^{15}N Nuclear Magnetic Resonance Studies of Iron(II) Low Spin Complexes of ^{15}N and ^{57}Fe Labelled Porphyrin

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Summary ^{15}N n.m.r. chemical shifts and $^1J(^{15}N-^{57}Fe)$ coupling constants have been obtained for Fe^{II} low spin bis(amine) complexes of [$^{15}N_4$, ^{57}Fe]-*meso*-tetraphenylporphyrin, and these are discussed in relation to the effect of the axial ligand on the iron–porphyrin binding profiles.

^{1}H and ^{13}C n.m.r. spectroscopy has become a powerful tool for characterizing the electronic structures and the nature of the binding of the ligand in various porphyrin and metalloporphyrin complexes.[1] Such studies have recently been complemented by ^{15}N n.m.r. spectroscopy for diamagnetic[2] and paramagnetic[3] porphyrin complexes where ^{15}N labelled porphyrin and ^{15}N enriched axial ligands are used. For diamagnetic porphyrin derivatives, ^{15}N n.m.r. studies have been reported[2] for metal free porphyrins and for metalloporphyrins with Zn, Ni, Mg, and Cd as the central metal ions. However, there has been no report on ^{15}N n.m.r. studies of iron(II) porphyrins. Here we report on the ^{15}N n.m.r. spectra of Fe^{II} low spin diamagnetic complexes of ^{15}N and ^{57}Fe labelled *meso*-tetraphenylporphyrin ([$^{15}N_4$, ^{57}Fe]-TPP), and, in particular, on the use of $^{15}N-^{57}Fe$ nuclear spin coupling constants as a probe for iron–porphyrin binding characteristics.

^{15}N-enriched TPP was prepared from ^{15}N-labelled pyrrole (Isocommerz, East Germany) by the usual method.[4] Incorporation of ^{57}Fe into this porphyrin was accomplished using Adlar's method[5] (isotopic enrichments of ^{15}N and ^{57}Fe were 95·7 and 90·96%, respectively). Bis(pyrrolidine), bis(morpholine), and bis(pyridine) Fe^{II} low spin complexes of [$^{15}N_4$, ^{57}Fe]-TPP were prepared by the reported methods.[6]

The ^{15}N n.m.r. spectra were recorded at 10·14 MHz in the pulse Fourier transform mode on a Jeol PFT-100 spectrometer with deuterium lock. The sample was placed in a 10 mm tube under appropriate solvent conditions (*ca.* 0·015 M). A pulse repetition time of 3 s was employed with 15 μs (45°) pulses. Chemical shifts are reported in p.p.m. from external H^{15}NO$_3$.

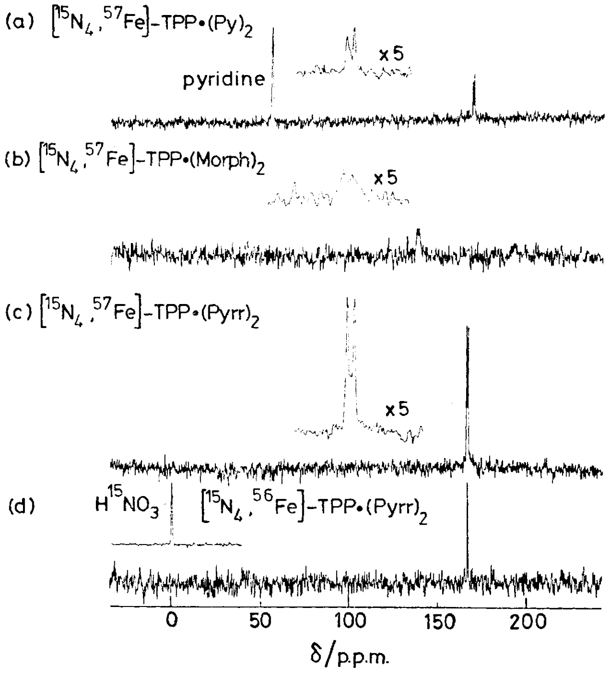

FIGURE. ^{15}N n.m.r. spectra of various Fe^{II} bis(amine) complexes of [$^{15}N_4$, ^{57}Fe]-*meso*-tetraphenylporphyrin (TPP). (a) Bis(pyridine)-[$^{15}N_4$, ^{57}Fe]-TPP in $C_5D_5N + D_2O$ (5 : 1) mixed solvent saturated with $Na_2S_2O_4$. 8K transients were accumulated without ^{1}H-noise decoupling. The slightly broadened ^{15}N signal is due to the residual porphyrin pyrrole $^1H-^{15}N$ coupling (<1 Hz). (b) Bis(morpholine)-[$^{15}N_4$, ^{57}Fe]-TPP in CDCl$_3$ containing 20% (v/v) morpholine. 20K transients were accumulated without ^{1}H-noise decoupling. (c) Bis(pyrrolidine)-[$^{15}N_4$, ^{57}Fe]-TPP in CDCl$_3$ containing 10% (v/v) pyrrolidine. 20K transients were collected with ^{1}H-noise decoupling. (d) Bis(pyrrolidine)-[$^{15}N_4$]-TPP with natural abundance Fe ion. Solvent as for (c). 15K transients were collected without ^{1}H-noise decoupling.

The ^{15}N n.m.r. spectra of various Fe$^{\text{II}}$ complexes of [^{15}N$_4$, ^{57}Fe]-TPP are shown in the Figure. For the bis(pyrrolidine) complex a doublet signal was observed at 165·8 p.p.m. with a spacing of 7·5 Hz. Using [^{15}N$_4$, ^{56}Fe-TPP] a singlet peak was observed (Figure d). This doublet can, therefore, be attributed to ^{15}N–^{57}Fe direct bond coupling. The corresponding ^1J(^{15}N–^{57}Fe) values for the bis(morpholine) and bis(pyridine) complexes are 8·0 and 7·8 Hz, respectively. There are no substantial differences in the ^1J (^{15}N–^{57}Fe) values between these complexes. To our knowledge, this is the first observation of ^{15}N–^{57}Fe coupling† of pyrrole nitrogen–central metal nuclear spin coupling in metalloporphyrin derivatives. The magnitude of ^1J(^{15}N–^{57}Fe) (*ca.* 7·5—8·0 Hz) appears to be very small for a direct bond nuclear spin coupling constant, and this may be due to the small value of the gyromagnetic ratio of ^{57}Fe (1/30 that of ^{1}H). However, as the ^{15}N–^{1}H coupling constant of iron-free TPP is 97 Hz,[2a] and the density of the *s* orbital at iron and the *s* bond order of N–Fe bonds are much larger than for an N–H bond, this value for ^1J (^{15}N–^{57}Fe) appears reasonable.

A small downfield bias of the ^{15}N shifts occurs on going from bis(pyridine) (169·7 p.p.m.) to bis(pyrrolidine) (165·8 p.p.m.) complexes. This is most probably attributed to the inductive effect of the axial ligand bound to the haem iron. The basicity of pyrrolidine nitrogen is larger than that of pyridine nitrogen, resulting in less *p* electron density on the porphyrin nitrogen (downfield shift) for the bis(pyrrolidine) complex. This *cis* inductive effect is not shown in the ^{15}N–^{57}Fe coupling constant.

It is of interest that there is a substantial difference in the ^{15}N shifts between zinc (175·2 p.p.m.)[2e] and iron complexes of [^{15}N$_4$]-TPP with a downfield bias of the ^{15}N shift for the iron(II) complex as compared with the zinc complex. The presence of axial nitrogen ligands in the iron complex appears to enhance the electronegativity of iron(II), resulting in a withdrawal of electron density from the porphyrin nitrogen (downfield shift).

For the bis(morpholine) complex, the ^{15}N resonance appeared as a slightly broadened doublet peak, ^1J(^{15}N–^{57}Fe) 8·0 Hz, δ = 144 p.p.m., downfield from those for pyrrolidine and pyridine complexes. This anomaly in the resonance position is most probably due to rapid exchange between Fe$^{\text{II}}$ low spin (diamagnetic) and Fe$^{\text{III}}$ low spin (paramagnetic) states, as has been reported in the mixed Fe$^{\text{II}}$ and Fe$^{\text{III}}$ haem bis(pyridine) complex.[7] Morpholine is not effective enough to reduce Fe$^{\text{III}}$ to Fe$^{\text{II}}$, compared with pyrrolidine or piperidine. The Fe$^{\text{II}}$ low spin morpholine complex is thus readily oxidized in solution. This large downfield bias of the ^{15}N shift indicates that the porphyrin nitrogen hyperfine shift for the Fe$^{\text{III}}$ low spin porphyrin complex should be far downfield.

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† The only reported example of a nuclear spin coupling constant for ^{57}Fe is ^1J(^{57}Fe–^{13}C) 23·4 Hz for ^{57}Fe(CO)$_5$. (B. E. Mann, *Chem. Comm.*, 1971, 1173; *J.C.S. Dalton*, 1973, 2012).

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