^{15}N Nuclear Magnetic Resonance Studies of the Iron–Axial Ligand Bond in Low Spin Iron(II) Complexes of Octaethylporphyrin

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Summary ^{15}N N.m.r. spectra have been obtained for bis(pyridine), bis(γ-picoline), CO, and octyl isocyanide complexes of iron(II)[^{15}N$_4$]-octaethylporphyrin and bromine complexes of cobalt(III) [^{15}N$_4$]-octaethylporphyrin; ^{15}N n.m.r. chemical shifts were found to be sensitive to the axial ligands and to reflect the nature of the ligand–metal bonding.

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^{15}N N.M.R. SPECTRA of porphyrins give unique information on the manner of the binding of the inner hydrogen atoms[1–5] and metal ions[2,3,5,6] to the central pyrrole nitrogen atoms. We have already reported ^{15}N n.m.r. spectra of several diamagnetic metal complexes of [^{15}N$_4$]-octaethylporphyrin {[^{15}N$_4$]-OEP} without axial ligands[2,5] and discussed the relationship between the chemical shifts and the metal–porphyrin bonding.[5] It is also expected that axial ligands on the central metal ion would have some effect on the chemical shifts of ^{15}N n.m.r. resonances of [^{15}N$_4$]-OEP, and we now report the ^{15}N n.m.r. spectra of iron(II) and cobalt(III) [^{15}N$_4$]-OEP co-ordinated with axial ligands. The chemical shifts were found to be sensitive to ligand replacement and gave a good indication of π type ligand–iron bonding.

Details of the synthesis of 98% ^{15}N-enriched octaethylporphyrin are described elsewhere.[5] The bis(pyridine) adduct {[^{15}N$_4$]-Fe^{2+}(OEP)(Py)$_2$} (**1**) and the bis(γ-picoline) adduct {[^{15}N$_4$]-Fe^{2+}(OEP)(γ-picoline)$_2$} (**2**) complexes were generated by reducing the iron(III) complexes with an excess of SnCl$_2$ in pyridine or in γ-picoline. The complexes {[^{15}N$_4$]-Fe^{2+}(OEP)(CO)(Py)} (**3**) and {[^{15}N$_4$]-Fe^{2+}(OEP)-(C$_8$H$_{17}$NC)(Py)} (**4**) were obtained *in situ* by the introduction of CO gas and octyl isocyanide to the pyridine adduct (**1**). The cobalt complexes {[^{15}N$_4$]Co^{3+}(OEP)BrX} (**5**) were prepared by the method of Clarke *et al.*[7] The concentrations of the samples were 0·02—0·04 M. ^{15}N N.m.r. spectra were obtained at 10·09 MHz with a JEOL PFT-100 pulse Fourier transform n.m.r. spectrometer. The spectra were recorded in the proton decoupled mode without nuclear Overhauser enhancement, and were accumulated 3 000—10 000 times with 10 s intervals.

Each of the ^{15}N n.m.r. spectra of the iron(II) low spin derivatives gave a single non-inverted signal in the range 180—230 p.p.m. upfield from the external $^{15}NO_3^-$. The ^{15}N resonance positions are summarized in the Table. The ^{15}N n.m.r. chemical shifts of the CO (**3**) and octyl isocyanide (**4**) complexes in pyridine solution are 43 and 23 p.p.m. upfield from that of the bis(pyridine) complex (**1**), respectively.

TABLE. ^{15}N N.m.r. chemical shifts of iron and cobalt complexes of [$^{15}N_4$]-OEP.

Compound	Solvent	Chemical shift[a]
{[$^{15}N_4$]-Fe^{2+}(OEP)$(Py)_2$}[b]	C_5D_5N	187·9
{[$^{15}N_4$]-Fe^{2+}(OEP)(γ-picoline)$_2$}	γ-Picoline	185·5
{[$^{15}N_4$]-Fe^{2+}(OEP)($C_8H_{17}NC$)(Py)}	C_5D_5N	210·6
{[$^{15}N_4$]-Fe^{2+}(OEP)(CO)(Py)}	C_5D_5N	231·3
{[$^{15}N_4$]-Co^{3+}(OEP)(Br)(Py)}	CD_2Cl_2	259·4
{[$^{15}N_4$]-Co^{3+}(OEP)(Br)(Py)}	C_5D_5N	260·0
{[$^{15}N_4$]-Co^{3+}(OEP)(Br)(4-acetyl-Py)}	4-Acetyl-Py	262·5
{[$^{15}N_4$]-Co^{3+}(OEP)(Br)(γ-picoline)}	γ-Picoline	260·3
{[$^{15}N_4$]-Mg(OEP)}	$CDCl_3$ + Py	179·9[c]
{[$^{15}N_4$]-Ni(OEP)}	$CDCl_3$	257·0[c]
{[$^{15}N_4$]-Zn(OEP)}	$CDCl_3$ + Py	179·2[c]
{[$^{15}N_4$]-Cd(OEP)}	C_5D_5N	173·1[c]

[a] Shifts are relative to external $NH_4{}^{15}NO_3$ in C_2D_6SO (p.p.m.). [b] Py denotes pyridine. [c] From ref. 5.

In our previous study, there was a correlation between the absorption maxima and the induced shifts due to the metal binding in {[$^{15}N_4$]-M(OEP)} (M = Mg, Ni, Zn, and Cd).[5] The shifts were attributed to energy differences between each orbital level ΔE_{ij} in the paramagnetic term σ_p of Ramsey's formula.[9] Since the absorption maxima of the Soret, α, β, and charge transfer bands of the iron(II) complexes studied here are fairly close to each other, the origin of the ligand induced shifts should be different from that for {[$^{15}N_4$]-M(OEP)}. In a previous Raman study it was shown that there are two kinds of iron(II) low spin states in haemoproteins which are specified by the binding nature of the sixth ligand to the haem iron.[8] Since the iron–axial ligand bond in (**3**) and (**4**) is predominantly of the π type and that of the complexes (**1**) and (**2**) is of the σ type, the present ^{15}N n.m.r. data also reflect the nature of the iron–ligand bonding. When CO binds to Fe as an axial ligand, the electrons in the π orbital are delocalized from the Fe–OEP system to the axial ligand π orbital. The paramagnetic shielding term σ_p depends on the ΔE_{ij} and the distribution of electrons ΣQ_{ij}. If ΔE_{ij} does not differ for each compound as in the CO, $C_8H_{17}NC$, pyridine, and γ-picoline complexes, σ_p may be affected by the magnitude of ΣQ_{ij}. The decrease of the latter term implies a decrease of the absolute value of σ_p and causes the upfield shift, as the sign of σ_p is positive. This prediction is consistent with the observed result that the ^{15}N of the CO adduct (**3**) resonates at higher magnetic field than that of the pyridine adduct (**1**).

The resonance frequency of the bis(picoline) complex (**2**) is almost the same as that of the pyridine complex (**1**). There are also quite small differences among the ^{15}N resonance positions of the cobalt complexes (**5**). The basicities of these axial ligands differ from each other, although such differences seem to have little influence on the chemical shift of the ^{15}N nuclei in the porphyrin ring. The change of the basicity in the axial ligands may give only second order perturbation to the ^{15}N n.m.r. chemical shift of the porphyrin ring compared with the change in the nature of the metal–ligand bond.

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[1] C. S. Irving and A. Lapidot, *J.C.S. Chem. Comm.*, 1977, 184.
[2] K. Kawano, Y. Ozaki, Y. Kyogoku, H. Ogoshi, H. Sugimoto, and Z. Yoshida, *J.C.S. Chem. Comm.*, 1977, 226.
[3] D. Gust and J. D. Roberts, *J. Amer. Chem. Soc.*, 1977, **99**, 3637.
[4] H. J. C. Yeh, M. Sato, and I. Morishima, *J. Magnetic Resonance*, 1977, **26**, 365.
[5] K. Kawano, Y. Ozaki, Y. Kyogoku, H. Ogoshi, H. Sugimoto, and Z. Yoshida, *J.C.S. Perkin II*, in the press.
[6] I. Morishima, T. Inubushi, and M. Sato, *J.C.S. Chem. Comm.*, 1978, 106.
[7] D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc.* (*C*), 1968, 881.
[8] T. Kitagawa, Y. Kyogoku, T. Iizuka, and M. Saito, *J. Amer. Chem. Soc.*, 1976, **98**, 5169.
[9] N. F. Ramsey, *Phys. Rev.*, 1950, **78**, 699.