Nuclear Magnetic Resonance Spectra of Nitrogen-15 Enriched Octaethylporphyrin and its Derivatives

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97% ^{15}N-Enriched octaethylporphyrin [$^{15}N_4$]OEPH$_2$ and its mono- and di-*N*-methyl derivatives were synthesized by the use of Na^{15}NO$_2$ as a starting material. ^{15}N N.m.r. at 10 MHz and ^{1}H n.m.r. spectra at 100 MHz were obtained for these compounds and the metal complexes of [$^{15}N_4$]OEP with Mg^{II}, Zn^{II}, Cd^{II}, Ni^{II}, and Fe^{II}. ^{13}C N.m.r. spectra at 25 MHz were also measured for the metal complexes. As shown previously ^{15}N and ^{1}H spectra of [$^{15}N_4$]OEPH$_2$ in CDCl$_3$ have indicated that the two central hydrogens move around the four nitrogen atoms rapidly enough to maintain four-fold symmetry on the n.m.r. time scale at higher temperatures, while they are fixed on two of the nitrogen atoms at lower temperatures. The temperature dependence of the spectra of [$^{15}N_4$]-OEPMeH and [$^{15}N_4$]OEPMe$_2$H$^+$ has also revealed that the hydrogen of OEPMeH is fixed on the nitrogen located opposite to *N*-methyl group, while that of OEPMe$_2$H$^+$ exchanges rapidly between two nitrogens even below room temperatures. The ^{15}N resonance of the Ni^{II} complex of [$^{15}N_4$]OEP is distinct from the other diamagnetic metal complexes and located at remarkably higher field. Similar distinct shifts were observed for the ^{13}C resonance of the α-carbon of the Ni complex. The ^{1}H spectrum of the methine proton of [$^{15}N_4$]OEPH$_2$ was shown to be coupled to two ^{15}N nuclei leading to a triplet. The metal complexes, however, showed more complicated spectral patterns. Their fine structures are due to ' virtual coupling ' and arise from the coupling between ^{15}N nuclei *via* the central metal ion. The extent of the coupling depends remarkably on the metal ions.

THE mechanism of NH tautomerism in free-base porphyrins has been examined by several spectroscopic techniques. I.r. spectra showed the existence of fairly strong though fairly normal hydrogen bonds.[1-4] *X*-Ray and neutron diffraction studies have given two types of

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information on the position of the central protons. Triclinic forms of TPP (tetraphenylporphin)[5] and OEP (octaethylporphyrin)[6] crystals show that the inner hydrogens are attached to the opposite pyrrole nitrogens, while the tetragonal form of TPP includes the NH arrangement distributed randomly.[7] *X*-Ray photoelectron spectroscopy has also revealed that hydrogen atoms are attached to opposing nitrogens.[8,9] In addition to this information for solids, dynamic aspects of NH tautomerism have been investigated by ^{1}H and ^{13}C n.m.r. spectroscopy. The data showed that two central hydrogen atoms are located at two opposing nitrogens at low temperatures but exchange sufficiently rapidly such that the chemical shift differences are averaged at higher temperatures.[10-14] For NH tautomerism, however, ^{15}N n.m.r. should give more detailed information, because of the direct participation of nitrogen atoms. In a preliminary communication we reported the ^{15}N n.m.r. spectrum of ^{15}N-enriched octaethylporphyrin ($[^{15}N_4]OEPH_2$) giving direct evidence for the tautomeric structure based on ^{1}H and ^{13}C data.[15] Similar conclusions resulting from ^{15}N n.m.r. data were recently reached by other groups for ^{15}N-enriched protoporphyrin-IX[16] and TPP.[17,18] Here we report the detailed results for $[^{15}N_4]OEPH_2$ and present new evidence for *N*-alkylated porphyrins such as *N*-methyl- and *NN'*-dimethyl-octaethylporphyrins ($[^{15}N_4]OEPMeH$ and $[^{15}N_4]OEPMe_2H^+$) about whose tautomerism little is known.[19,20]

When metal ions are incorporated in the porphyrins, the electron density on nitrogen is affected by the nature of the metal–nitrogen bonding.[21] In this paper the ^{15}N resonance signals of some diamagnetic metal complexes of $[^{15}N_4]OEP$ are reported. In the course of the study it was found that the ^{1}H resonance signal of the methine proton is split by coupling to ^{15}N and the fine structure of the signal is caused by ^{15}N–^{15}N spin–spin coupling *via* the central metal ion. The chemical shifts and spin–spin coupling constants indicate the nature of the metal–nitrogen bonding in the metalloporphyrin.

EXPERIMENTAL

The ^{15}N label was incorporated into $OEPH_2$ by Knorr synthesis of ethyl 3-acetyl-4-ethyl-2-methylpyrrole-5-carboxylate using $Na^{15}NO_2$ (97.3 atom%; Merck). The ^{15}N content was confirmed by mass spectroscopy. Details of the synthesis of $OEPH_2$, its Mg^{II}, Cd^{II}, Ni^{II}, Zn^{II}, and Fe^{II} chelates,[22] and OEPMeH and $OEPMe_2H^+$[19] are described in the literature. The samples were dissolved in $CDCl_3$, and the spectra of the dications were measured in trifluoroacetic acid. To keep the iron(II) low spin state the $Fe^{II}OEP$ complex was stored in pyridine containing an excess of $SnCl_2$. ^{15}N Spectra were obtained at 10.09 MHz with a JEOL PFT-100 pulse Fourier transform n.m.r. spectrometer. Spectra were recorded with noise modulated ^{1}H decoupling (2.5 KHz), and in some measurements of the free bases, spectra were taken in the gated proton irradiation mode allowing the observation of proton coupled but intensity enhanced spectra by the nuclear Overhauser effect (NOE). On the other hand ^{15}N n.m.r. of metal complexes were obtained in the proton decoupled mode without NOE to reduce the decrease in intensity with negative NOE. Spectra were spread over 5 kHz with 8 192 data points; resolution due to digitalization was 1.22 Hz, *i.e.* 0.12 p.p.m. for ^{15}N. The normal operating conditions employed were: pulse width 20 μs (50° flip angle) and pulse delay 2 s. For the measurement of metal complexes 10 s was taken as the interval because of the long relaxation times. Sample tubes were 10 mm in diameter with a 2 mm coaxial tube containing $^{15}NH_4{}^{15}NO_3$ solution in C_2D_6SO, which provides the reference standard and external field-frequency lock. The chemical shifts were measured upfield in p.p.m. relative to external $^{15}NO_3{}^-$. The temperature of the probe was *ca.* 28°. ^{1}H and ^{13}C n.m.r. spectra were obtained in the Fourier transform mode on a JEOL FX-100 spectrometer operating at 99.6 and 25.05 MHz, respectively, with tetramethylsilane as standard. ^{1}H–^{15}N Heteronuclear INDOR was performed on a JEOL PFT-100 spectrometer equipped with a PA-1 amplifying unit and fitted with a matching network tuned for 10 MHz. The radiofrequency field was changed manually and spectra were monitored on the display unit of a EC-100 computer.

RESULTS AND DISCUSSION

NH *Tautomerism of Free Base Octaethylporphyrin*.—The proton decoupled ^{15}N n.m.r. spectrum of $OEPH_2$ at −53 °C shows two signals with negative NOE (Figure 1, left). The position of the upper field resonance is comparable with that of pyrrole[23] and the dication $[^{15}N_4]OEPH_4{}^{2+}$ in trifluoroacetic acid (TFA), and thus the signal was assigned to the protonated nitrogen (Table 1). The lower resonance appears 104 p.p.m. downfield from the higher. As it is known that the nitrogen resonance of pyridine shifts upfield on

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protonation by *ca.* 100 p.p.m.,[24,25] the lower signal is assignable to the non-protonated nitrogen. Since we can distinguish two kinds of nitrogens, the two central hydrogens seem to be fixed on two of the four nitrogen atoms at lower temperatures. The two protons are on opposing and not on adjacent nitrogens, since the methine protons (–CH=) in [$^{15}N_4$]OEPH$_2$ give a single resonance signal indicative of C_{2v} symmetry. The negative NOE of the lower field signal of the proton-free nitrogens in OEPH$_2$ is also observed for [$^{15}N_4$]-pheophytin a [26] and [$^{15}N_4$]TPP [17] probably due to exchange being slow on the chemical shift time scale but fast on the T_1 time scale, and/or to their proximity to the fixed hydrogens.[27,28] The two resonance signals coalesced around room temperature and a sharp inverted signal is seen at the central position of the two signals at higher temperatures. This indicates that the two central protons move around the four nitrogen atoms rapidly enough to maintain four-fold symmetry on the n.m.r. time scale at higher temperatures (Figure 2). The appearance of a single sharp nitrogen signal for the dication [$^{15}N_4$]OEPH$_4{}^{2+}$ shows the equivalence of the four protonated nitrogens. The shift values listed in Table 1 roughly agree with those of [$^{15}N_4$]TPP,[17,18] and [$^{15}N_4$]-pheophytin a except for the nitrogen in the reduced ring IV.[26]

TABLE 1

^{15}N Chemical shifts and coupling constants $J(^{15}N–H)$ of [$^{15}N_4$]OEP derivatives

Compounds	Solvent	T/°C	Chemical shifts * (p.p.m.)	Assignment	$^1J(^{15}N–H)$/Hz
[$^{15}N_4$]OEPH$_2$	CDCl$_3$	28	191.0	N $\rightleftharpoons$ NH	24
		−53	139.7	N	
			243.3	NH	97
[$^{15}N_4$]OEPH$_4{}^{2+}$	TFA	R.t.†	253.7	NH	93
[$^{15}N_4$]OEPMeH	CDCl$_3$	R.t.	125.8	N	
			243.3	NH	100
			256.0	NMe	
[$^{15}N_4$]OEPMeH$_3{}^{2+}$	TFA	R.t.	251.3	NH (adjacent)	92
			252.9	NH (opposite)	
			259.0	NMe	
[$^{15}N_4$]OEPMe$_2$H$^+$	CDCl$_3$	R.t.	183.5	N $\rightleftharpoons$ NH$^+$	48
			256.3	NMe	
[$^{15}N_4$]OEPMe$_2$H$_2{}^{2+}$	TFA	R.t.	254.5	NH	
			260.8	NMe	

* Shifts are relative to external NH$_4{}^{15}$NO$_3$ in [$^2H_6$]DMSO. † R.t. = room temperature.

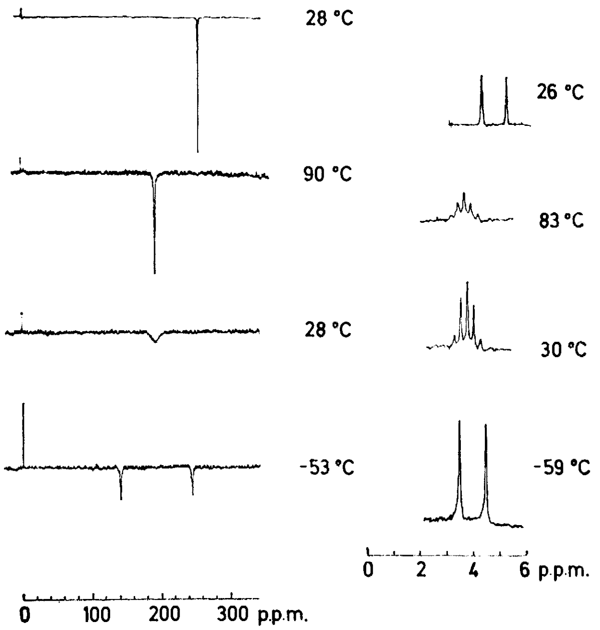

FIGURE 1 Temperature dependence of the proton decoupled ^{15}N n.m.r. spectra (left) and ^{1}H resonances of the NH groups (right) of [$^{15}N_4$]OEPH$_2$ in CDCl$_3$. The concentration of the solution was 0.019M and each spectrum was accumulated 20 000 times. The top spectra are those of the dication [$^{15}N_4$]-OEPH$_4{}^{2+}$ in TFA. ^{15}N Chemical shifts are in p.p.m. upfield from external NH$_4{}^{15}$NO$_3$ in C$_2$D$_6$SO and ^{1}H chemical shifts are from internal Me$_4$Si

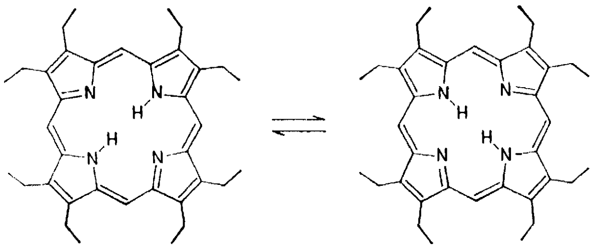

FIGURE 2 Tautomeric structures for [$^{15}N_4$]OEPH$_2$ at and above room temperature

The quintet for the NH protons at higher temperatures collapsed at *ca.* −20 °C and changed into a doublet [$^1J(^{15}N–H)$ 98 Hz] at lower temperatures (Figure

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1, right). The coupling constant is identical with those reported for [$^{15}N_4$]pheophytin a,[26] [$^{15}N_4$]protoporphyrin-IX methyl ester,[16] and [$^{15}N_4$]TPP [18] and is typical of sp^2-hybridized nitrogen.[29] The quintet for the NH protons and the triplet for the central nitrogens are unique phenomena compared with the usual n.m.r. exchange processes in which spin multiplets collapse to a singlet by increasing the exchange rate. This result is caused by intramolecular exchange of the protons among the four nitrogens, while normal exchange processes involve intermolecular exchange among an infinite number of sites.

It is known that the NH proton resonance in porphyrins has variable shift and is sometimes very broad.[11] In our preliminary work the NH proton signal appeared as a broad singlet at room temperature. However Irving and Lapidot [16] observed a multiplet for NH protons of [$^{15}N_4$]protoporphyrin-IX methyl ester in which a quintet was overlaid with a quartet. On the other hand, they obtained broad resonances for the NH protons of [$^{15}N_4$]coproporphyrin-III methyl ester. We have also succeeded in observing a quintet for the NH protons of OEPH$_2$ (Figure 1), when a solution of [$^{15}N_4$]OEPH$_2$ in CDCl$_3$ was shaken with the same amount of distilled water and the water phase removed. However, the sharp quintet broadened when the solution of [$^{15}N_4$]-OEPH$_2$ was held in a n.m.r. tube for a long time or exposed to intense light. Water treatment of the solution made the signal sharp again. A deuteriated pyridine solution of [$^{15}N_4$]OEPH$_2$, on the contrary, gives a sharp quintet without water treatment and is affected neither by long standing of the solution nor exposure to intense light. One possible explanation for the phenomena is the interaction of free base porphyrin with water soluble paramagnetic substances such as the radical produced by decomposition of chloroform. However, it is difficult to rule out the possibility of broadening resulting from proton exchange between the NH groups and contaminated water.

The quintet for the NH proton resonance also reveals that the two inner protons are equally coupled to four nitrogens with a coupling constant [$^1J(^{15}N\text{-}H)$ 24.5 Hz] which is a quarter of the coupling constant obtained at lower temperatures. From this, it is expected that proton-coupled ^{15}N n.m.r. provides a triplet with the same coupling constant at higher temperatures. This was actually observed for a deuteriated pyridine solution of [$^{15}N_4$]OEPH$_2$ at 70 °C and the value of 23 ± 3 Hz is in agreement with that of the NH proton.

It is known that octaethylporphyrin in TFA has a dication structure. It gave a single sharp resonance at δ 253.7 p.p.m. at 30°. The resonance position is 10—15 p.p.m. higher than that of TPP dication,[17] which was measured in chloroform solution with an excess of TFA. The NH proton resonance of the dication in TFA appeared as a doublet [$^1J(^{15}N\text{-}H)$ 93 Hz] whose value suggested that the nitrogens have sp^3 character to some extent. The appearance of the NH proton resonance indicates slow exchange with the protons of TFA.

NH *Tautomerism of* N-*Methyloctaethylporphyrin*.—In the proton-decoupled ^{15}N n.m.r. spectrum of [$^{15}N_4$]-OEPMeH there are three signals with a negative NOE over the temperature range examined (Figure 3, left). The position of the central intense resonance coincides with that of the protonated nitrogen in OEPH$_2$ at lower temperatures and is thus reasonably assigned to the protonated nitrogen (Table 1). The weak upper field resonance is located at a position near the chemical shift of the protonated nitrogen and is assignable to the NMe nitrogen. As it is known that there is little effect on the nitrogen chemical shift by replacing H with Me on pyrrole-type nitrogen atoms,[23] the upfield shift of NMe compared with that of NH of [$^{15}N_4$]OEPH$_2$ and [$^{15}N_4$]OEPMeH may be due to the sp^3 hybridization [30] of the nitrogen. The weak lowest field resonance is positioned around the chemical shift of the nonprotonated nitrogen in OEPH$_2$ at lower temperatures and is ascribed to the two nonprotonated nitrogens. Thus the central hydrogen of OEPMeH appears to be fixed on the opposite nitrogen to NMe at room temperature (Figure 4A). The negative NOE of the two peaks of the proton-free nitrogens may be due to the remote methyl protons [27,28] rather than slow exchange of the NH protons as for OEPH$_2$.

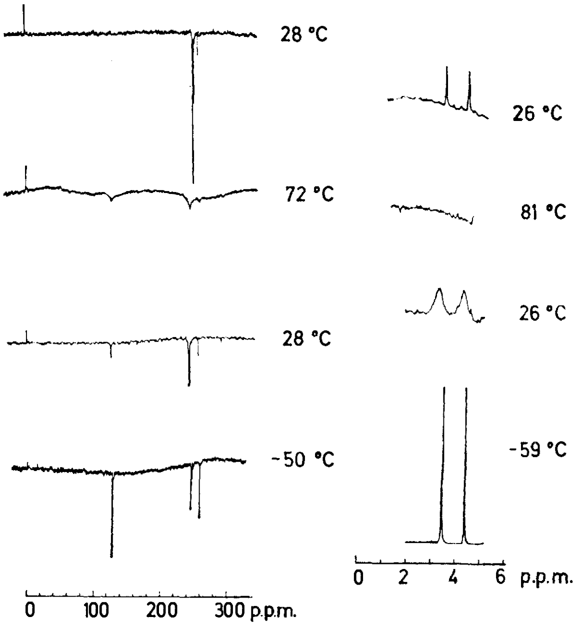

FIGURE 3 Temperature dependence of the proton decoupled ^{15}N n.m.r. spectra (left) and ^1H resonances of the NH groups (right) of [$^{15}N_4$]OEPMeH in CDCl$_3$. The concentration of the solution was 0.030M and each spectrum was accumulated 10 000—20 000 times. The top spectra are those of the dication [$^{15}N_4$]OEPMeH$_3^{2+}$ in TFA

The NH proton resonance of [$^{15}N_4$]OEPMeH appeared as a sharp doublet with an N–H coupling constant of 101 Hz (Figure 3, right). Raising the temperature allowed NH to be observed as a broad

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doublet which was not sharpened by water treatment. As the chemical shift of the NH proton was very dependent upon temperature and the imino proton signal of non-labelled OEPMeH was also broad, the broadening was probably due to intermolecular proton exchange among the NH protons or with contaminated water in $CDCl_3$ solution. The difference in the behaviour of protons between $OEPH_2$ and OEPMeH may be attributed to the enhanced basicity of nitrogen in OEP-MeH.[19,20]

The dication of OEPMeH in trifluoroacetic acid gave three inverted signals at *ca.* δ 250 p.p.m. The highest resonance peak was assigned to the methylated nitrogen based on comparison with the resonance positions of free acid OEPMeH and the dication of *NN'*-dimethyl-OEP discussed below. The intensity of the signal at δ 251.3 p.p.m. is twice that of the peak at δ 252.9 p.p.m. Thus the former resonance is assigned to the nitrogen atoms adjacent to the methylated nitrogen.

^1H N.m.r. of the NH protons of the dication $[^{15}N_4]$-$OEPMeH_3^+$ in TFA showed a doublet with NH coupling of 92 Hz, similar to that of $OEPH_4^{2+}$.

NH *Tautomerism of* NN'*-Dimethyloctaethylporphyrin.*—The proton-decoupled ^{15}N n.m.r. spectra of $[^{15}N_4]$-$OEPMe_2H^+$ where two adjacent nitrogens are methylated in a *trans*-manner above and below the porphyrin plane exhibited two nitrogen signals at room temperature (Figure 5, left). The upper field weak resonance is at the same position as the NMe signal of $[^{15}N_4]$-OEPMeH and is assigned to the methylated nitrogens. The negative NOE of the signal may be ascribed the same cause as for monomethylated OEP. The lower field intense inverted peak is positioned just at the centre of the protonated and non-protonated nitrogen resonances of $[^{15}N_4]$OEPMeH (Table 1). It means that the central proton exchanges rapidly between the two nitrogens (Figure 4B). If so, the inner hydrogen is equally coupled to the two nitrogens and the H–^{15}N coupling constant should be half that of a fixed hydrogen. Actually, a doublet $[^1J(^{15}N–H)$ 48 Hz] was observed in the proton-coupled ^{15}N n.m.r. spectrum.

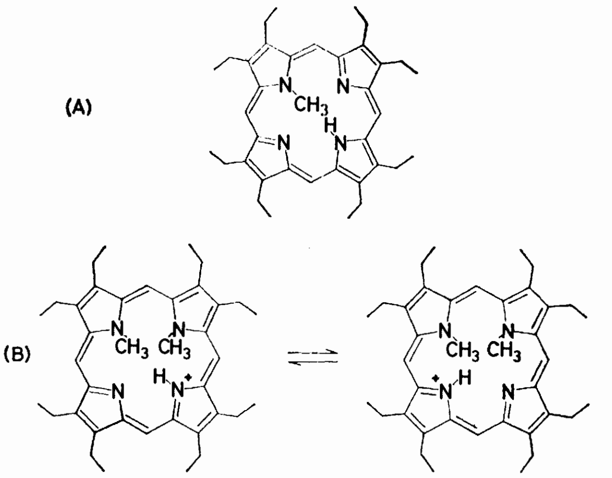

FIGURE 4 Tautomeric structures of (A) $[^{15}N_4]$OEPMeH and (B) $[^{15}N_4]OEPMe_2H^+$

The ^1H n.m.r. spectrum of $[^{15}N_4]OEPMe_2H^+$ confirmed the above explanation. The NH proton resonance appeared as a triplet with an N–H coupling constant of 48 Hz at and below the room temperature (Figure 5, right). The appearance of the triplet for the NH proton at −59 °C and two peaks in the ^{15}N spectrum at −50 °C reveals that the proton exchanges rapidly on two nitrogens and is not fixed even at such low temperatures. Its behaviour is distinct from those of the fixed protons in $OEPH_2$. The discrepancy between the two compounds may be attributed to the high basicity of dimethylOEP and to the nature of monocation.

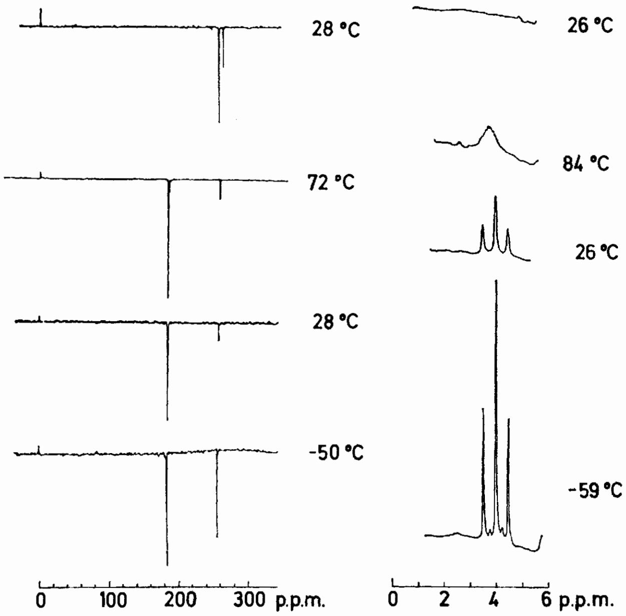

FIGURE 5 Temperature dependence of the proton decoupled ^{15}N n.m.r. spectra (left) and ^1H resonances of the NH groups (right) of $[^{15}N_3]OEPMe_2H^+Cl^-$ in $CDCl_3$. The concentration of the solution was 0.030M and each spectrum was accumulated 10 000—20 000 times. The top spectra are those of the dication $[^{15}N_4]OEPMe_2H_2^{2+}$ in TFA

An NH proton resonance for the dication $[^{15}N_4]$-$OEPMe_2H_2^{2+}$ in TFA was not observed. A previous paper on non-labelled $OEPMe_2H_2^{2+}$ reported none for the proton chemical shift.[20] The disappearance of the NH resonance may be attributed to proton exchange between the dication and solvent TFA.

^{15}N *Chemical Shifts of the Metal Complexes of Octaethylporphyrin.*—The ^{15}N n.m.r. spectra of the metal complexes of $[^{15}N_4]$octaethylporphyrin with Mg^{II}, Zn^{II}, Cd^{II}, Ni^{II}, and Fe^{II} ions gave single non-inverted signals and the shift values are collected in Table 2. Although it was difficult to obtain spectra with high signal to noise ratios because of the long relaxation time of the proton-free ^{15}N nuclei, the resonance positions were confirmed by INDOR by monitoring the methine proton resonances which were split by coupling to ^{15}N nuclei. The Fe complex can be maintained in the iron(II) low spin state in pyridine solution in the presence of excess of $SnCl_2$ in a sealed tube. Otherwise, the ^{15}N resonance could not be seen because of broadening due to the presence of paramagnetic species. On the other hand the Ni complex in pyridine produces paramagnetic species and its signal is hard to detect. For the other metal complexes a different solvent was used in each case mainly because of solubility. The solvent effect on chemical shifts is within a few p.p.m. judged from the shifts in mixed solvents.

TABLE 2

^{15}N Chemical shifts of metal complexes of $[^{15}N_4]OEP$

Compounds	Solvent	Chemical shifts (p.p.m.) *
$[^{15}N_4]Mg(OEP)$	$CDCl_3$ + py †	179.9
$[^{15}N_4]Fe^{II}(OEP)(py)_2$	$[^2H_5]py$	187.9
$[^{15}N_4]Ni(OEP)$	$CDCl_3$	257.0
$[^{15}N_4]Zn(OEP)$	$CDCl_3$ + py	179.2
$[^{15}N_4]Cd(OEP)$	$[^2H_5]py$	173.1 (165.6, 180.6) ‡

* Shifts are relative to external $NH_4{}^{15}NO_3$ in $[^2H_6]DMSO$. † py means the addition of a trace of pyridine. Concentrations were in the range 0.02—0.06M; spectra are accumulated 7 000—10 000 times with 10 s intervals. ‡ Satellite peaks due to spin–spin coupling with ^{111}Cd or ^{113}Cd $[^1J(^{15}N–Cd)$ 151.4 Hz].

The observed nitrogen chemical shifts of the metal complexes are δ 33—41 p.p.m. upfield from the shifts of non-protonated nitrogens of $[^{15}N_4]OEPH_2$ except for the Ni complex. The resonance position of the Zn complex, δ 179.2 p.p.m., corresponds to δ 175.2 p.p.m. of Zn-$[^{15}N_4]TPP$ reported previously.[17] It is also interesting to compare the nitrogen chemical shift of the Mg complex with those of $[^{15}N_4]$chlorophyll-a,[26] *i.e.*, the three nitrogens except that of the reduced ring in chlorophyll-a resonate near the frequency for those of MgOEP. Two satellite peaks at δ 165.6 and 180.6 p.p.m. with 10% intensity of the central peak of CdOEP were observed. Natural Cd contains two isotopes with spin 1/2, ^{111}Cd and ^{113}Cd. Their abundances are 12.9 and 12.3%, respectively. The satellite peaks must be due to coupling with ^{111}Cd and/or ^{113}Cd.

TABLE 3

^{13}C Chemical shifts of $[^{15}N_4]OEPH_2$, $[^{15}N_4]OEPH_4{}^{2+}$, and metal complexes of $[^{15}N_4]OEP$

		Chemical shift (p.p.m.) *				
Compounds	Solvent	Cα	Cβ	Methine	CH_2	CH_3
$OEPH_2$	$CDCl_3$	144.1br	141.4	96.5	19.8	18.5
$OEPH_4{}^{2+}$	TFA	143.6 †	147.8	100.9	21.7	18.2
Mg(OEP)	$CDCl_3$ + py	147.6	142.4	98.0	20.1	19.0
$Fe^{II}(OEP)(py)_2$	py	145.5br	145.0	97.5	20.2	19.0
Ni(OEP)	$CDCl_3$	140.3br	142.4	96.8	19.7	18.3
Zn(OEP)	$CDCl_3$ + py	147.3	141.7	96.7	19.9	18.8
Cd(OEP)	$CDCl_3$ + py	148.7	142.2	97.8	20.0	18.9

* Chemical shifts are relative to tetramethylsilane. † Split into a doublet coupled to ^{15}N $[^1J(^{13}C—^{15}N)$ 13.4 Hz].

It is known that the resonance position of ^{14}N shifts to higher field by *ca.* 50 p.p.m. when free ammonia is complexed with a diamagnetic cobalt ion in $[Co(NH_3)_6]^{3+}$.[31] This is mainly attributed to the paramagnetic term σ_p in the shielding constant arising from magnetic mixing of excited states with the ground state.[21,32] As shown in Ramsey's formula,[33] σ_p depends upon the values of excitation energy ΔD_i, which are sometimes substituted by the longer wavelength optical absorption maxima.[21,32] The narrow range of distribution of the ^{15}N chemical shifts of the metal complexes of OEP may be attributable to their similar absorption maxima.[34] The Ni^{II} complex, however, gives a resonance at higher field than the others. As the metal–^{15}N bond is stabilized, the value of ΔE seems to increase, the absolute value of σ_p decreases, and the ^{15}N resonance shifts to higher field. The larger ΔE of the Ni complex is revealed by the shorter wavelength absorptions of the Soret α and β bands.[35] The evidence of a strong Ni–N bond is also manifested in the higher Ni–N vibrational stretching frequency than those of other metal complexes.[36] These facts accord with the high field shift of the ^{15}N resonance of the Ni complex. The absorption maxima of $Fe^{II}(OEP)(py)_2$, however are close to those of the Ni complex, though its ^{15}N chemical shift falls around those of the Mg, Cd, and Zn complexes. In the case of Fe complexes the ^{15}N chemical shifts depend on the nature of the bonding between Fe and the fifth and sixth ligands; this will be discussed elsewhere.[37]

To confirm the occurrence of strong Ni–N bonding, ^{13}C resonances were observed for the metal complexes. As shown in Table 3 the resonance of the α-carbon of the Ni complex is remarkably higher compared with those of the other complexes. The effect of Ni–N bonding is still seen in the chemical shift of the second nearest nucleus.

^{15}N–^{15}N *Coupling in Metal Complexes of Octaethylporphyrin.*—^1H N.m.r. spectra of the methine protons in free base $[^{15}N_4]OEPH_2$ and its metal complexes are shown in Figure 6. The methine protons in the free base appeared as a triplet with $^3J(^{15}N–H)$ of 4.7 Hz owing to coupling to two ^{15}N nuclei, three bonds removed. On complexation with the metal ion, however, additional couplings were observed as shoulders and are attributable to coupling between the nitrogens through the central metal ion. The multiplets collapsed to singlets upon irradiation at the ^{15}N resonance frequency. This

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apparent long range coupling is known as 'virtual coupling',[38] and has been observed for the metal complexes containing phosphorus.[39] The spectra were analysed by simulation taking the coupling constants $^{3}J(^{15}\mathrm{N{-}H})$ and $^{2}J(^{15}\mathrm{N{-}M{-}}^{15}\mathrm{N})$ into account. Though the spectra should be simulated as an eight-spin system, they were approximated as a six-spin system $\mathrm{AA'X_2X_2'}$ where A' is the methine proton opposite to A and X the near and X' the far nitrogens to A. As it is known that the coupling between two phosphorus nuclei *trans* to each other ^{2}J(P–M–P *trans*) is usually greater than the corresponding ^{2}J(P–M–P *cis*) in the case of phosphine–metal complexes,[39] the coupling constant $^{2}J(^{15}\mathrm{N{-}M{-}}^{15}\mathrm{N}$ *cis*) was neglected in simulation. Actually, simulation involving $^{2}J(^{15}\mathrm{N{-}M{-}}^{15}\mathrm{N}$ *cis*) provided a complex spectrum. Setting $^{3}J(^{15}\mathrm{N{-}H})$ and $^{2}J(^{15}\mathrm{N{-}M{-}}^{15}\mathrm{N}$ *trans*) as 5.0 and 50.0 Hz, respectively, the simulated NH protons appeared as a quintet (Figure 7). The signs of the coupling constants had no effect on the pattern of the simulated spectra. A heptet was obtained by decreasing $^{2}J(^{15}\mathrm{N{-}M{-}}^{15}\mathrm{N}$ *trans*) to 7.0 Hz, and a triplet with shoulders was simulated by taking a value of 2.5 Hz. Thus the patterns of the methine protons in Zn[$^{15}\mathrm{N}_4$]OEP and Cd[$^{15}\mathrm{N}_4$]OEP correspond to the simulated pattern (B) in Figure 7 and those in Mg[$^{15}\mathrm{N}_4$]OEP, Ni[$^{15}\mathrm{N}_4$]OEP, and Fe[$^{15}\mathrm{N}_4$]OEP to (C).

In the $^{15}\mathrm{N}$–$^{15}\mathrm{N}$ spin–spin coupling constant the contribution of the spin–orbital interaction becomes important in addition to the contact term which is predominant in the proton–proton spin–spin coupling. The latter effect depends on the electron density at the core nuclei and on the extent of polarization of the intermediate electron cloud, while the former term reflects the magnitude of the magnetic field induced by the electron orbital motion and the spin–orbit term is related to the total electrons in the system. The virtual coupling constants in the simulated spectra depend on the atomic number of the central metal and thus the contribution of the spin–orbit terms seems important to the magnitude of $^{15}\mathrm{N}$–$^{15}\mathrm{N}$ coupling constants. Although the coupling constant may provide some informations on the nature of the M–N bonding, it is not directly correlated with that obtained from chemical shift data. In the $^{1}\mathrm{H}$ spectrum of [$^{15}\mathrm{N}_4$]chlorophyll-a,[26] additional couplings have also been observed as small peaks on both sides of the central lines of the methine triplets, and attributed to long range N–H coupling across the central Mg atom. However, they did not try to simulate the multiplicity of the methine proton signals as 'virtual coupling'.

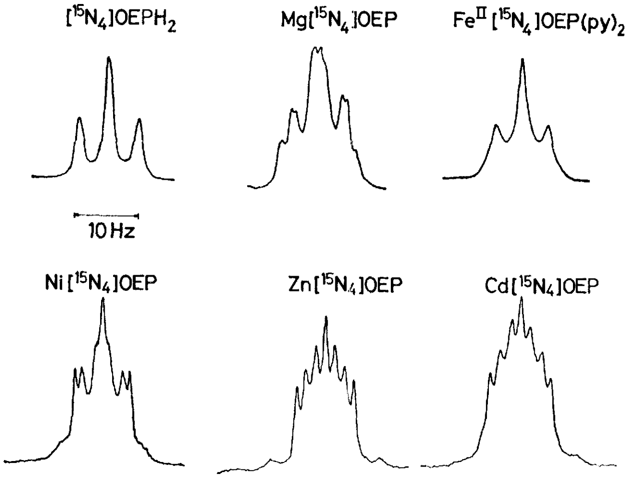

FIGURE 6 ^{1}H N.m.r. spectra of the methine protons in metal complexes of [$^{15}\mathrm{N}_4$]OEP

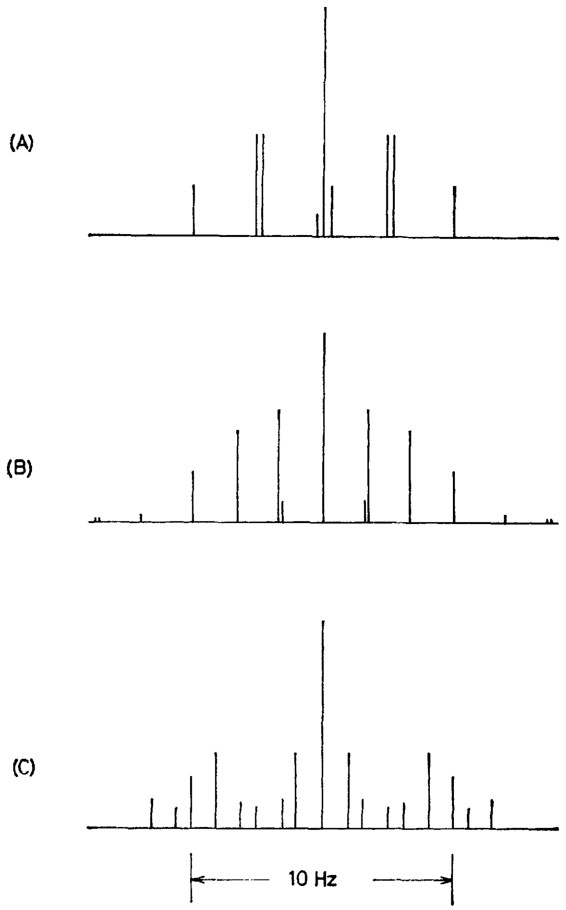

FIGURE 7 Simulated spectra of the methine protons of metal [$^{15}\mathrm{N}_4$]octaethylporphyrins as a part of $\mathrm{AA'X_2X'_2}$ system with the constants ν_{A} 100 and ν_{B} 10 MHz and $J_{\mathrm{AX'}} = J_{\mathrm{AA'}} = J_{\mathrm{XX'}}$ [$^{2}J(^{15}\mathrm{N{-}M{-}}^{15}\mathrm{N}$ *cis*)] 0.0 Hz. (A) $^{2}J(^{15}\mathrm{N{-}M{-}}^{15}\mathrm{N}$ *trans*) 50, (B) 7, and (C) 2.5 Hz

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[8/142 *Received, 27th January,* 1978]

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