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Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Iron (III) Porphyrin–Imidazole Complexes

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Summary Upfield ^{13}C n.m.r. hyperfine shifts for co-ordinated imidazole resonances and most porphyrin resonances are discussed in terms of unpaired spin delocalization and assignment of haemoprotein signals.

Co-ordination of an imidazole residue of histidine to the iron porphyrin prosthetic group is required for function of all well characterized haemoproteins. ^{1}H N.m.r. spectroscopy of paramagnetic metalloporphyrin–imidazole complexes has been especially productive in elucidating bonding and thermodynamic, kinetic, and electronic structural information.[1,2] ^{13}C N.m.r. spectroscopy has been utilized to a lesser extent in model studies of paramagnetic iron porphyrins,[3–5] although examples of applications to metal-free porphyrins and diamagnetic metalloporphyrins are numerous.[6] Spectra have been reported for porphyrin[3] and cyanide[4] carbon resonances in low-spin iron(III) porphyrin–cyanide complexes, in high-spin halide complexes,[5] and in μ-oxo-bridged iron(III) porphyrin dimers.[5] Iron porphyrin–imidazole complexes have not previously been investigated by ^{13}C n.m.r. spectroscopy despite the potential relevance of such studies to the parent haemoprotein compounds. Low molecular weight haemoproteins have been the subject of several ^{13}C n.m.r. investigations,[7] and a resonance for the quaternary imidazole carbon of co-ordinated histidine has been assigned without benefit of iron porphyrin–imidazole spectra. Preliminary results of model studies are reported here to facilitate assignments and provide strategy for incorporation of ^{13}C labels in haemoproteins, as well as to evaluate earlier ^{1}H n.m.r. analysis of unpaired spin delocalization mechanisms.[2]

Substituted iron(III) tetraphenylporphyrin chloride [Fe(TPP)], iron(III) octaethylporphyrin chloride [Fe(OEP)], and iron(III) protoporphyrin IX dimethyl ester chloride [Fe(PPDME)] complexes with variously substituted imidazoles have been examined. The spectrum of Fe(TPP)-(1-MeIm)$_2$·Cl (Im = imidazole), shown in the Figure,

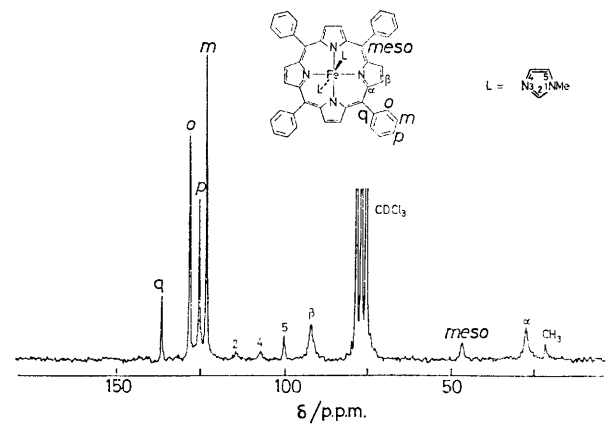

Figure. Proton decoupled ^{13}C n.m.r. spectrum of Fe(TPP)·Cl (0·05 M) and 1-MeIm (0·10 M) in $CDCl_3$ at 2 °C, referenced to Me_4Si; downfield shifts are positive.

clearly indicates resolved signals for all eleven carbon atoms of the complex. Similar imidazole resonances were observed for Fe(OEP)(1-MeIm)$_2$·Cl and porphyrin signals were recorded at −22 °C: δ 7·4 (α-C of pyrrole), 133·8 (β-C of pyrrole), 6·3 (*meso*-carbon), −32·3 (CH_2), and 88·3 (Me) p.p.m. The pattern of hyperfine shifts in Fe(PPDME)-(1-MeIm)$_2$·Cl parallels that for the Fe(OEP) complex. Spectra resemble those reported for cyanide complexes[3]

with some important differences. In particular, *meso*-carbon resonances show large upfield hyperfine shifts and phenyl carbon signals are also shifted upfield in Fe(TPP)–imidazole species. Using Co(TPP)(1-MeIm)$_2$·Cl as a diamagnetic reference compound, the hyperfine shifts for phenyl carbon atoms (*o*, −6·9; *m*, −3·5; and *p*, −2·7 p.p.m.) parallel the relative geometric factor values normalized to the *ortho*-shift (*o*, −6·9; *m*, −3·8; and *p*, −3·3 p.p.m.) suggesting shift contributions largely from a metal-centred dipolar term at these carbon atoms. The upfield bias for other carbon resonances is unexpected in relation to previous ^{1}H n.m.r. work describing unpaired spin delocalization through π-type M.O.'s.[2] ^{1}H Contact shifts are also upfield, but contact shifts for carbon and attached protons are expected to be opposite in direction for π-spin delocalization. A σ-spin polarization mechanism for carbon-13 may be invoked to explain these seemingly anomalous results.

Single resonances of non-protonated aromatic carbons have been assigned for low molecular weight haemoproteins.[7] In the paramagnetic cyanoferricytochrome c a signal at 123·6 p.p.m. (36 °C) was tentatively assigned to the 5-carbon of co-ordinated histidine.[7] For iron(III) porphyrin complexes of 5-methyl imidazole (chloroform solvent) and *N*-acetylhistidine (2 : 1 chloroform–methanol solvent) resonance positions of 114 and 111 p.p.m., respectively, at 36 °C are obtained by extrapolation from lower temperature values. The narrow linewidth and proximity to the haem make the 5-carbon imidazole resonance attractive for monitoring the haem environment. Significant differences between resonances in model compounds and proteins must reflect effects of the *trans* ligand and nature of haem environments.

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