the porphyrin ring. We are currently examining amphiphilic derivatives of these porphyrins as Langmuir–Blodgett films and the macroscopic NLO properties of these assemblies.

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Supplementary Material Available: Spectroscopic and analytical data for $H_3(an_3Por)$, $H_2(\textit{trans}\text{-}a_2n_2Por)$, $H_2(\textit{cis}\text{-}a_2n_2Por)$, and $H_2(a_3nPor)$ (4 pages). Ordering information is given on any current masthead page.

Rapid Detection of ^{57}Fe NMR Chemical Shifts of Model Hemes: An Approximate Correlation between ^{57}Fe and ^{31}P Chemical Shifts of Fe(II) Porphyrins Bound to Phosphine Axial Ligands

Larry M. Mink, Kenner A. Christensen, and F. Ann Walker*

Department of Chemistry, University of Arizona
Tucson, Arizona 85721

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The NMR chemical shift range of the ^{57}Fe nucleus is at least 12 000 ppm.[1-4] Therefore, ^{57}Fe NMR spectroscopy is potentially an extremely sensitive, direct probe of the electron density and asymmetry at the heme iron. However, the combination of low natural abundance (2.19%) and a low magnetogyric ratio makes the ^{57}Fe nucleus in natural abundance only 7.4×10^{-7} times as sensitive as the proton. Direct detection of ^{57}Fe resonances of model hemes and heme proteins[4-9] has therefore utilized isotopic enrichment of ^{57}Fe. Nevertheless, the direct detection of ^{57}Fe signals typically requires hours of NMR time and large volumes of enriched sample. Thus, indirect detection of ^{57}Fe rsonance frequencies is an attractive alternative method. La Mar and co-workers[10] showed some time ago that such double resonance techniques could allow the determination of ^{57}Fe chemical shifts of carbon monoxy complexes of heme proteins using ^{13}CO- and ^{57}Fe-enriches samples. Morishima[11] and Nozawa[12] have similarly determined ^{57}Fe chemical shifts using ^{15}N-enriched porphyrins. Koridze and co-workers[13] have utilized similar techniques, with ^{13}C as the observed nucleus, for ^{57}Fe-enriched ferrocenes and ferrocenyl cations, without ^{13}C enrichment. Benn and co-workers have utilized both ^{13}C[14] and ^{31}P[2,3] as the observed nucleus for investigating a number of ferrocenes[14] and phosphine-coordinated organometallic complexes of a number of low-γ metal nuclei.[2,3] The latter authors have also demonstrated the increased enhancement obtained by inverse 2D polarization transfer techniques.[2,3]

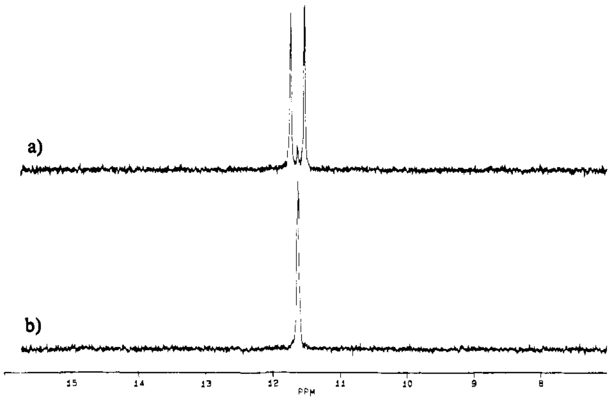

Figure 1. ^{31}P spectra of 95% ^{57}Fe-enriched $[(p\text{-}OCH_3)_4TPPFe(PMe_3)_2]$ at 25 °C in C_6D_6 (12 mM), recorded on a Bruker AM-500 spectrometer in the presence of broad band proton decoupling:[25] (a) off-resonance ^{57}Fe irradiation (128 acquisitions); (b) on-resonance ^{57}Fe irradiation, resulting in decoupling of the ^{31}P–^{57}Fe doublet (64 acquisitions). Chemical shifts are vs external 85% H_3PO_4; sample concentration was ~6 mM. Stepping through the ^{57}Fe frequency range around 16.2 MHz with a decoupling power of 0.5 W (bandwidth ~100 Hz) causes the ^{31}P doublet ($J_{Fe\text{-}P}$ = 35–59 Hz) to collapse when the resonant frequency of ^{57}Fe is reached.

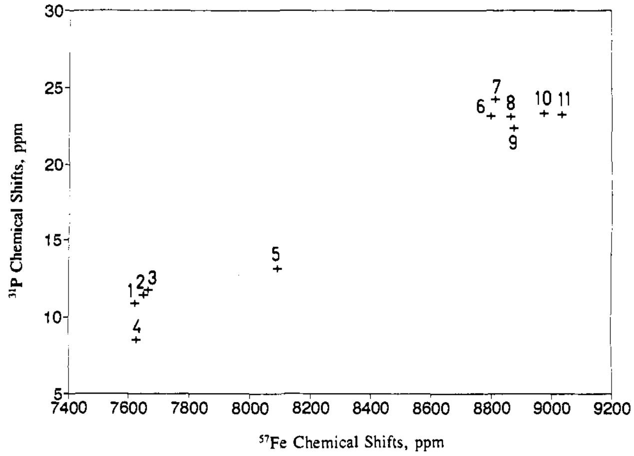

Figure 2. Correlation between ^{31}P and ^{57}Fe chemical shifts at 21 °C in C_6D_6, with ^{57}Fe shifts relative to external 90% $Fe(CO)_5$ in C_6D_6 and ^{31}P shifts relative to external 85% H_3PO_4: $[(p\text{-}Cl)_4TPPFe(PMe_3)_2]$ (1); $[TPPFe(PMe_3)_2]$ (2); $[(p\text{-}OCH_3)_4TPPFe(PMe_3)_2]$ (3); $[TPPFe(PMe)(CO)]$ (4); $[TPPFe(PMe_3)(n\text{-}BuNC)]$ (5); $[TPPFe(PMe_3)(n\text{-}BuNH_2)]$ (6); $[TPPFe(PMe_3)(PhCH_2SCH_3)]$ (7); $[TPPFe(PMe_3)(NMeIm)]$ (8); $[TPPFe(PMe_3)(4\text{-}NMe_2Py)]$ (9); $[TPPFe(PMe_3)(Py)]$ (10); $[TPPFe(PMe_3)(4\text{-}CNPy)]$ (11).

We have applied the 1D indirect method utilizing the sensitive ^{31}P nucleus as the detected signal to a series of model hemes of the type $[(RTPP)^{57}Fe(PMe_3)(L)]$[15-19] (RTPP = a symmetrical, R-substituted tetraphenylporphyrin, L = PMe_3, CO, isonitrile, aliphatic amine, imidazole, pyridine, or thioether). The coordination of one or two phosphine ligands to the axial positions of Fe(II) model hemes has allowed us to determine ^{57}Fe chemical shifts of new complexes by decoupling the ^{57}Fe–^{31}P doublet of enriched ^{57}Fe(II) porphyrins, as shown in Figure 1. While it might be expected that finding the proper ^{57}Fe frequency to

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(15) ^{57}Fe metal, 95% enriched, was purchased from New England Nuclear and inserted into the tetraphenylporphyrins as described previously.[16] The yields of TPP^{57}FeCl and the para-substituted TPP^{57}FeCl derivatives were 80–90%, based on ^{57}Fe as the limiting reagent.

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decouple the ^{31}P signal would be a time-consuming process (because of the large chemical shift range of ^{57}Fe), we have found that *a correlation exists between the ^{31}P and the ^{57}Fe chemical shifts*, as shown in Figure 2. This correlation makes it easy to predict the ^{57}Fe chemical shift of a new complex, thus simplifying the search for the proper decoupling frequency and allowing determination the ^{57}Fe chemical shift of a new complex in about 20 min.

Replacement of electron-withdrawing groups, Cl, by electron-donating groups, OCH_3, at the para positions of the phenyl rings of TPP causes shifts of ^{57}Fe and ^{31}P resonances to lower shielding, as summarized in Figure 2. (Actual chemical shifts and coupling constants are given in the supplementary material, Table S-1.) For the ^{57}Fe case, this is the predicted direction, based on the paramagnetic contribution to the screening constant being the dominant factor for heavy nuclei, especially those with unfilled d-shells such as these low-spin d^6 complexes.[20] The spread of the ^{57}Fe shifts is somewhat larger than that of the ^{59}Co chemical shifts reported earlier for the same series of para-substituted $[TPPCo(NMeIm)_2]^+$ complexes.[21] Substitution of one PMe_3 by CO, both good π-acids,[22] yields a similar ^{57}Fe chemical shift (but a smaller ^{31}P chemical shift), while substitution by a number of aromatic and aliphatic amines or benzyl methy sulfide shifts the iron resonance to lower shielding by $\sim$1200 ppm. The isonitrile ligand is expected to be a good σ-donor but a poorer π-acceptor than CO or the phosphine,[22] consistent with its intermediate ^{57}Fe and ^{31}P chemical shifts. *N*-Methylimidazole,[23] 4-(dimethylamino)pyridine,[23] and benzyl methyl sulfide are expected to be both good σ- and π-donors, while 4-cyanopyridine[23] is expected to be a weak σ-donor and fairly good π-acceptor and *N*-butylamine is only a σ-donor, yet they all display fairly similar ^{57}Fe and ^{31}P shifts. The observed relationship between ^{57}Fe and ^{31}P chemical shifts (Figure 2) suggests a possible synergism in the σ- and π-bonding effects of phosphine–L trans axial ligand combinations, such that when a strong σ- or π-donor ligand is present trans to a phosphine, it has the effect of decreasing the shielding of both the metal and the phosphine nuclei. (However, the effect is not a simple one, since the trend among the three pyridines is the reverse of that expected in terms of either σ- or π-donor characteristics, i.e., $\delta(4\text{-NMe}_2\text{Py}) < \delta(\text{Py}) < \delta(4\text{-CNPy})$.) The increase in coupling constants $J_{\text{Fe–P}}$ upon a change in L from CO (36 Hz) to the nitrogen donors and the thioether (47–59 Hz) (Table S-1) also suggests synergism in the σ- and π-bonding of these ligand combinations. Investigations of additional mixed-ligand complexes aimed at probing the factors that affect the ^{57}Fe and ^{31}P chemical shifts and the coupling constants are underway.

The temperature dependences of the ^{57}Fe and ^{31}P chemical shifts were investigated over the range −61 to +30 °C in toluene-d_8 and from 20 to 55 °C in benzene-d_6. Linear shifts of both resonances with temperature were observed, with the ^{57}Fe and ^{31}P chemical shifts having opposite temperature dependences (Table S-1). Both $[TPPZnPMe_3]$ and PMe_3 itself also display smaller shifts of the ^{31}P signal to higher shielding with increasing temperature (−0.014 and −0.005 ppm/°C, respectively), and a similar temperature dependence of the ^{31}P chemical shifts has been reported for a series of dimeric Pd(I) complexes of the type $[Pd_2(dppm)_2X_2]$.[24] Neither ^{31}P nor ^{57}Fe chemical shifts were concentration dependent over the range 6–24 mM. Solvent effects are also very small.

Most model hemes and heme proteins investigated thus far,[5-11] including those presented in Table S-1, have ^{57}Fe chemical shifts ranging from 7200 to 9200 ppm vs $Fe(CO)_5$. However, the ^{57}Fe resonance of cytochrome *c* is observed at 11197 ppm,[4] which is dramatically shifted to lower shielding by 3000. Due to this dramatic shift for the cytochrome *c* resonance, we had anticipated that the thioether complex of our study would display an ^{57}Fe chemical shift significantly different from that of the *N*-methylimidazole and other nitrogen donor complexes. However, this is not the case (Figure 2). We thus suggest that the unusual ^{57}Fe chemical shift of cytochrome *c*[4] may include a contribution not found in model hemes: the contribution of fixed axial ligand orientation. In model hemes at ambient temperatures, axial ligands are expected to rotate rapidly. We are currently investigating specially designed model heme complexes in which axial ligand rotation is hindered in order to determine the effect of fixed axial ligand plane orientation on the ^{57}Fe and ^{31}P chemical shifts and chemical shift anisotropies.

Acknowledgment. The financial support of the National Institutes of Health (DK 31038) is gratefully acknowledged. The authors also wish to thank Professor Richard S. Glass for supplying the sample of benzyl methyl sulfide and Professor David E. Wigley for providing the cylinder of CO.

Supplementary Material Available: A table of ^{57}Fe and ^{31}P chemical shifts of Fe(II) tetraphenylporphyrins bound to trimethylphosphine (Table S-1) (1 page). Ordering information is given on any current masthead page.

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Experimental Evidence by EXAFS of the Second Hydration Shell in Dilute Solutions of Cr^{3+}

Adela Muñoz-Paez*[†] and Enrique Sánchez Marcos[‡]

Departamento de Química Inorgânica e Instituto de
Ciencias de Materiales, Facultad de Química
Universidad de Sevilla, 41012-Sevilla, Spain
Departamento de Química Física, Facultad de Química
Universidad de Sevilla, 41012-Sevilla, Spain

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Since Frank and Evans[1] proposed their concentric shell model, concepts of the first and second hydration shell have been widely used for understanding the structure of solvated ions and, as a consequence, the rationalization of a large number of chemical properties of electrolyte-containing solutions.[2] Direct experimental evidence of ionic solution structure has been obtained from X-ray and neutron diffraction.[3] In particular, a description of the first hydration shell for a large number of monoatomic cations and anions has been reported;[4] however, for the second hydration shell, available information is not so general. An important limitation of these techniques is that the species to be studied must be quite concentrated, namely, up to 1.0 M.

Information about the local environment around cations in highly dilute solutions (ca. 10^{-3} M) can be obtained by the EXAFS technique (extended X-ray absorption fine structure), which is an excellent tool to study short-range order about a specific type of atom. This technique has allowed us to examine an experimental system closer to the ideal concept of infinitely dilute solutions, where the ion–solvent interactions are not disturbed by the ion–ion interactions. Decrease of sensitivity of the absorber–backscatterer distance inherent in this technique has precluded, until now, the unambiguous determination of the second

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[†] Departamento de Química Inorgânica e Instituto de Ciencias de Materiales.

[‡] Departamento de Química Física.

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