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^{15}N Nuclear Magnetic Resonance Studies of Ligand Binding to Zinc Tetraphenylporphyrin

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Summary Porphyrin ^{15}N chemical shifts of complexes formed by zinc *meso*-tetraphenylporphyrin and substituted pyridines may be correlated with the electron donating ability of the pyridine substituent.

SEVERAL recent reports¹⁻⁶ have demonstrated the practicality of ^{15}N n.m.r. studies of porphyrins. It is now of interest to determine the kinds of chemical information which can be derived from the n.m.r. parameters. Studies of unsymmetrical porphyrins and related molecules¹ suggest that the nitrogen chemical shifts are greatly influenced by substitution at the periphery of the porphyrin ring. However, the biological role of porphyrins is also strongly dependent upon the interaction of the metal atom of a metallated porphyrin with additional ligands. Reported here are the results of an investigation of the effects of interactions of this type on porphyrin ^{15}N chemical shifts.

Zinc *meso*-tetraphenylporphyrin is readily studied using ^{15}N n.m.r. spectroscopy,^{2,3} and forms 1:1 complexes with organic amines,⁷ including pyridine derivatives.⁸ Zinc *meso*-tetraphenylporphyrin (96% ^{15}N) (**1**) was synthesized as described previously.³ Complexes of (**1**) with *meta*- or *para*-substituted pyridine derivatives were prepared by treating a 0.02 M chloroform solution of (**1**) with a quantity of neat ligand sufficient to produce essentially complete complexation of the porphyrin, as calculated from published⁸ equilibrium constants. The ^{15}N chemical shifts of the porphyrin nitrogen atoms of the complexes are reported in the Table in p.p.m. upfield from external 1 M $\text{Na}^{15}\text{NO}_3$ in D_2O . The chemical shift values were determined at 9.12 MHz and are reproducible to about ± 0.03 p.p.m. Doubling the amount of ligand had no effect on the chemical shifts, and the

observed changes in chemical shift are therefore not merely medium effects. This is as expected, because the amount of amine added was only *ca.* 1% of the total sample volume.

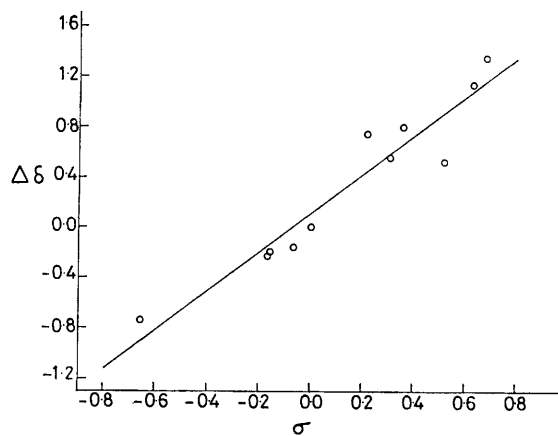


FIGURE. Hammett plot for substituted pyridine-zinc tetraphenylporphyrin complexes.

It is evident from the Table that the ^{15}N chemical shifts of the porphyrin nitrogen nuclei are sensitive to changes in the nature of the fifth ligand to zinc. The chemical shift changes for the series of closely related pyridine ligands are small, but easily measurable. It might be suspected that the ^{15}N shifts would correlate to some degree with the electron donating ability of the ligand and/or the stability of the complex. In order to determine whether any such relationship exists, the

chemical shift difference between each substituted pyridine complex and the unsubstituted pyridine complex ($\Delta\delta$) was plotted (Figure) against the Hammett σ constant for that substituent,⁹ which is a measure of electron donation or withdrawal.^{9,10} Although such treatments have generally been applied to benzene derivatives, applications to pyridine

TABLE. Porphyrin ¹⁵N chemical shifts for complexes of zinc tetraphenylporphyrin and substituted pyridines.

Ligand	δ /p.p.m.	Ligand	δ /p.p.m.
None	175.99	4-Acetylpyridine	175.00
3-Cyanopyridine	175.82	Pyridine	174.49
4-Cyanopyridine	175.61	3-Methylpyridine	174.33
Pyridine-3-carbaldehyde	175.27	4-Methylpyridine	174.26
Pyridine-4-carbaldehyde	175.23	3-Aminopyridine	174.23
3-Acetylpyridine	175.03	4-Aminopyridine	173.75

systems have been reported.^{8,11} The slope of the theoretical line,¹⁰ ρ , is 1.53 (correlation coefficient 0.955). The trend is very clear: increased electron donation by the substituent results in a downfield shift of the porphyrin ¹⁵N resonance. Because it has been reported⁸ that the stabilities of substituted pyridine complexes correlate well with σ values, it can be assumed that the ¹⁵N chemical shifts also correlate with the stability constant (K). This is indeed the case, and for the seven complexes for which such constants are available⁸ a plot of $\Delta\delta$ against $\log K$ gives a straight

line of the form $\Delta\delta = -1.16 \log K + 4.48$ with a correlation coefficient of 0.986.

For all the examples, complex formation resulted in a downfield shift of the ¹⁵N resonance, and increased electron donation from the substituent (with consequent enhancement of complex stability) increased the amount of downfield shift. In order to determine whether or not this downfield shift is unique to the pyridine series, the complex of (1) with piperidine was studied. In this complex, the porphyrin ¹⁵N chemical shift (174.81 p.p.m.) is again downfield of that in (1) itself. In this connection, it is interesting that the ¹⁵N shift of the bis(pyrrolidine)-Fe¹¹ low-spin complex of [¹⁵N₄,⁵⁷Fe]tetraphenylporphyrin is slightly downfield of that of the bis(pyridine) complex.¹²

The results reported here suggest that the measurement of porphyrin ¹⁵N chemical shifts may prove to be a valuable method for studying the binding of additional ligands to the porphyrin metal centre.

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