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# Do NMR and ESR Provide Comparable Information in the Investigation of Metalloporphyrin Aggregation?

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It is well known that porphyrins and metalloporphyrins aggregate in solution [1, 2]. EPR spectra of copper, silver and vanadyl complexes provide evidence of dimers with S = 1 spin state [3–8]; the spectral analysis has allowed us to determine the spin Hamiltonian parameters and to obtain structural information on the dimer complexes [3–8]. The data are consistent with a face-to-face structure of the aggregate. An EPR study on aggregation of complexes of mesoporphyrin(IX) dimethyl ester with some metal ions has shown that only dimers are present in detectable amount in solution [7].

$^{1}$H NMR spectra have also been used to obtain thermodynamic and structural information in porphyrins and metalloporphyrins [9–16]. A model based on the porphyrin ring current has provided some structural information, in particular quite large porphyrin–porphyrin distances were found [9, 13, 14].

In this research we have investigated the association of Fe(III)PCl (where P is mesoporphyrin(IX) dimethyl ester) and the interaction between FePCl and CuP. From a previous EPR study [7], the dimerization of the iron porphyrin was estimated to be $<1$ M$^{-1}$, whereas the heterodimer formation constant for FePCl–CuP was 34.7 M$^{-1}$.

Previous $^{1}$H NMR investigation on high spin iron(III) porphyrin complexes [15] indicated a very complex situation that cannot be interpreted with a simple dimerization equilibrium, nor with a higher degree of aggregation. The $^{1}$H NMR investigation of systems like FePCl and FePCl–CuP, for which independent information is available, seemed particularly worthy of attention.

The complexes were prepared as reported elsewhere [7]. The $^{1}$H NMR spectra were obtained on a Bruker CXP 300 at 25 °C with TMS as internal standard. The spectra of FePCl in $CDCl_3$ are shown in Fig. 1, together with the assignment of the signals which had already been proposed [17]. In particular, four signals and a shoulder for the 2,4,6,7 $\alpha$-$CH_2$ and two signals for the 1,3,5,8 $\alpha$-$CH_3$ signals were observed. Their positions are concentration-dependent up to an observed variation in the shift

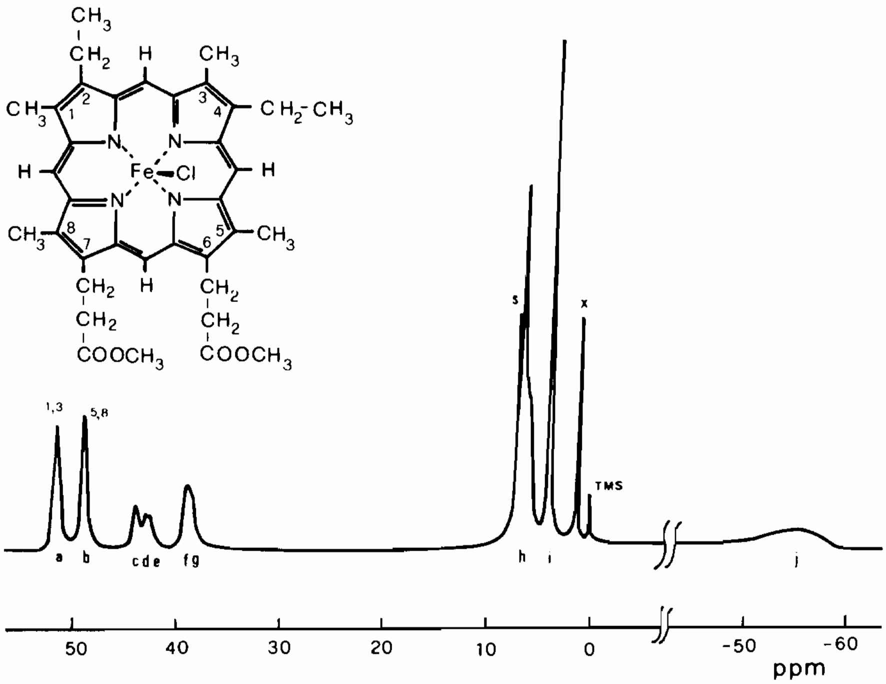

Fig. 1. 300 MHz $^{1}$H NMR spectrum at 25 °C in $CDCl_3$ of FePCl. Assignment of the signals: a, b = $\alpha$-$CH_3$; c, d, e, f, g = $\alpha$-$CH_2$; h = $\beta$-$CH_2$, $\beta$-$CH_3$; i = O–$CH_3$; j = *meta*-H; X = impurity; S = solvent.

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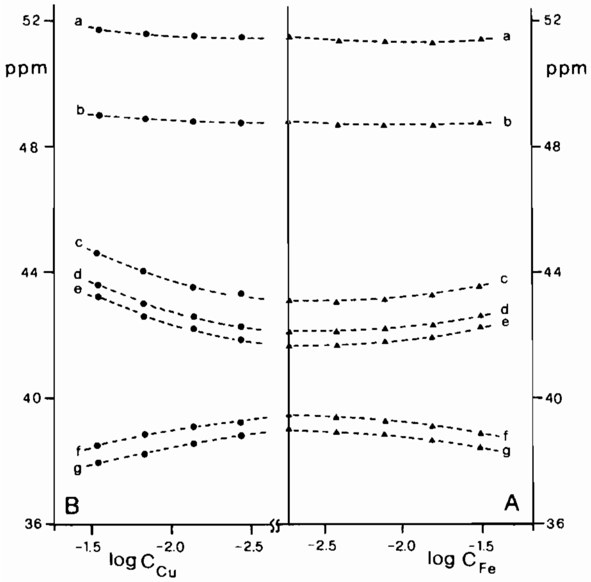

Fig. 2. Plot of chemical shifts as a function of the concentration of: A) FePCl; B) CuP–FePCl, in $CDCl_3$ at 25 °C, for the α-$CH_3$ (a, b) and α-$CH_2$ (c, d, e, f, g (shoulder)) signals d and e are presumably due to the resolved diasterotopic splitting of one α-$CH_2$.

of 0.6 ppm. The linewidths are also concentration dependent, however, the relative variation of the shifts are affected by smaller errors. The dependence of the chemical shifts with the concentration are shown in Fig. 2A.

The nature of the shifts is essentially due to contact contribution [18]. The change of the shift of the signals with concentration could be due to the change of the contact contribution, to an induced dipolar shift from a second interacting metalloporphyrin, or to ring current. It will be shown later that the latter possibility occurs. It is however surprising that the four α-$CH_2$ signals shift pairwise in opposite directions with the change in concentration. This observation has not a straightforward explanation; however, it shows that association does not provide a symmetrical aggregate. Since the α-$CH_3$ signals move in the same direction upon change in concentration, it seems that the behaviour of the α-$CH_2$ signals is due to their belonging to a flexible group. It is unfortunate that it is not possible to have a detailed assignment of the α-$CH_2$ signals. It is noteworthy that the *meso*-H signal is not concentration dependent within the uncertain linewidth. This shows that the nature of the shifts is not essentially due to a variation of the electron–nucleus coupling.

The variation of the shifts are, at first glance, consistent with a low value for the monomer-dimer equilibrium constant, consistent with the EPR data. However, every formation constant that reproduces the experimental points gives values for the limit isotropic shifts of the homodimers that are unreasonable for FeP systems. For example, with a constant value of 1 $M^{-1}$ the d line of the α-$CH_2$ signals would experience a shift of 120 ppm downfield with respect to the monomeric species. It is confirmed therefore that the $^1H$ NMR spectra are not explained by a simple model for porphyrin aggregation [15].

Addition of increasing amounts of Cu(II)P to a Fe(III)PCl solution provided variations in the shift of the protons of the latter complex larger than those found in the FePCl solutions; the pattern of the shifts with the concentration is shown in Fig. 2B. A model based on a face-to-face dimer, with a distance of 4.1 Å between the porphyrin plane as proposed for the CuP–CuP dimer, allowed us to calculate the dipolar shift induced by the CuP moiety on FePCl through the following equation [19], using the $g$ values of the CuP monomer:

$$\left(\frac{\Delta H}{H}\right)^{\mathrm{dip}} = \frac{\beta^2 S(S+1)}{9kTr^3}\,(1 - 3\cos^2\theta)(g_{\parallel}^2 - g_{\perp}^2)$$

The dipolar shifts on FePCl are at most 0.6 ppm for the pure dimer*. Therefore this calculation shows that the observed shift variations with concentration are not due to dipolar shifts. Indeed, the induced shifts by the diamagnetic NiP complex on FePCl have been found to be intermediate between those found for FePCl alone and for FePCl–CuP systems. It seems therefore that ring current effects are the most responsible for the shift variations.

The shift pattern again indicates that the interaction between the porphyrins does not provide symmetric aggregates. If the dimer formation constant of FePCl–CuP obtained through EPR spectroscopy is used, the shift pattern is not reproduced with any reasonable value for the CuP–FePCl limit shift: apparently only very low constant values reproduce the pattern of the shifts. However, the limit shifts for the CuP–FePCl species are still completely unreasonable. Apparently, the dimer detected through EPR spectroscopy is silent with respect to the NMR investigation.

This research shows that EPR and NMR techniques monitor different kinds of interaction and, in a way, account for the long-debated discrepancy between the calculated porphyrin–porphyrin distances by using the data of the two spectroscopies.

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*This value is obtained for a θ angle of 90°. If the metal–metal line is perpendicular to the porphyrin plane, then θ is such that the dipolar shift decreases one order of magnitude.

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