N.M.R. Studies of Tin(IV) Porphyrins: Evidence for 'Through-space' ^{13}C–^{1}H Coupling in Dihydroxo-5,10,15,20-Tetraphenylporphyrinatotin(IV)

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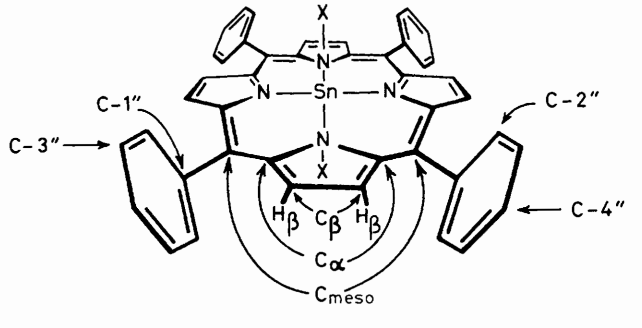
^{1}H and ^{13}C N.m.r. spectra of the title compound are reported, the latter showing unusual ^{13}C–^{1}H residual couplings which are rationalised by 'through-space' interactions between the centrally co-ordinated hydroxy hydrogen and porphyrin carbon nuclei.

In the ^{1}H n.m.r. spectra of axially-co-ordinated metalloporphyrins,[1] hydrogen-containing ligands experience large up-field shifts[2] due to the macrocycle's diamagnetic ring-current. Previous workers have reported difficulty in detecting hydroxy ligands by ^{1}H n.m.r. spectroscopy in thallium and other metalloporphyrins,[3] but they have been observed, to high field of Me_4Si, for aluminium(III),[4] phosphorus(V),[5] and germanium(IV)[6] porphyrins. However, an unusual effect of hydroxy ligands on the ^{13}C n.m.r. spectra of tin(IV) metalloporphyrins has, to our knowledge, gone unnoted, and we therefore report ^{1}H and ^{13}C n.m.r. spectra of dihydroxo-5,10,15,20-tetraphenylporphyrinatotin(IV) ($Sn^{IV}(TPP)(OH_2]$ (**1**). In the former, the hydroxy ligands, and their tin satellites, appear at high field while, in the latter, residual couplings are observed which we ascribe to long-range ^{13}C–^{1}H spin–spin interactions for the hydroxy protons to several of the porphyrin carbon nuclei. We suggest a 'through-space' mechanism for these couplings.

Metalloporphyrin (**1**) was prepared *via* a literature method[7] from $SnCl_2$ and TPP in refluxing acetic acid. The acetate ligands were replaced by hydroxy groups using the method of Maskasky and Kenney for $Ge^{IV}(TPP)(OH)_2$.[6] After thorough drying, (**1**) gave a satisfactory microanalysis and mass spectrum. In the i.r. spectrum of (**1**), a sharp peak at 3610 cm^{-1} was assigned to the non-hydrogen-bonded hydroxy ligands.

The ^{1}H n.m.r. data, recorded in dry $CDCl_3$,† are shown in Table 1. The hydroxy peaks appear at δ −7.46 with tin satellites, due to two-bond ^{1}H–$^{117,119}Sn$ coupling (J 37 Hz[8]), flanking the main peak. In Table 1, the data are compared with those of $Sn^{IV}(TPP)Cl_2$ (**2**), where no high-field peak is observed. On shaking with D_2O, the high-field peak of (**1**) disappears. For both (**1**) and (**2**), satellites are observed flanking the β-pyrrole proton resonance, which are assigned to long-range coupling to the tin nucleus over four bonds. This coupling constant (see Table 1) is greater for (**2**) than (**1**), a phenomenon previously reported in dichloro and dihydroxo complexes of phosphorus(V) TPP derivatives.[5] This may be due to the overall effect of p_π–d_π back-bonding from chlorine to tin.



(**1**) X = OH
(**2**) X = Cl

Because all six tin-co-ordinating groups (four porphyrin nitrogens and two axial chlorines) can engage in this type of bonding, the p_π–d_π back-bonding by the axial ligands effectively 'tightens' *all* co-ordination to the tin nucleus. This will augment σ-overlap between tin and the nitrogen moieties, increasing Fermi contact and, implicitly, transmission of spin–spin coupling to the β-pyrrole protons.[9] We propose that chlorine is better equipped to do this than oxygen because the former has two residual $3p_\pi$ orbitals, compared to oxygen's one $2p_\pi$ orbital, and that these are energetically more compatible with tin's empty $5d_{xz}$ and $5d_{yz}$ orbitals.

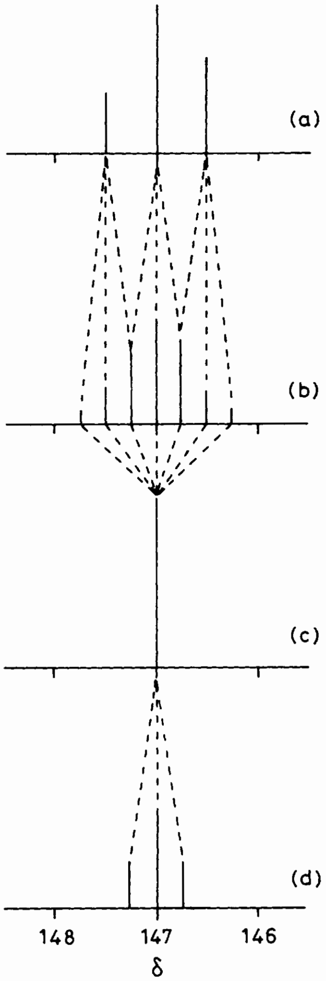


Figure 2. Splitting (diagrammatic) of C_α ^{13}C resonance under conditions of proton decoupling and coupling for (**1**) and its dihydrate; J values in Hz. (a) Proton-decoupled (**1**), J ^{13}C–$^{1}H(OH)$ 18; (b) proton-coupled (**1**), J ^{13}C–$^{1}H(\beta)$ 9; (c) proton-decoupled (**1**) dihydrate, no ^{13}C–$^{1}H(OH)$ coupling; (d) proton-coupled (**1**) dihydrate, J ^{13}C–$^{1}H(\beta)$ 9.

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† ^{1}H and ^{13}C N.m.r. spectra were recorded on a Bruker WM 250 spectrometer at 250 and 62.9 MHz, respectively.

Table 1. ^{1}H Chemical shifts (δ) and ^{1}H–$^{117,119}Sn$ coupling constants (in Hz) for compounds (**1**) and (**2**).

Compound[a]	Pyrrole β-H	Phenyl *o*-H	Phenyl *m*- and *p*-H	Sn–OH
(**1**)	9.12 (9.5 Hz)	8.31	7.81	−7.46 (37 Hz)
(**2**)	9.20 (15.5 Hz)	8.32	7.83	—

[a] The spectra were recorded in $CDCl_3$ with Me_4Si (TMS) as internal reference.

Table 2. ^{13}C Chemical shifts (δ) for (**1**) and (**2**) and ^{13}C–$^{1}H(OH)$ couplings contants for (**1**).

Compound[a]	C_α	C_β	C_{meso}	C-1″	C-2″	C-3″	C-4″
(**1**)	147.0 (18 Hz)	132.5 (7 Hz)	121.5 (12.5 Hz)	141.5	135.1 (6 Hz)	126.9	128.2
(**2**)	146.4	132.6 (30.5 Hz)[b]	121.2	140.7	134.9	127.1	128.5

[a] The spectra were recorded in $CDCl_3$ with TMS as internal reference. [b] This is a ^{13}C–$^{117,119}Sn$ coupling constant over three bonds.[13]

In the proton-decoupled ^{13}C n.m.r. spectrum of (**1**), recorded in dry $CDCl_3$,† four of the peaks in the typical seven-line spectrum[10] appear, unusually, as triplets. The *J* values decrease in the order $C_\alpha > C_{meso} > C_\beta \sim$ C-2″ (see Figure 1 and Table 2) and the triplet peak intensities are roughly in the ratio 1:2:1. This precludes ^{13}C–$^{117,119}Sn$ coupling as the cause of the triplet structures for two reasons: (i) the triplet peak intensity ratio is too large for the known natural abundance of ^{117}Sn and ^{119}Sn isotopes (7.65 and 8.68%, respectively), and (ii) previously recorded carbon–metal *J* values in metalloporphyrins[10,11] decrease in the order $C_{meso} > C_\beta > C_\alpha \sim$ C-2″ (if coupled).

A plausible explanation for the triplet structure on the four carbon resonances is residual ^{13}C–^{1}H coupling originating with the two centrally co-ordinated hydroxy protons. Initially, the proton-decoupled ^{13}C n.m.r. spectrum of (**1**) was recorded with the centre of the decoupled range tuned nominally to δ 5. This covers a span ~16 p.p.m. wide, from δ +13 to −3, so effectively leaving the hydroxy protons (at δ −7.46) undecoupled.

A further ^{13}C n.m.r. spectrum of (**1**) was recorded with the centre of the decoupling radiation shifted upfield to δ ~0, covering the range from δ +8 to −8. This would adequately decouple the hydroxy as well as the porphyrin protons. Significantly, all the triplets collapsed to singlets. Shaking with D_2O also removed the triplet structure on all four peaks.

These triplets occur only where the sample of (**1**) and the $CDCl_3$ are thoroughly dried. If either contains residual water, no triplet structures are observed. Presumably, proton exchange is too rapid, on the n.m.r. time-scale, for this type of ^{13}C–^{1}H coupling to occur. The point is further illustrated by the proton-*coupled* ^{13}C n.m.r. spectrum of both (**1**) and its dihydrate. In the former, C_α carbons appear as a septet, while in the latter they appear as a 1:2:1 triplet [$J(^{13}C$–$^{1}H)$ 9 Hz].

This last coupling constant is explained by each C_α carbon coupling equally, over two and three bonds, to its two neighbouring (see Figure 1) β-pyrrole protons. A precedent exists in the triplet structure assigned to the proton-coupled C_α carbons in 2,5-dimethyl pyrrole.[12]

The 9 Hz coupling constant is approximately half that of the hydroxy coupling to the C_α carbons (*J* 18 Hz, see Table 2) in the initial proton-decoupled ^{13}C n.m.r. spectrum of (**1**). We therefore rationalise the septet structure on the C_α carbon resonance, in the proton-*coupled* spectrum of (**1**) as an overlapping triplet of triplets (see Figure 2).

The number of intervening bonds between the hydroxy ligands and the C_α, C_{meso}, C_β, and C-2″ carbons, is four, five, five, and seven, respectively. The magnitudes of the ^{13}C–$^{1}H(OH)$ coupling constants to these carbons (see Table 2) from the initial proton-decoupled ^{13}C n.m.r. spectrum of (**1**) would appear inconsistent with a simple through-bond coupling mechanism. Molecular models show that the distance of the freely rotating hydroxy protons from these four carbon nuclei, through space, increases in the order $C_\alpha < C_{meso} < C_\beta <$ C-2″. We therefore suggest that the ^{13}C–$^{1}H(OH)$ couplings reported here can be explained by a 'through-space' mechanism. We are currently investigating the transmission of spin–spin coupling in these systems.

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