in perpendicular planes over the meso positions. The chemical exchange cross peaks are indicative of interconversion of all resonances of a particular type, due to rotation of the axial ligands rather than axial ligand exchange. This interpretation is confirmed by the fact that there are no cross peaks observed between free and coordinated 2-MeImH resonances at any of the temperatures investigated. Rotation of the 2-MeImH ligands requires that alternate phenyl rings "flap" up and down as the ligands rotate. The coupling pattern between the pyrrole-H protons is consistent with that expected on the basis of the extrapolated intercepts of the Curie plot.

Introduction

Metal complexes of tetrakis(2,6-disubstituted phenyl)porphyrins such as tetramesitylporphyrin ($TMPH_2$) or tetrakis(2,6-difluoro,-dichloro-, or dibromophenyl)porphyrins have found considerable utility in the investigation of hydroxylation reactions which attempt to model those of cytochrome P450.[3-12] In addition to these uses as model compounds, Nakamura and Groves have recently shown for the bis-2-methylimidazole complex of (tetramesitylporphinato)iron(III) chloride ($TMPFe^{III}Cl$), that ortho-phenyl substituents hinder the rotation of the planar axial ligands about the metal–ligand bond[13] on the NMR time scale, as evidenced by dynamic one-dimensional (1-D) proton NMR studies. They concluded that the pattern and number of ^1H signals observed were consistent with the two axial ligand planes of 2-methylimidazole lying over the porphyrin nitrogen N(1)–N(3) and N(2)–N(4) axes, in perpendicular planes, with the resulting structure having C_2 symmetry.

On the basis of two-dimensional (2-D) NOESY (nuclear Overhauser and exchange spectroscopy) experiments performed at −29, −54, and −74 °C for the 2-methylimidazole (2-MeImH) complex of TMPFeCl, which has short spin–lattice (T_1) and spin–spin (T_2) relaxation times, we offer a novel alternative interpretation of the results obtained by Nakamura and Groves[13] and illustrate the utility of NOESY spectra collected at several temperatures in separating the contributions from through-space correlations due to the nuclear Overhauser effect and those due to chemical exchange. We will further show that variable-temperature NOESY experiments can successfully be used to demonstrate the dynamic flexibility of the porphyrin ring for the complex investigated. Due to the extreme mobility ("flapping") of the phenyl rings and the meso carbon atoms as the axial 2-MeImH ligands rotate, chemical exchange is the predominant contribution to the NOESY map at −29 °C. At low temperatures the rotation and flapping motion is reduced, chemical exchange is somewhat (−54 °C) or completely (−74 °C) suppressed, and only nuclear Overhauser effects contribute to the cross correlation pattern observed at −74 °C.[14] This pattern and the number of resonances obtained is only explicable if the 2-MeImH ligands are positioned over the meso carbon atoms in perpendicular planes. This viewpoint, which is supported by results of X-ray crystal structure determinations of similar low-spin $TMPFe^{III}$ complexes,[15,16] is discussed below.

Experimental Section

$TMPH_2$ was synthesized by the BF_3–ethanol cocatalysis method described by Lindsey[17] and purified as described.[17] Iron was inserted and

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(1) A preliminary account of this work was reported at the 200th National Meeting of the American Chemical Society, Washington, DC, August 1990.

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(15) X-ray crystal structures of five bispyridine complexes of $TMPFe^{III}$, including those of 3-ethyl- and 3-chloropyridine,[16] have shown that in each case the axial ligands are in approximately perpendicular planes lying over the meso positions.

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the complex converted to the high-spin chloroiron(III) form by methods described previously.[18] The $(2,6\text{-}Cl_2)_4TPPFeCl$ was prepared by shaking a methylene chloride solution of $(2,6\text{-}Cl_2)_4TPPFeClO_4$ twice with 0.5 M HCl, followed once with distilled water. The methylene chloride layer was dried over Na_2SO_4 and evaporated to dryness. The solid was redissolved in methylene chloride, and gaseous HCl was bubbled through the solution for 30 s; it was then evaporated to dryness. Proton NMR studies were performed on 10 mM solutions of the Fe(III) porphyrin in CD_2Cl_2 (99.8%, Cambridge Isotopes); 2-MeImH (Aldrich, 1 M stock solution in CD_2Cl_2) was titrated into the solution until the 1-D NMR spectrum at 0 °C showed no evidence of high-spin Fe(III) porphyrin, as evidenced by the disappearance of the pyrrole-H resonance at +86 ppm. For optimal NOESY spectral acquisition, with the longest possible T_1s, samples were degassed by bubbling with argon for 10 min prior to NMR spectroscopic investigation.

Proton NMR spectra were recorded at San Francisco State University on a General Electric GN-300WB spectrometer operating at 300.10 MHz. Typically, 1-D spectra were acquired with 128 free induction decays of 16K data points over a spectral bandwidth of about 18 kHz, using a 30° pulse (3.2 μs). Due to very short spin–lattice relaxation times T_1 (3 ms < T_1 < 360 ms) a short relaxation delay of 600 ms was used. Data were typically processed with 10-Hz exponential apodization prior to Fourier transformation. Chemical shifts were referenced to residual $CHDCl_2$ (5.32 ppm). NOESY spectra were collected on the same instrument using 128 t_1 blocks of 32 scans each over a spectral bandwidth of about 18 kHz and using 256 complex t_2 points to give a total experiment time of 1.37 h. The typical $90\text{–}t_1\text{–}90\text{–}\tau_m\text{–}90\text{–}t_2$ pulse sequence with a composite 180° pulse applied during the mixing period to suppress unwanted cross peaks arising from scalar interactions was used to obtain the data sets. The mixing times at individual temperatures were optimized by trial and error to give maximum intensity of cross peaks, including those between protons of T_1s differing by as much as a factor of 5. Typically, mixing times which produced optimal intensities of all cross peaks were those which were 15–30% longer than the shortest T_1s of protons which were correlated. This is in contrast to the widely accepted practice for diamagnetic compounds of using mixing times of the order of the longest T_1.[19] Data were processed with a 30°-phase shifted sine-bell-window function in both dimensions, zero-filled once to 256 t_1 × 256 t_2 points prior to Fourier transformation, magnitude calculation, and symmetrization.

Results and Discussion

Two-dimensional NMR experiments, including NOESY and COSY (homonuclear correlation spectroscopy) experiments have been utilized to determine structural and dynamic properties of diamagnetic molecules, both relatively small organic molecules[20] and macromolecules including proteins,[21] oligosaccharides,[22] DNA fragments,[23] and RNAs.[24] Relatively few successful applications of these experiments to paramagnetic molecules have been reported[25,26] because (1) hyperfine shifts (contact and/or dipolar) broaden the resonances, thus obscuring the scalar couplings between protons, (2) the paramagnetically induced relaxations shorten both spin–spin (T_2) and spin–lattice (T_1) relaxation times, sometimes so dramatically that the detection of significant NOESY cross peak intensity is prevented, and (3) for the COSY experiment, short T_2s decrease the time available for buildup of coherence as well as obliterate cross peaks due to overlap, and hence cancellation of the antiphase components often occurs,[26,27] precluding the observation of any COSY cross correlations at all. Such is the case for the present system, where the $T_2{}^*$s of the proton signals of interest are as short as 1.5 ms. Thus all attempts to observe COSY cross peaks at any temperature failed.

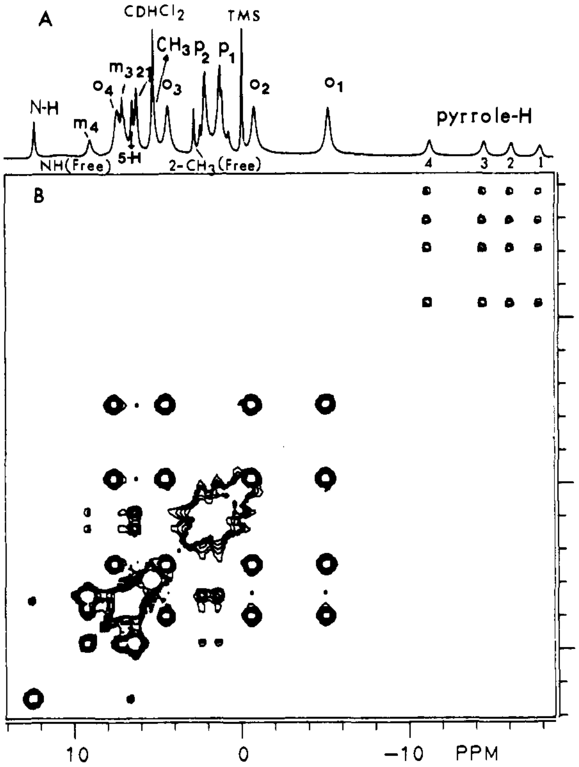

Figure 1. (A) The 300-MHz ^1H NMR spectrum of a 10 mM sample of $[TMPFe(2\text{-}MeImH)_2]Cl$ in CD_2Cl_2 at −29 °C with assignments of all resonances. (B) NOESY map collected with optimized 80-ms mixing time showing chemical exchange (EXSY) cross peaks and 2-D NOE cross peaks. The latter are observed between the NH and 5-H resonances of coordinated 2-MeImH, while a combination of NOESY and EXSY correlations are observed between para CH_3 and meta H resonances and between ortho CH_3 and meta H signals. The expected location of EXSY cross peaks between the methyl resonances of free and coordinated 2-MeImH if chemical exchange of the axial ligand were involved would be 2.85, 5.29 ppm and 5.29, 2.85 ppm.

For the NOESY experiment, where cross peak detection is less sensitive to the short T_2s of paramagnetic samples than is the COSY experiment, the choice of the values for the parameters (mixing time, τ_m, block size, $2N$, and spectral bandwidth, F), utilized for successful acquisition of the NOESY maps, is crucial. In order to observe NOESY cross peaks for the iron complex it was necessary to set the acquisition time (t_2) to some value not significantly greater than T_2, such that there would still be detectable coherence following the third 90° pulse, even for later t_1 data increments. Since the acquisition time $A_t = N/2F$, where N is the total number of real data points in the t_2 dimension, an acquisition time of the order of magnitude of T_2 (<2 ms) leads to severe limitations in block size and spectral bandwidth. For the current experiment, NOESY spectra could be obtained with $N = 256$ and $F = 18$ kHz, for which the acquisition time was thus 7 ms. This fixes the digital resolution ($1/A_t$) at 141 Hz. Using a larger block size simply lengthens the acquisition time, which, in comparison to the $T_2 < 2$ ms, leaves no signal to be acquired during time period t_2 for many of the later t_1 data sets.

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In addition to the constraints imposed on achievable digital resolution by the short T_2s of the protons of [TMPFe(2-MeImH)$_2$]Cl, the wide range of T_1s (3–360 ms) among the protons of the molecule required optimization of the mixing time τ_m to observe cross peaks. Since the T_1s of the correlated protons were very different, and decreased with decreasing temperature,[28] changes in τ_m had dramatic effects on cross peak intensity (or absence). As a rule, the optimum mixing times required to detect NOESY or chemical exchange cross correlations were found to be 1.15–1.3 times the shorter T_1 of the two protons for which couplings were sought.

Figure 1A shows the 1-D proton NMR spectrum of [TMPFe(2-MeImH)$_2$]Cl at −29 °C in CD_2Cl_2. All peak assignments agree with those of Nakamura and Groves.[13,29] (A similar peak pattern is observed for the [(2,6-Cl$_2$)$_4$TPPFe(2-MeImH)$_2$]Cl complex in CD_2Cl_2 at −29 °C, except for the absence of the ortho CH_3 resonances and the replacement of the two para CH_3 peaks by two para H resonances.[30,31]) The 2-D NOESY map at −29 °C, collected with optimized 80 ms mixing time, is shown in Figure 1B. Very strong cross peaks are observed between all four pyrrole H resonances, all four ortho CH_3 resonances, all four meta H signals, and the two para CH_3 resonances. Clearly, this suggests that these sets of cross peaks arise from chemical exchange, and hence all protons of a particular type are in chemical exchange with each other. A combination of chemical exchange (EXSY) and NOE cross correlations are apparent between the two para CH_3 resonances and both meta H resonances at 9.03 and 6.26 ppm and between the two most upfield-shifted ortho CH_3 signals and the meta H signals at 6.26 ppm. The cross peaks observed between the NH and the 5 H resonance of coordinated 2-MeImH cannot arise from chemical exchange (because the scalar coupled protons should also be dipolar (through space) coupled), and therefore must result from nuclear Overhauser effect interactions. Notably absent in this NOESY map are cross peaks between the methyl groups of free and coordinated 2-MeImH, even though ligand exchange at this temperature is expected to be more rapid than at the lower temperatures studied. The chemical shift positions of the expected cross peaks would be at 2.85, 5.29 and 5.29, 2.85 ppm in Figure 1B. The absence of these EXSY cross peaks suggests that the chemical exchange process is not the dissociation of 2-MeImH, but rather hindered rotation of the axially coordinated ligands, consistent with observations made by Nakamura and Groves.[13]

Figure 2A shows the 1-D proton NMR spectrum of [TMPFe(2-MeImH)$_2$]Cl in CD_2Cl_2 at −54 °C, and Figure 2B shows the corresponding NOESY map at −54 °C obtained with an optimized mixing time of 76 ms. Again, the 2-D contour plot shows cross correlations among all four ortho CH_3 resonances, all meta resonances, and the two para CH_3 resonances, and all of the pyrrole H resonances (at a deeper contour level than that shown). At −54 °C (Figure 2B), in comparison to the contour plot at −29 °C (Figure 1B), the chemical exchange (EXSY) cross peaks are somewhat suppressed; the cross correlations between the two para CH_3 signals and each of the meta H resonances, each of the four ortho CH_3 resonances and the afore-mentioned meta H, and between the coordinated 2-MeImH N-H and 5-H signals are relatively more pronounced. Some cross peaks among the phenyl substituents arise from chemical exchange; a number of them disappear at −74 °C, as will be discussed below. In addition to these cross peaks observed at both −29 and −54 °C, the NOESY spectrum at −54 °C also exhibits NOE cross correlations between ortho CH_3(2) and pyrrole H(4) and ortho CH_3(3) and pyrrole H(2) and -(3) signals (Figure 2B). However, there is only one set of cross peaks observed between an ortho CH_3 signal, that of ortho CH_3(1), at −6.07 ppm, and the methyl resonances of coordinated 2-MeImH at 4.99 ppm (marked by arrows in Figure 2B). Thus, ortho CH_3(1) must be spatially near the methyl group of the coordinated ligand.

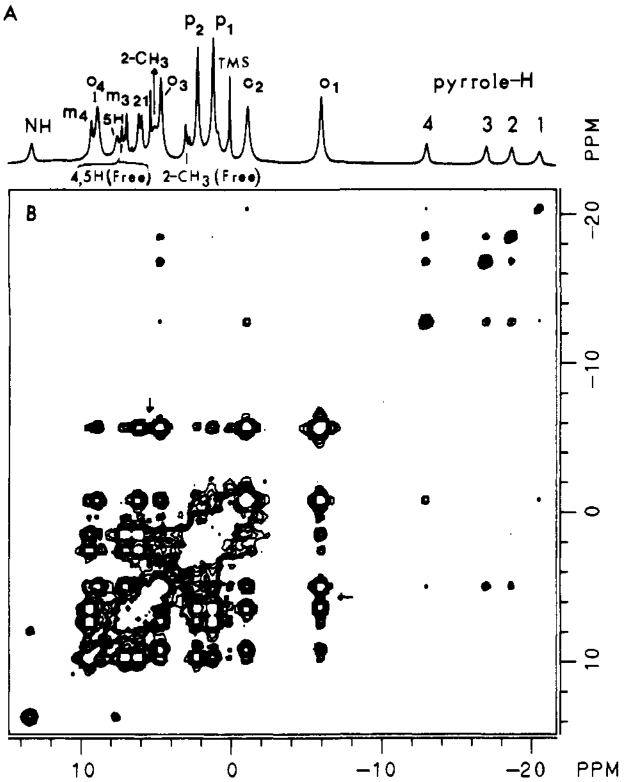

Figure 2. (A) The 300-MHz ^1H NMR spectrum of a 10 mM sample of [TMPFe(2-MeImH)$_2$]Cl in CD_2Cl_2 at −54 °C with assignments of all resonances. (B) NOESY map collected with optimized 76 ms mixing time showing chemical exchange (EXSY) cross peaks and 2-D NOE cross peaks. The latter are observed between the NH and 5-H resonances of coordinated 2-MeImH, while a combination of NOESY and EXSY correlations are observed between para CH_3 and meta H resonances and ortho CH_3 and meta H signals. The NOE cross peaks between ortho CH_3(1) and the methyl group of coordinated 2-MeImH are marked by arrows.

Upon lowering the temperature in increments of 5° from −54 to −74 °C, some cross peaks disappear; they are therefore assigned as EXSY cross peaks. At −74 °C EXSY cross peaks are entirely suppressed, and all cross peaks still detected are NOE correlations. All resonances exhibit extreme broadening, as shown in the 1-D NMR spectrum of the complex in Figure 3A. The following NOE cross correlations among the phenyl substituents are observed, as shown in the expanded region of the spectrum in Figure 3B: meta H(1) to para CH_3(1) and ortho CH_3(1); meta H(2) to para CH_3(2) and ortho CH_3(2); meta H(3) to para CH_3(1) and ortho CH_3(3); and meta H(4) to para CH_3(2) and ortho CH_3(4). Complete suppression of the EXSY cross peaks allows the observation of only one set of 2-D NOE cross peaks between the pyrrole H resonances, as shown at a deep contour level in Figure 4A, indicating that signals (4) and (2) are derived from protons within the same pyrrole ring. No cross peaks were detected between pyrrole signals (1) and (3) under any experimental condition.

The NOESY cross peak pattern observed at −74 °C (Figures 3 and 4A) is consistent with the structure proposed in Figure 4B,

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(28) Approximate T_1s at −29 °C of the protons of Figure 1A and 3 ms (4-$H_{(coord)}$), 48 ms (N-$H_{(coord)}$), 87 ms (2-$CH_{3(coord)}$), 60–70 ms (meta H), 70 ms (ortho CH_3), 360 ms (para CH_3), ca. 40 ms (pyrrole H). At −54 °C the T_1s of the N-$H_{(coord)}$ had shortened to 33 ms, both the meta H and ortho CH_3 had shortened to ca. 58 ms, the para CH_3 to 290 ms, and the pyrrole H to 36–29 ms. At −74 °C the T_1s of the N-$H_{(coord)}$ had shortened to 27 ms, the meta H to ca. 28 ms, the ortho CH_3 to 21–36 ms, the para CH_3 to 200 ms, and the pyrrole H to 24–20 ms.

(29) The broad resonance of the 4-H protons of coordinated 2-MeImH (26.61 ppm) is not included in Figure 1A.

(30) Simonis, U.; Walker, F. A., unpublished data.

(31) The [(2,6-Cl$_2$)$_4$TPPFe(2-MeImH)$_2$]Cl complex shows four pyrrole H, four meta H, and two para H signals, but preliminary studies suggest that in this case the spin–lattice relaxation times, T_1, are too different to allow the buildup of NOESY cross peaks, as has been discussed by others.[26,27,32]

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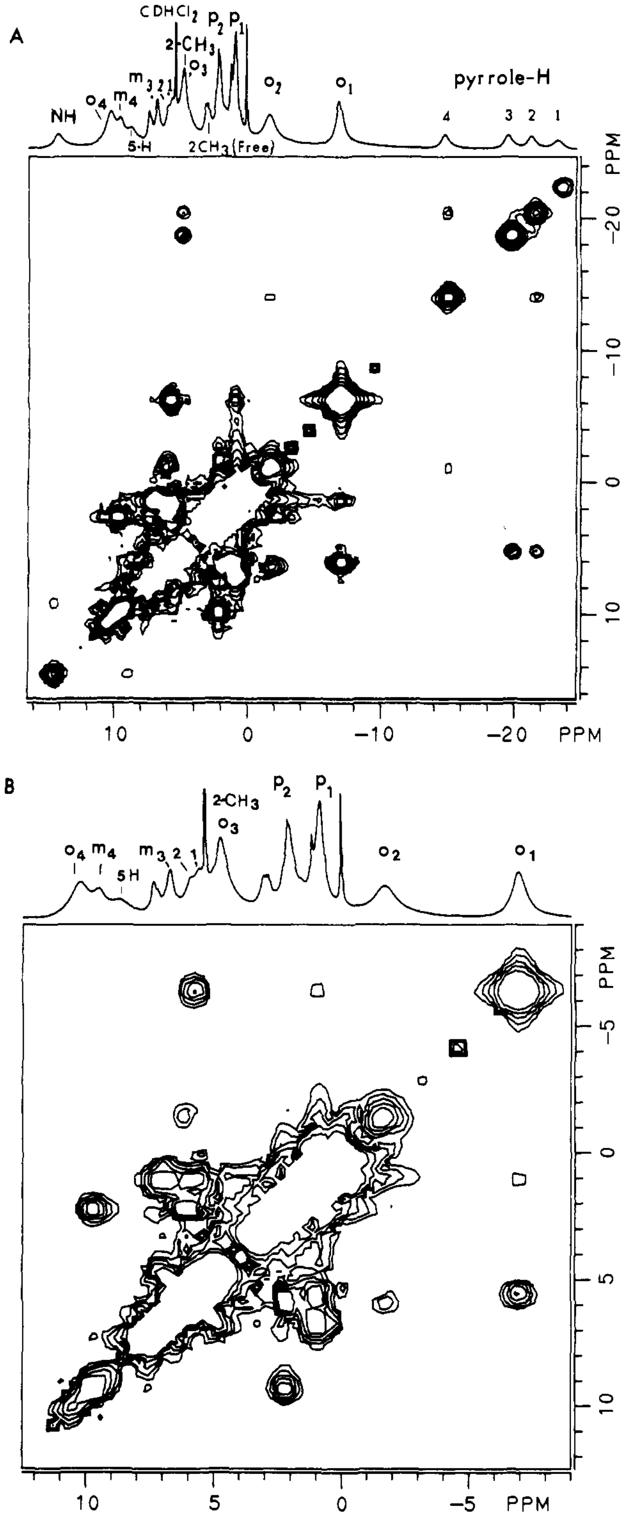

Figure 3. Proton 1-D spectrum and NOESY map collected at -74 °C with optimized mixing time of 50 ms showing 2-D NOE cross peaks (A) at a level deep enough to show the cross peaks between ortho CH_3 and pyrrole H resonances, and (B) on an expanded scale at a higher level which shows the cross peaks between particular ortho CH_3 and meta H and meta H and para CH_3 resonances.

in which the ortho and para CH_3 and meta H resonances of the two types of phenyl rings should show NOE cross correlations within each ring, e.g., meta H(1) should exhibit through-space couplings to para $CH_3(1)$ and ortho $CH_3(1)$ etc. The inequivalence of the pyrrole H signals must be caused by the off-axis binding of the 2-MeImH ligands due to the 2-methyl substituent and not simply by the lower symmetry of the 2-MeImH ligand, since the binding of unsymmetrical pyridines such as 3-methylpyridine to TMPFeCl does not cause splitting of the pyrrole H resonances.[30] From consideration of the NOESY cross peaks observed in the 2-D spectrum at -74 °C (Figures 3 and 4A) and that observed between ortho $CH_3(1)$ and the 2-CH_3 signal of coordinated 2-MeImH in the NOESY map at both -54 and -74 °C (Figure 2B)[33] it is possible to make a unique assignment of all resonances. In terms of the pyrrole H resonances, H_a gives rise to peak (3), H_b to (2), H_c to (4), and H_d to (1). The assignments of the ortho and para CH_3 and meta H resonances of the phenyl rings are given in Figure 4B. The 2-CH_3 group of the axial ligand is close to ortho $CH_3(1)$, as shown. The ortho $CH_3(3)$ group is in close proximity to both pyrrole H_a and H_b, and the ortho $CH_3(2)$ group is spatially close to pyrrole H_c (Figures 3A and 4B).

While the assignments of the pyrrole H resonances given in Figure 4B may at first consideration seem unexpected, we must consider not the pyrrole H pattern observed at -74 °C but rather the temperature dependence of these proton resonances extrapolated to $1/T = 0$, where the pattern of unpaired electron density is indicative of the "in-plane" or "rhombic magnetic anisotropy" due to the second-order Zeeman interaction.[34] Since pyrrole H(4) has a much weaker temperature dependence than the other three, as shown in Figure 5, its extrapolated intercept is the least positive, making the order of the intercepts $4 < 1 \sim 2 < 3$. Hence the assignments of the pyrrole H resonances are totally consistent with the pattern of unpaired electron delocalization expected for a low-spin Fe(III) porphyrin in which the symmetry plane of the orbital of the unpaired electron passes through the porphyrin nitrogens of the rings that contain H_b and H_c.[34] If we assume that the off-axis binding of the 2-MeImH ligands increases the unpaired electron delocalization to the pyrrole positions to which H_a and H_b are bound and decreases the delocalization to the positions to which H_c and H_d are bound, as shown diagrammatically in the insert of Figure 5, then we can account for the pyrrole H coupling pattern observed.

As mentioned above, the interpretation of the number of proton NMR signals observed for $[TMPFe(2\text{-}MeImH)_2]Cl$ in terms of off-axis binding of the 2-MeImH ligand is strengthened by the fact that the binding of 3-methylpyridine to TMPFeCl does not cause splitting of the pyrrole H resonances,[30] although the molecular structure of five bispyridine complexes of $TMPFe^{III}ClO_4$ all show that the pyridine ligands are oriented with their axial ligand planes lying over opposite meso positions,[16] as shown in Figure 9a of ref 35. *Thus, the paramagnetic Fe(III) center apparently does not sense lowered axial ligand symmetry unless that lowered symmetry causes the Fe–N_{ax} bond axis to be distorted from the heme normal.* Such a distortion (as is expected in the 2-MeImH case) creates four different types of pyrrole H, four ortho CH_3, two para CH_3, and four meta H environments, each of which experiences a different contact and dipolar shift. Only two of the four different types of pyrrole H should show 2-D NOE cross peaks. This viewpoint is in accord with results of previous X-ray crystallographic investigations of the bis-2-methylimidazole complex of $TPPFe^{III}$, which showed[36,37] that "hindered" ligands such as 2-MeImH must lie over the meso positions if a low-spin complex is to result. (The X-ray structure of single crystals of the related bisbenzimidazole complex of $TPPFe^{III}$ demonstrates that when the ligands lie over the porphyrin nitrogens, the complex is high-spin.[38]) For other low-spin Fe(III)

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[33] Unfortunately, at -74 °C, the 2-CH_3 signal is superimposed on the ortho $CH_3(3)$ signal.

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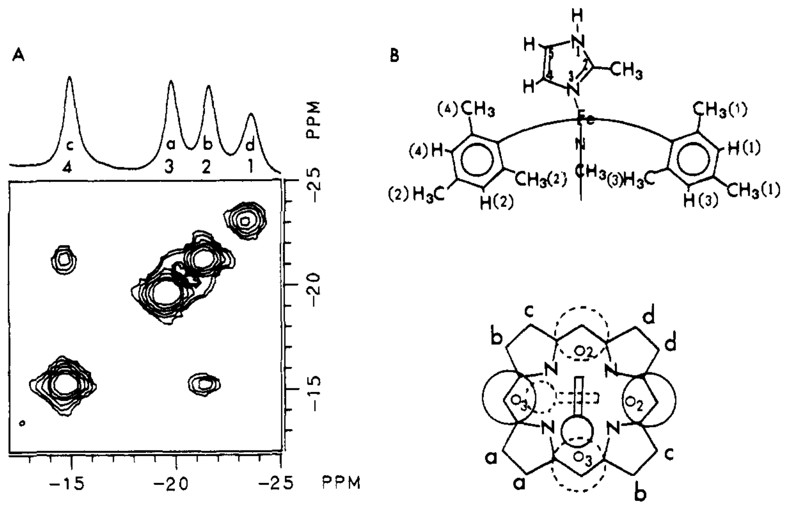

Figure 4. (A) The pyrrole H region of the NOESY map of $[TMPFe(2\text{-}MeImH)_2]Cl$ at -74 °C at a low contour level, showing only one set of cross peaks, between pyrrole signals 4 and 2. (B) Proposed model of the structure of $[TMPFe(2\text{-}MeImH)_2]Cl$, showing the schematic representation of the ruffling of the porphyrin ring which bends the mesityl groups to move the ortho CH_3 out of the way of the upper axial ligand. The opposite bend of the other two mesityl groups provides an oblong binding cavity for the lower axial ligand, at right angles to that shown. The unique pyrrole H protons are labeled a–d in accord with the symmetry of the molecule. From information discussed in the text, H_a gives rise to peak (3), H_b to (2), H_c to (4), and H_d to (1). Assignments of phenyl resonances are given in parentheses in Figure 4B. Solid circles and lines represent ortho CH_3 groups and ligands above the plane, while dotted symbols represent those below the plane.

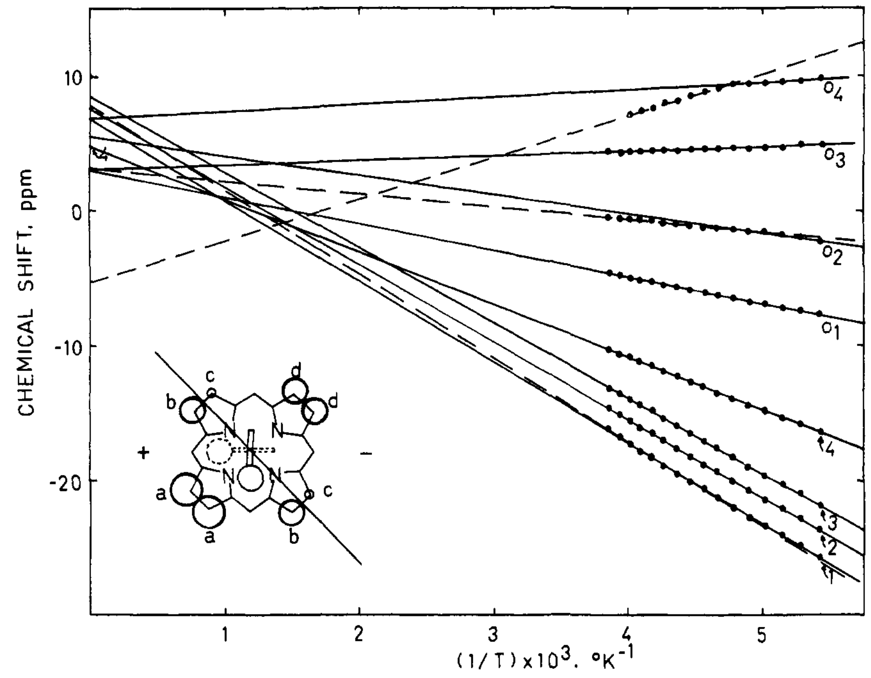

Figure 5. Curie plot of the pyrrole H and ortho CH_3 peaks of $[TMPFe(2\text{-}MeImH)_2]Cl$. Note that the line for pyrrole H(4) crosses those of the other three and has the least positive intercept. Pyrrole H(1) and ortho $CH_3(2)$ and -(4) exhibit changes in slope at $1/T = 0.00480\ K^{-1}$ or -65 °C. The temperature dependence of these three resonances above -65 °C is represented by the dashed line in each case. Insert: Diagram of the electron density distribution in the orbital of the unpaired electron, based on the relative intercepts of the pyrrole protons.[34] The (+) and (−) notation on the left and right side of the structure indicate the regions on either side of the nodal plane bisecting the porphyrin ring where electron density appears to be increased and decreased, respectively, over that expected for simply the average effect of the two planar ligands. This increased and decreased electron density is believed to be the result of the off-axis binding of 2-MeImH to iron, which is caused by the steric effect of the 2-methyl substituent.

complexes of TMP[16,35] and $(2,6\text{-}Cl_2)_4TPP$[16,39] it has been shown that planar axial ligands are able to bind to Fe(III) porphyrins with their ligand planes lying over the meso positions even though steric repulsions are expected between the mesityl ortho CH_3 and the methyl groups of 2-MeImH. These nonbonded interactions between the methyl groups of the 2-MeImH ligands and the mesityl groups for this orientation of the axial ligand are minimized by tipping the ortho mesityl groups away from the 2-methylimidazole ring, producing a strongly ruffled porphyrin core having two oblong "cavities" at right angles to each other, which hold the "hindered" axial ligands in perpendicular planes over the meso positions.[16,35]

The slope of the Curie plot of the proton signal of ortho $CH_3(4)$ changes sharply at 208 K or -65 °C (Figure 5, dashed line). Since the isotropic shifts of phenyl substituents in low-spin Fe(III) complexes have been shown to be overwhelmingly dipolar in nature,[40] the sharp change in slope of ortho $CH_3(4)$ is indicative of a change in the relative importance of the axial and rhombic contributions to the dipolar shift at -65 °C. In particular, the in-plane, or rhombic anisotropy term, whose angular dependence

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$(\sin^2 \Theta \cos 2\Omega)$[34,40,41] is expected to be averaged to zero by ligand rotation, must be of opposite sign, but smaller in magnitude than the axial term, whose angular dependence $(3 \cos^2 \Theta - 1)$[34,40,41] does not average to zero as the ligands rotate. Less pronounced changes in slope were also observed for ortho $CH_3(2)$ and pyrrole H(1), which we have assigned as H_d (Figure 5, dashed lines). All three of these groups are nearest the 5-H of the two 2-MeImH ligands. This region of the complex is relatively less sterically encumbered than is the opposite end, near H_a and ortho $CH_3(1)$ and -(3). The change in slopes of the Curie plots for protons H_d and ortho $CH_3(2)$ and -(4) at −65 °C may indicate the temperature at which rotation ceases as the structure of the molecule is locked into the strongly ruffled form. This form may not only have a different rhombic but also a different axial contribution to the dipolar shift to the three protons whose slopes change at −65 °C than does the freely rotating form, since the value of $3 \cos^2 \Theta - 1$ will be different for the locked ruffled form than for the average of the forms which are subjected to rotation of the axial ligands.

The EPR spectra of the 2-MeImH complexes of $TMPFe^{III}$ and $(2,6\text{-}Cl_2)_4TPPFe^{III}$ in frozen glasses of CH_2Cl_2 have only one resolved feature, with $g \geq 3.0$.[35] This "large g_{max}" type of EPR signal has previously been shown to occur for bispyridine or hindered imidazole complexes of low-spin Fe(III) porphyrins in which the axial ligands are in perpendicular planes.[16,35,37]

The presence of all possible EXSY cross peaks between chemically equivalent protons (Figure 1B and 2B), together with the absence of cross peaks between free and bound 2-MeImH (as evidenced most clearly in the NOESY map at −29 °C, Figure 1B, in which resonances overlap less than at lower temperatures), indicates that the mechanism of the chemical exchange process is rotation of the bound ligands, as originally suggested by Nakamura and Groves.[13] Such rotation would cause sequential switching of the up/down ruffling distortion of individual *meso*-phenyl groups and indicates that there must be large amplitude motions of the phenyl groups in homogeneous solution, even at relatively low temperatures, if such rotation is to take place. Such fluxionality is seldom detectable, since in the absence of ortho phenyl substituents and/or sterically hindered ligands, preliminary NMR data suggest that axial ligands appear to rotate rapidly, even at −95 °C.[30] In light of the difference in structural model proposed here, the activation parameters measured by Nakamura and Groves[13] for the rotation of the axial 2-MeImH ligands, $\Delta H^{\ddagger} = 12.9$ Kcal/mol, $\Delta S^{\ddagger} = 3.7$ eu,[13] represent the combination of those for ligand rotation and fluxional distortion of the TMP ligand necessary to allow that rotation. Despite the large amplitude motions necessary, these activation barriers are much lower than those due to ligand exchange ($\Delta H^{\ddagger} = 20.1$ Kcal/mol, $\Delta S^{\ddagger} = 40$ eu[42]), and clearly represent those of a totally different chemical exchange process. Further investigations of axial ligand rotation in these "cavity" type porphyrins are currently underway.

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Charge Transfer across Oblique Bisporphyrins: Two-Center Photoactive Molecules

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Abstract: A bisporphyrin, comprising gold(III) and zinc(II) porphyrins held in an oblique orientation via a 1,10-phenanthroline spacer, undergoes intramolecular electron transfer with almost unit quantum efficiency on excitation with visible light. The reaction pathway and kinetics vary according to which porphyrin absorbs the incident photon, but the net reaction involves intramolecular electron transfer from zinc porphyrin (ZnP) to gold porphyrin (AuP^+). Thus, the ZnP excited singlet state transfers an electron to the appended AuP^+. Excitation of the AuP^+ generates the triplet excited state which abstracts an electron from the ZnP (77%) or transfers electronic energy to it (15%). The ZnP triplet state also transfers an electron to the appended AuP^+. Similar processes are observed with the corresponding gold/free-base bisporphyrin.

Photoinduced energy or electron transfer between porphyrins, which is of interest both for understanding natural photosynthesis and for the design of molecular electronic devices, has been demonstrated for various supramolecular systems.[1-7] Singlet energy transfer, occurring by the Förster mechanism, has been described for a range of covalently linked zinc(II)/free-base bisporphyrins possessing different types of spacer group.[5] These studies have been extended to larger arrays in an effort to mimic

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