Valence Electron Cloud Asymmetry from Two Points of View: A Correlation between Mössbauer Quadrupole Splittings and ^{57}Fe NMR Chemical Shifts of Diamagnetic Iron(II) Porphyrinates

Jayapal Reddy Polam,[1a] Joshua L. Wright,[1a] Kenner A. Christensen,[1a] F. Ann Walker,*[,1a] Holger Flint,[1b] Heiner Winkler,[1b] Michael Grodzicki,[1b] and Alfred X. Trautwein*[,1b]

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721, and Institut für Physik, Medizinische Universität zu Lübeck, Ratzeburgerallee 160, 2400 Lübeck, Germany

Received December 6, 1995[⊗]

Abstract: We have prepared a series of 94.5%-enriched ^{57}Fe(II) complexes of tetramesitylporphyrin and octaethylporphyrin having various bis- or mixed axial ligation and investigated them by both NMR and Mössbauer spectroscopy. The results obtained, and literature values for MbCO and cytochrome *c*, show a rough correlation between ΔE_Q and δ_{Fe}. This correlation suggested that the previously-reported chemical shifts of the complexes [TPPFeL$_2$], L = pyridine-d_5, and pyrrolidine (Nozawa, T.; Sato, M.; Hatano, M.; Kobayashi, N.; Osa, T. *Chem. Lett.* **1983**, 1289) might be incorrect; we have thus used the rapid pulsing method of Schwenck to detect the signal of the bis-pyridine-d_5 complex at 11 715 ppm, within its predicted chemical shift range, based upon the δ_{Fe} *vs* ΔE_Q correlation, and ~4,400 ppm to lower shielding than originally reported. These findings emphasize the value of the Mössbauer−NMR correlation in aiding the detection of ^{57}Fe NMR signals, as well as the perils of seeking these easily "folded" signals without such a correlation.

Introduction

The ^{57}Fe nucleus has an extremely low NMR frequency (~16.3 MHz at 11.75 T) and is therefore only 3.4×10^{-5} as sensitive as ^{1}H at equal isotopic concentration. ^{57}Fe also has a large chemical shift range (>12 000 ppm), and for both the low sensitivity and large chemical shift range reasons, it is thus extremely difficult to detect ^{57}Fe signals by direct methods. For this reason, we have previously used indirect methods that rely upon ~16.3 MHz decoupling of the ~202.5 MHz ^{31}P doublet (J = 36−59 Hz) that results from scalar coupling of ^{57}Fe to ^{31}P for a series of Fe(II) porphyrinate complexes having at least one trimethylphosphine (PMe$_3$) axial ligand.[2,3] However, since phosphines are not naturally-occurring ligands for heme proteins, we sought other means of predicting the approximate ^{57}Fe chemical shifts of diamagnetic iron(II) porphyrinates of biological importance and, hence, simplifying the search for the signals. Silver and co-workers previously reported an apparent correlation between the Mössbauer quadrupole splittings, ΔE_Q, and the iron-57 chemical shifts, δ_{Fe}, of a series of ferrocenes and related Fe(II) arene complexes,[4] and we reasoned that a similar correlation might be observed for Fe(II) porphyrinates. Since Mössbauer spectra have frequently been reported for low-spin Fe(II) model hemes and heme proteins, values of ΔE_Q[5−11] are already available for some of the systems for which ^{57}Fe chemical shifts are known.[12−18] In order to expand the body of available Mössbauer spectroscopic data to include the complexes having at least one trimethylphosphine ligand,[2,3] we have prepared a series of 94.5%-enriched ^{57}Fe(II) complexes of tetramesitylporphyrin (TMP) and octaethylporphyrin (OEP) having various bis- or mixed axial ligation, have used them for NMR studies,[2,3] and have now investigated them by Mössbauer spectroscopy. We have found that a correlation exists between Mössbauer quadrupole splittings and ^{57}Fe NMR chemical shifts, although opposite that reported by Silver and co-workers,[4] that is useful for detecting possible errors in reported ^{57}Fe chemical shifts and for predicting the chemical shift range to be expected for a given iron(II) porphyrinate complex.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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S0002-7863(95)04096-0 CCC: $12.00

Experimental Section

Chloroiron(III) porphyrinates (94.5% enriched with ^{57}Fe, Isotec) were synthesized and purified as described previously.[2,3] Mössbauer samples were prepared by dissolution of the desired ^{57}Fe(III) porphyrinate plus a 5-fold ratio of the desired axial ligand in dimethylacetamide (Aldrich), followed by addition of a 10-fold excess of zinc amalgam and stirring for 1 h in an inert atmosphere glovebox. For preparation of mixed-ligand complexes containing one trimethylphosphine ligand, 1 equiv of 1.0 M PMe_3 in toluene (Aldrich) was added after reduction. In each case, the resulting solution of Fe(II) porphyrinate−axial ligand complex was filtered and transferred into a Delrin Mössbauer sample holder, capped tightly, removed from the glovebox, and immediately frozen in liquid nitrogen.

Mössbauer spectra were recorded at 77 K on a constant-acceleration-type Mössbauer spectrometer, and the raw quadrupole doublet data were fit to Lorentzian line shapes. The zero velocity is referred to the centroid of the room-temperature Mössbauer spectrum of metallic iron foil. The direct-detected ^{57}Fe NMR spectra were recorded in a 10 mm NMR tube at 15, 25, and 35 °C on a Bruker AM-500 NMR spectrometer equipped with a Bruker 10 mm broad-band probe tuned to 16.394 MHz. The ^{2}H lock and ^{1}H decoupler were not used because they created artifactual signals. The rapid pulsing technique of Schwenck[19] was used, with a pulse width of 26.4 μs, a 20.8 kHz spectral bandwidth, an acquisition time of 9.8−98 ms (26 ms appears optimal), and no relaxation delay. The number of transients varied from 4×10^5 to 5×10^6. The spectra were multiplied by an exponential decay function with a 20 Hz line broadening and zero-filled twice before Fourier transformation. The zero reference was external neat $Fe(CO)_5$.

Results and Discussion

Mössbauer spectra of mixed-ligand (PMe_3)-L and bis-L complexes of TMPFe(II) and OEPFe(II) were measured at 77 K in frozen dimethylacetamide solution. Dimethylacetamide was used as solvent because of its relatively high melting point, which allowed investigation of the temperature dependence of the quadrupole splitting of several samples. Only the bis-PMe_3 complex of TMPFe(II) showed measureable temperature dependence of the quadrupole splitting above 150 K. A preliminary explanation of this temperature dependence is that the PMe_3 ligands begin to rotate as the temperature is raised above 150 K, but further studies of this system are under way. Typical Mössbauer spectra are shown in Figure 1, where it can be seen that the quadrupole splitting varies considerably as the axial ligands are varied from two trimethylphosphine to two N-methylimidazole to two 2-methylimidazole ligands. The quadrupole splittings and isomer shifts are summarized in Table 1, where it can be seen that the isomer shifts of the low-spin Fe(II) complexes vary very little among the complexes investigated (0.36−0.46 mm/s), while the quadrupole splittings vary significantly (0.35−1.73 mm/s). Available Mössbauer data on other Fe(II) porphyrinates and heme proteins are also included in Table 1. In addition, ^{57}Fe NMR chemical shifts obtained in this laboratory[2,3] and by other investigators are also included.

In Figure 2 is shown a plot of the quadrupole splitting, ΔE_Q, *vs* ^{57}Fe chemical shift, δ_{Fe}, obtained from the data of Table 1. It is evident that a rough correlation exists, except for two data points, those for [TPPFe(pyrrolidine)$_2$] and [TPPFe(pyridine)$_2$].[12] On the basis of the rough correlation observed in Figure 2, we predicted that the 7258 and 7341 ppm chemical shifts, respectively, of the two complexes mentioned above might be in error. We therefore used our correlation to aid in the search for the true chemical shift of the bis-pyridine complex, which we expected to be between 11 000 and 13 000 ppm. Using the rapid pulsing technique of Schwenck,[19] the ^{57}Fe signal of [TPPFe(Py-d_5)$_2$] in pyridine-d_5 was detected at 11 715 ppm relative to external $Fe(CO)_5$ (Figure 3), after acquisition of 4.2×10^5 transients (~8 h).

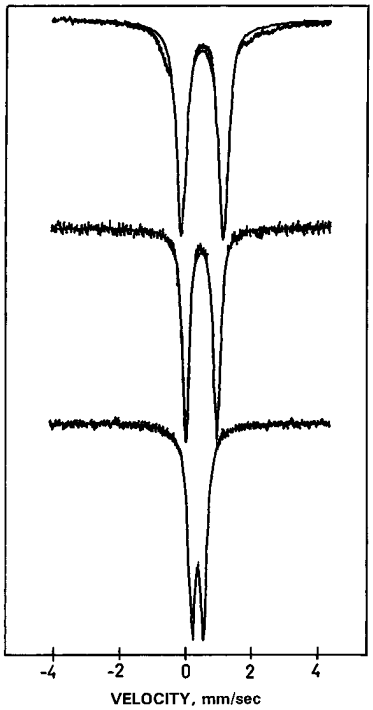

Figure 1. Mössbauer spectra of ~10 mM (a) [OEPFe(PMe_3)$_2$], (b) [OEPFe(NMeIm)$_2$], and (c) [OEPFe(2MeImH)$_2$] in frozen dimethylacetamide at 77 K. Percent effects are 96, 92, and 96, respectively.

The ^{57}Fe signal is easily folded. We also found apparent signals at 9188 and 10 389 ppm when using a large spectral bandwidth (20 kHz) and lower carrier frequencies, but in each case, the signal moved when the carrier frequency was changed and disappeared when the spectral bandwidth was narrowed. The true signal, observed at 11 715 ppm at 25 °C, did not move when the carrier frequency was either increased or decreased by 10 kHz, or when the spectral bandwidth was reduced from 20 to 10.4 kHz. The temperature dependence of the signal was found to be +2.9 ppm/°C, similar to the ~+2−3 ppm/°C found previously for other ^{57}Fe porphyrinates.[2,3,20]

This is the largest ^{57}Fe chemical shift reported thus far for Fe(II) porphyrinates, and its value confirms that the 11 197 ppm value reported for ferrocytochrome *c*[20] is reasonable based on the observed Mössbauer−NMR correlation. This correlation furthermore predicts chemical shifts of ~11 000−13 000 ppm for most bis-pyridine and nonhindered imidazole complexes of model hemes and cytochrome b_5 because of their similar values of ΔE_Q (1.0−1.2 mm/s)[5−9,21] and much larger chemical shifts of perhaps 14 000−16 000 ppm for the bis-2-methylimidazole and -1,2-dimethylimidazole complexes of TMPFe(II),[22,23] which have much larger quadrupole splittings ($\Delta E_Q = 1.64$ and 1.73 mm/s, respectively). Unfortunately, the larger the chemical shift, the larger the expected chemical shift anisotropy[20] (see below) and, thus, the larger the expected line width[24] and the more easily the signal will be buried in the noise. Also, most bis-pyridine and bis(nonhindered imidazole) complexes are quite

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Table 1. ^{57}Fe Mössbauer and NMR Data for a Series of Fe(II) Porphyrinates

	Mössbauer data			NMR data		
complex	*T*, K	isomer shift, mm/s	ΔE_Q, mm/s	*T*, K	δ_{Fe}, ppm	apparent $\delta_{\parallel}$,[a] ppm
cytochrome *c*	4.2	0.45[10]	+1.17[10]	298	11197[20]	15591
myoglobin CO	4.2	0.27[11]	+0.35[11]	296	8227[17]	6681
				288	8234[18]	6702
myoglobin *n*-BuNC				293	9238[24]	9714
cytochrome b_5	4.2	0.43[21]	+1.04[21]			
[(p-OMe)$_4$TPPFe(Py)CO]	298	0.19[5]	0.49[5]	296	8211[13,14,32]	6633
[(p-OMe)$_4$TPPFe(ImH)CO]	298	0.18[5]	0.36[5]	298	8151[16,14,32]	6453
[TpivPPFe(N-MeIm)CO]	4.2	0.27[6]	0.27[6]	298	8110[15]	6330
[TMPFe(PMe$_3$)$_2$]	77	0.36[33]	+0.47[33]	294	7743[3]	5229
[OEPFe(PMe$_3$)$_2$]	77	0.36[33]	+0.35[33]	294	7873[3]	5369
[TMPFe(PMe$_3$)(4-NMe$_2$Py)]	77	0.38[33]	+0.85[33]	294	8883[3,34]	8649
[TMPFe(PMe$_3$)(4-CNPy)]	77	0.39[33]	+0.88[33]	294	9033[3]	9099
[TMPFe(PMe$_3$)(N-MeIm)]	77	0.38[33]	+0.75[33]	294	8827[3]	8481
[OEPFe(PMe$_3$)(2-MeImH)]	77	0.44[33]	+1.05[33]	294	8893[3,35]	8679
[(*p*-Cl)$_4$TPPFe(Pyrr)$_2$]	298	0.40[7]	1.27[7]			
[(*p*-Me)$_4$TPPFe(Pyrr)$_2$]	298	0.42[7]	1.36[7]			
[TPPFe(Pyrr)$_2$]				302	7258[12]	
[TPPFe(Py)$_2$]	77	0.40[8]	1.15[8]	302	7341[12]	
				298	11715[33]	17169
[TMPFe(4-NMe$_2$Py)$_2$]	77	0.39[33]	+1.20[33]			
[OEPFe(4-NMe$_2$Py)$_2$]	77	0.45[33]	+1.02[33]			
[TMPFe(4-CNPy)$_2$]	77	0.28[33]	+1.12[33]			
[OEPFe(4-CNPy)$_2$]	77	0.32[33]	+1.10[33]			
[TMPFe(N-MeIm)$_2$]	77	0.45[33]	+1.11[33]			
[OEPFe(N-MeIm)$_2$]	77	0.46[33]	+0.96[33]			
[TMPFe(2-MeImH)$_2$]	77	0.39[33]	+1.64[33]			
[TMPFe(1,2-Me$_2$Im)$_2$]	77	0.39[33]	+1.73[33]			
[OEPFe(2-MeImH)$_2$]	77	0.34[33]	+1.67[33]			
[TMPFe(PhCH$_2$SCH$_3$)$_2$][b]	77	0.41[33]	+0.60[33]			
		0.48[33]	+1.45[33]			

[a] Calculated from the observed chemical shift, assuming $\delta_{\perp} = 9000$ ppm.[20] [b] Two Fe(II) signals observed, relative abundances about 5:2.

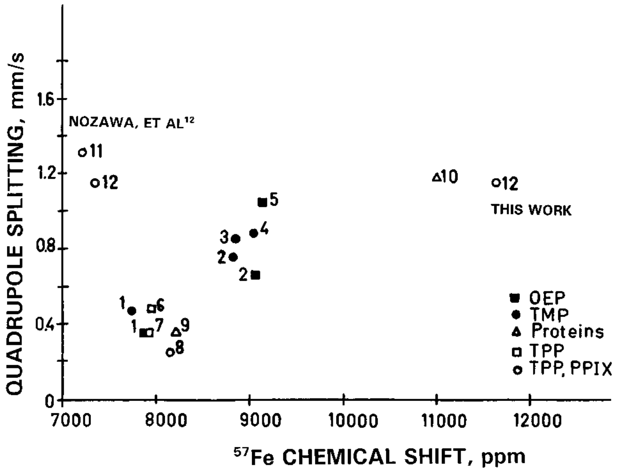

Figure 2. Correlation between Mössbauer quadrupole splitting, ΔE_Q, and ^{57}Fe chemical shift, δ_{Fe}. Note the symbol identification of the porphyrinate ligand in the figure. Ligand combinations: (1) two PMe$_3$;[33] (2) PMe$_3$, NMeIm;[33] (3) PMe$_3$, 4-NMe$_2$Py;[33,34] (4) PMe$_3$, 4-CNPy;[33] (5) PMe$_3$, 2-MeImH;[33,35,36] (6) CO, Py;[5,13,32,36] (7) CO, ImH;[5,14,32,36] (8) CO, N-MeIm;[6,15,36] (9) CO, Histidine;[11,17,18] (10) Methionine, Histidine;[10,20] (11) 2 Pyrrolidine;[7,12,36] (12) two Py-d_5.[8,12,36]

insoluble in most solvents, and hence, concentrations similar to those of [TPP^{57}Fe(Py-d_5)$_2$] in pyridine-d_5 (~10 mM) cannot often be achieved.

The existence of the Mössbauer–NMR correlation results from the related effects of bonding interactions of the porphyrinate and axial ligands on the energies and occupancy of metal orbitals for the two kinds of spectroscopy: ΔE_Q values are approximately related to the ansiotropy of the valence charge distribution in the metal 3d and 4p orbitals, as expressed by the Townes–Dailey approximation:[25,26]

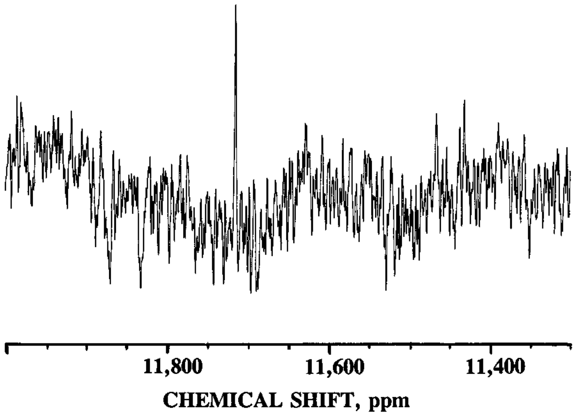

Figure 3. ^{57}Fe NMR signal for a 10 mM solution of [TPP^{57}Fe(d$_5$Py)$_2$] in pyridine-d_5, recorded in a 10 mm NMR tube at 25 °C in a Bruker AM-500 broad-band probe: number of transients, 4.2 × 10^5; 8 h total acquisition time; line broadening, 20 Hz. The signal is referenced to neat Fe(CO)$_5$.

$$q_{val} = {}^4\!/_5\langle r^{-3}\rangle_p[-N_{p_z} + {}^1\!/_2(N_{p_x} + N_{p_y})] + {}^4\!/_7\langle r^{-3}\rangle_d \times [N_{d_x}2{-}y2 - N_{d_z}2 + N_{d_{xy}} - {}^1\!/_2(N_{d_{xz}} + N_{d_{yz}})] \quad (1)$$

where N_p and N_d are the effective populations of the appropriate 4p and 3d iron orbitals, respectively, and $\langle r^{-3}\rangle$ is the expectation value of $1/r^3$ taken over the appropriate 3d and 4p radial

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functions. Deviations from this approximation may be found by MO calculations. Detailed discussion of the use of the Townes−Dailey approximation in predicting or explaining Mössbauer quadrupole splittings has appeared elsewhere.[26]

^{57}Fe NMR shifts are believed to be controlled by the paramagnetic shielding contribution to the screening constant[27,28] where

$$\sigma = \sigma^{\text{dia}} + \sigma^{\text{para}} \tag{2}$$

$$\sigma^{\text{para}} = -(\mu_0 e^2/8\pi m^2)\sum(1/\Delta E_{\text{o},n})[\langle 0|\sum r_j - 3l_{j\alpha}|n\rangle \times \langle n|\sum l_{j\beta}|0\rangle + \langle 0|\sum l_{j\beta}|n\rangle\langle n|\sum r_j - 3l_{j\alpha}|0\rangle] \tag{3}$$

and the matrix elements result from the unquenched orbital angular momentum of the paired electrons in the compounds of open-shell heavy atoms. For complexes of approximate D_{4h} or C_{4v} symmetry, such as the 6-coordinate iron porphyrinates of this study, this equation has two leading terms, arising from two similar $\Delta\mathrm{E}_{\mathrm{o,n}}$, which are much smaller than any others, and hence dominate eq 3. These $\Delta E_{\text{o},n}$ have been shown to arise from the splitting of the lowest-energy transition of a d^6 octahedral complex into two low-energy ligand field transitions for the symmetry groups D_{4h} or C_{4v},[27,28] and because of their similarity in energy, we will henceforth refer to them collectively as ΔE_{opt}.

N_{p} and N_{d}, the sizes of the matrix elements in eq 3, and ΔE_{opt} are all expected to be controlled by the σ donor, π donor/acceptor properties of the axial ligands. For d^6 complexes, good π acceptor ligands such as CO or PMe$_3$ are expected to cause $N_{\text{d}_{xz}}$ and $N_{\text{d}_{yz}}$ to be less than 2.0 because of π back-bonding to the ligands, thus causing the low-spin d^6 electron configuration to have a small excess population of d$_{xy}$ as compared to d$_{xz}$,d$_{yz}$, thereby producing a small positive value of q_{val} and ΔE_{Q}. The same π acceptor interactions are expected to lead to more mixing of axial ligand and porphyrinate wave function character into the d$_{xz}$ and d$_{yz}$ wave functions that contribute to the matrix elements of eq 3, thus decreasing their population, as well as increasing ΔE_{opt}. Thus, both the numerator and denominator of eq 3 contribute to the production of a small value of $|\sigma_{\text{para}}|$ and a relatively small ^{57}Fe chemical shift.

In comparison, for ligands such as imidazoles or pyridines that are both strong σ and strong π donors, we must consider the importance of σ donation to the metal d$_{z^2}$ and p$_z$ orbitals and π donation to the metal p$_x$ and p$_y$ orbitals. With regard to Mössbauer quadrupole splittings, σ donation to either the d$_{z^2}$ or p$_z$ orbitals would lead to a decrease in quadrupole splitting (eq 1), while π donation to the p$_x$ and p$_y$ orbitals of the metal would lead to an increase in ΔE_{Q}. Scheidt and Chipman[29] have reported charge iterative extended Hückel calculations that show that there is significant π donation from the ligands to the 4p orbitals of the metal. Such π donation to the 4p orbitals is expected to increase N_{p_x} and/or N_{p_y} and produce a larger positive value of ΔE_{Q} (eq 1). At the same time, the energies of the filled d$_{xz}$ and d$_{yz}$ orbitals will be raised by the π donor (filled−filled) interaction, leading to an increase in the contributions from the matrix elements of eq 3 and a decrease in ΔE_{opt} for π donor axial ligands. Both of these effects will lead to an increase in $|\sigma_{\text{para}}|$ and the ^{57}Fe chemical shift. Hence, a correlation is observed between Mössbauer quadrupole splittings and ^{57}Fe NMR chemical shifts, with larger quadrupole splittings correlating with larger chemical shifts for pseudo-octahedral d^6 systems, as shown in Figure 2.

It should be noted that the slope of the correlation shown in Figure 2 is opposite to that observed by Silver and co-workers for ferrocene derivatives and related arene sandwich complexes.[4] These investigators have identified variations in the populations of the filled e$_2$ symmetry d$_{xy}$,d$_{x^2-y^2}$ and empty e$_1$ symmetry d$_{xz}$,d$_{yz}$ orbitals as being the main contributors to changes in the Mössbauer quadrupole splittings[30] with electron-donating and -withdrawing substituents on the cyclopentadiene or other arene ring. In this case, because of the difference in symmetry and hence the difference in occupation of the d orbitals, the predictions of the Townes−Dailey approximation are opposite those for octahedral-based complexes, since it is the d$_{xy}$ and d$_{x^2-y^2}$ orbitals, which contribute positively to the quadrupole splitting, that are filled. (In addition, the contribution of electrons in these orbitals to the valence charge and hence the quadrupole splitting is twice that of d$_{xz}$,d$_{yz}$ electrons, eq 1.) Removal of electron density by donation from the metal to electron-deficient cyclopentadiene or arene π orbitals is thus expected to decrease the populations of the d$_{xy}$,d$_{x^2-y^2}$ orbitals, thereby decreasing the quadrupole splitting, the same trend as predicted for the Fe(II) porphyrinates bound to π acceptor ligands, but arising from different orbital contributions. Thus, it is the trend in ^{57}Fe chemical shifts which is reversed in these ferrocene derivatives: π acceptor ligands produce *larger* values of δ_{Fe}, indicating either larger contributions from the matrix elements or a smaller ΔE_{opt}, or both, when π acceptor cyclopentadienes or arenes are present. Though larger values of δ_{Fe} were attributed by the authors to "loss of electron density on the iron atom", [4] we would identify the main contribution as being *a smaller value of* ΔE_{opt}, resulting from stabilization of the e$_1$ symmetry empty d$_{xz}$,d$_{yz}$ set due to better energy matching with the π^* orbitals of the π acceptor cyclopentadiene or arene rings. Thus, the difference in symmetry makes the d$_{xz}$,d$_{yz}$ set the LUMOs of the iron "sandwich" complexes, while they are the HOMOs of the iron porphyrinates, and interaction with π acceptor ligands has the opposite effect on ΔE_{opt} in the two cases, thus leading to opposite trends in ^{57}Fe chemical shifts.

Baltzer[20] and Oldfield and co-workers[24] have suggested that the chemical shift anisotropy, $\Delta\delta = |\delta_\perp - \delta_{||}|$, determines the T_1 and T_2 relaxation times and hence the line widths of ^{57}Fe signals by providing an effective mechanism of nuclear spin relaxation:

$$1/T_1 = (1/15)\gamma^2 H_{\text{o}}^{\,2}(\delta_\perp - \delta_{||})^2\{2\tau_{\text{R}}/(1 + \omega^2\tau_{\text{R}}^{\,2})\} \tag{4}$$

$$1/T_2 = (1/90)\gamma^2 H_{\text{o}}^{\,2}(\delta_\perp - \delta_{||})^2\{8\tau_{\text{R}} + 6\tau_{\text{R}}/(1 + \omega^2\tau_{\text{R}}^{\,2})\} \tag{5}$$

where τ_{R} is the rotational correlation time of the molecule. It has been proposed by Baltzer[20] that the value of $\delta_\perp$ is approximately constant for all iron porphyrinates at about 9000 ppm, while the value of $\delta_{||}$ is determined by the axial ligands, and varies widely. Based upon this premise and the fact that the average chemical shift $\delta = (1/3)\delta_{||} + (2/3)\delta_\perp$, we have calculated the values of the parallel contribution to the chemical shift, $\delta_{||}$, and listed the values in the last column of Table 1. Clearly, ferrocytochrome *c* and [TPPFe(Py)$_2$] have by far the largest chemical shift anisotropies. The T_1 of ferrocytochrome *c* is estimated to be 4 ms,[20,24] while those of myoglobin CO[17] and myoglobin *n*-BuNC[24] are estimated to be 17 and 152 ms, respectively. The magnitudes of $\Delta\delta$ calculated for these three

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proteins on the basis of $\delta_\perp = 9000$ ppm are 6591, 2319, and 714 ppm, which are fairly consistent with their T_1's.[24] Although we have not measured the T_1 of [TPPFe(Py)$_2$], the value of T_2 calculated from the corrected line width of about 64 Hz (corrected for the exponential line broadening of the FID (20 Hz)) is ~5.0 ms. (The T_1 is undoubtedly very similar because this relatively small model heme complex is close to the T_1 minimum ($\tau_R \sim 2.6$ ns for the slightly larger tetramesitylporphyrin ion-paired complex [TMPFe(2-MeImH)$_2$]$^+$ClO$_4^-$,[31] so τ_R is probably ~2 ns for [TPPFe(Py)$_2$], and this yields $\omega^2\tau_R^2$ ~0.04).) Using eq 5 above we obtain a value of $\Delta\delta = 8570$ ppm, as compared to the value of 8159 ppm obtained from Baltzer's assumption.[20] Thus, to within our ability to estimate τ_R, Baltzer's assumption that $\delta_\perp$ is fairly constant at 9000 ppm again appears to be upheld.

In conclusion, it should be noted that the true chemical shift of [TPPFe(Py-d_5)$_2$] is ~4400 ppm to lower shielding than originally reported[12] and is the largest chemical shift reported for Fe(II) thus far. The original report of the 7341 ppm shift for this complex mentioned that the signal disappeared when the spectral bandwidth was increased.[12] The lower magnetic field strength instrument available to these workers in 1983 (and hence the lower sensitivity of the signal) and the reports of similar ^{57}Fe chemical shifts for other complexes (mainly having CO,imidazole axial ligand combinations) available at that time undoubtedly both contributed to the fact that the "folding" of the signal was not detected. This emphasizes the value of the Mössbauer–NMR correlation in aiding the search for ^{57}Fe NMR signals as well as the perils of seeking these easily "folded" signals without the aid of such a correlation.

Acknowledgment. Support of this research by the U.S. National Institutes of Health Grant DK 31038 (F.A.W.), the University of Arizona Undergraduate Biology Research Program (UBRP) and BRAVO! summer international research program (J.L.W.), the University of Arizona Materials Characterization Program, and the Deutsche Forschungsgemeinschaft (A.X.T.) is gratefully acknowledged.

JA954096M

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