^{13}C NMR Spectra of Tetra(3,4,5-trimethoxyphenyl)porphyrin and its Zinc and Iron(III) Complexes

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During the past few years several reports have appeared on the ^{13}C NMR spectra of porphyrins and some metalloporphyrins [1−11]. The porphyrins have included, besides porphin itself, several *meso*-tetraarylporphyrins, octaethylporphyrin and various coproporphyrins, protoporphyrins, etc. Metal derivatives have included those with zinc(II), cadmium(II), mercury(II), ruthenium(II), thallium(III), indium-(III), iron(III), titanium(IV), etc. Measurement of spectra is hampered in some cases (especially in the popular *meso*-tetraaryl series) by the limited solubility of the porphyrin or metalloporphyrin, with the consequent necessity of long data collection times with unenriched samples.

We have measured the ^{13}C NMR spectra of some metalloporphyrins, including both high and low spin iron(III) derivatives, and have found that $\alpha,\beta,\gamma,\delta$-tetra(3,4,5-trimethoxyphenyl)porphyrin has particularly attractive properties for NMR investigations.

Experimental

All solvents and starting materials were reagent grade. Pyrrole, 3,4,5-trimethoxyaniline and 3,4,5-trimethoxybenzaldehyde were obtained from Aldrich Chemical Company.

Tetra(3,4,5-trimethoxyphenyl)porphyrin (MX3-PPH$_2$) was prepared from pyrrole and 3,4,5-trimethoxybenzaldehyde in refluxing propionic acid [12]. and purified by column chromatography on alumina. The zinc(II) [MX3PPZn] and hemin chloride [MX3-PPFeCl] complexes were prepared in dimethylformamide [13], and recrystallized from methylene chloride−ether mixtures. The binuclear μ-oxo complex [(MX3PPFe)$_2$O] was prepared by treatment of a methylene chloride solution of the hemin chloride with aqueous potassium hydroxide, precipitation with ether, column chromatography, and recrystallization from methylene chloride−ether.

A Jeol FX-60 pulsed Fourier transform NMR spectrometer, operating at 15 MHz with internal deuterium lock and proton noise decoupling, was used to record ^{13}C NMR spectra at natural abundance, at 34 °C. Shifts were calculated in ppm relative to internal tetramethylsilane. These were the same when TMS was used as an external standard in the several cases investigated. A spectral width of 2.5 kHz was used for the diamagnetic samples, and a width of 4 kHz for the paramagnetic samples. A 50--80° pulse and an acquisition time of about 1 s were standard. Shifts are accurate to ±0.10 ppm.

Results

^{13}C spectra of the free porphyrin MX3PPH$_2$, the zinc(II) complex [MX3PPZn], the binuclear complex [(MX3PPFe)$_2$O], the low-spin bisimidazole hemichrome [MX3PPFe·2Im]Cl, and the high-spin hemin chloride [MX3PPFeCl] were measured in deuterochloroform and, for the zinc complex, also in dimethyl sulfoxide. There was no apparent dependence of peak positions on the concentrations used, even in the three paramagnetic cases. In all cases, partially decoupled spectra were also determined to aid in peak assignments. Peaks were generally narrow, except for the α-carbon resonances.

Peak assignments for the trimethoxyphenyl group are based on literature values for mescaline hydrochloride [14] and a 3,4,5-trimethoxyaniline spectrum recorded by us. Porphyrin ring assignments are based on literature values for tetraphenylporphyrin and its metal derivatives [2, 7−10]. Dimethyl sulfoxide and imidazole values were taken from ref. 15. There was no difficulty in completely assigning the peaks in the spectra of the free porphyrin and its zinc complex. Most of the peaks in the binuclear μ-oxo complex and the bisimidazole hemichrome could also be assigned unambiguously, but the spectrum of the hemin chloride proved more difficult to interpret. Even in this spectrum, however, the methoxy carbons were easily identified. In all cases the number of peaks in the partially proton-decoupled spectra agree with the assignment.

Data are given in Scheme 1, in ppm relative to tetramethylsilane. All peaks were downfield from the TMS resonance. Atom numbering is also given in Scheme 1.

Discussion

Tetra(3,4,5-trimethoxyphenyl)porphyrin and its zinc and mononuclear iron complexes are soluble to at least the extent of about 0.1 M in chloroform, which is perhaps five times the solubility of tetraphenylporphyrin and its metal derivatives. This enables excellent quality spectra to be quickly measured. An additional advantage of this easily prepared porphyrin

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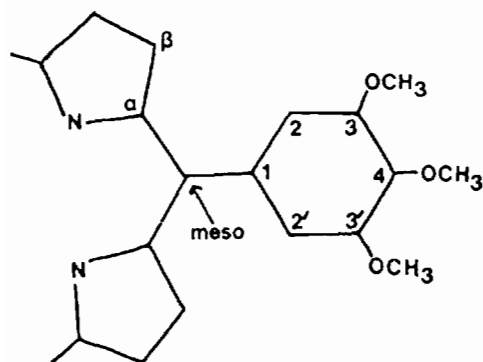
MX3PPH₂ in CDCl₃: 151.29 (3,3'); 146.66 (broad,α); 137.98 (1 or 4); 137.49 (4 or 1); 131.08 (β); 120.04 (*meso*); 112.90 (2,2'); 61.28 (*p*-OCH₃); 56.41 (*m*-OCH₃).

[MX3PPZn] in CDCl₃: 151.47 (3,3'); 150.58 (α); 138.47 (1 or 4); 137.98 (4 or 1); 132.30 (β); 121.34 (*meso*); 113.05 (2,2'); 61.48 (*p*-OCH₃); 56.61 (*m*-OCH₃).

[MX3PPZn] in (CH₃)₂SO: 151.47 (3,3'); 150.25 (α); 139.29 (1 or 4); 137.83 (4 or 1); 132.14 (β); 120.85 (*meso*); 113.46 (2,2'); 61.40 (*p*-OCH₃); 56.69 (*m*-OCH₃); 41.01 (DMSO).

[(MX3PPFe)₂O] in CDCl₃ (concentrations: 45 and 77 mg/ml): ~240 (broad, α or *meso*); ~214 (broad, *meso* or α); 152.20 and 151.55 (3,3'); 138.43 (1 or 4); 130.64 (4 or 1); 125.71 (weak, broad, β); 121.68 (2,2'); 61.42 (*p*-OCH₃); 58.18 and 56.10 (*m*-OCH₃).

[MX3PPFeCl] in CDCl₃ (concentrations: 40 and 55 mg/ml): 265 (broad, *meso*); 248.5 (broad, 2,2'); 179.20, 173.61 (shoulder) and 173.09 (3,3' and 4); 153.99; 71.08 (*p*-OCH₃); 57.70 and 57.05 (*m*-OCH₃).

[MX3PPFeCl] + excess imidazole, in CDCl₃ (concentrations: 40 and 55 mg/ml): 149.36(3,3'); 136.45(4); 135.96 (C-2 of free imidazole); 133.52 (*meso*); 122.56 (C-4,5 of free imidazole); 108.26 (2,2'); 96.33 (?, very weak); 94.46 (broad, β); 60.51 (*p*-OCH₃); 55.96 (*m*-OCH₃); 39.23 (broad, weak, α); 37.36 (?, very weak).

Scheme 1.

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arises from the strong and unambiguously identifiable methoxy carbon resonances (in both *meta* and *para* positions on the phenyl rings) and the expected splitting of the *m*-methoxy resonances in five-coordinated metal derivatives.

Although the methoxy carbons are far removed from the metal center, and occur on phenyl rings which are probably nearly perpendicular to the porphyrin ring, there are noticeable changes in the positions of these resonances in going from the free porphyrin to the zinc and iron complexes. Thus, in the zinc complex, both *m*- and *p*-methoxy resonances are shifted downfield by the same amount, 0.20 ppm in CDCl₃, and by 0.12 and 0.28 ppm in (CH₃)₂SO, from the free base values. Although zinc porphyrins are known to bind one axial group rather strongly [16], there is no evidence for splitting of the *o*- and *m*-phenyl carbons, nor of the *m*-methoxy carbons for [MX3PPZn] in DMSO, which strongly

indicates that the zinc is not statically five-coordinated in this case.

In the spectrum of the low-spin hemichrome [MX3PPFe·2Im]Cl, there is clearly only one type of *o*- and *m*-phenyl carbons and one *m*-methoxy carbon, confirming the symmetrical axial ligation expected in this complex. The shift of the *p*-methoxy carbons from the free base value (−0.71 ppm) is much greater than the shift of the *m*-methoxy carbon (−0.45 ppm). (Similarly, Wüthrich and Baumann [5] found a larger shift for the *p*-phenyl carbon than for the *m*-phenyl carbons in the low-spin tetraphenylporphyrin hemichrome [TPPFe(CN)₂]⁻.) However, the overall spectrum is somewhat more complex than expected, in that the α and β pyrrole carbon resonances appear to be each split by the same amount, 1.87 ppm. This is the only case for which such splittings are found, which suggests some type of interaction with the imidazole ligands. No peaks unambiguously assignable to coordinated imidazole are found. These should be at most about one-fourth the intensity of the next strongest peaks, and no special effort was made to locate them.

The binuclear μ-oxo complex [(MX3PPFe)₂O], which contains high-spin iron(III) centers antiferromagnetically coupled, gives an excellent spectrum. There is a very large splitting, 2.08 ppm, of the *m*-methoxy carbons in this five-coordinated iron complex. The position of the *p*-methoxy resonance changes very little (0.06 ppm) from that in the diamagnetic zinc complex. The *m*-methoxy resonance at 56.10 ppm also changes little (0.5 ppm), and this peak probably belongs to the methoxy groups pointing away from the μ-oxo bridge.

The spectrum of the high-spin hemin [MX3PPFeCl] shows large shifts of many of the peaks, although not as large as those found for the high-spin tetraphenylporphyriniron(III) iodide [9] and sulfate [10]. The assignments in Scheme 1 are tentative, except for the methoxy peaks which are easily identifiable. They show the expected splitting of the *m*-methoxy groups (0.65 ppm), but these are not shifted very far from their positions in the free base or zinc complex. On the other hand, the *p*-methoxy resonance is shifted downfield by 9.60 ppm. The α and β carbon resonances either lie outside the range investigated or are too broad to be observed (as suggested for the hemin iodide [9] and sulfate [10] cases, and recently confirmed Goff *et al.* [11] for several [TPPFeX] derivatives).

These data show that electronic effects from the metal center are transmitted to the π-system of the aryl groups in tetraarylporphyrinatoiron(III) complexes, resulting in significant shifts in *para*- and *meta*-methoxy substituents. Also, the *meta*-methoxy resonance is clearly split in the five-coordinated iron(III) cases. Splitting of the proton NMR peaks of both *ortho* and *meta* protons in tetraarylpor-

phyrinatoiron(III) halides has been reported by LaMar and Walker [17]; thus these ^{13}C NMR splittings are not unexpected.

Acknowledgements

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