Mechanisms of Aggregation in Metalloporphyrins: Demonstration of a Mechanistic Dichotomy

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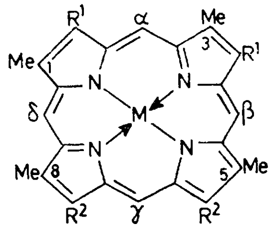
Summary N.m.r. spectroscopy is used to demonstrate that the predominant interaction in aggregations of magnesium(II) porphyrins [*e.g.* (**1**)] involves the metal atom in one molecule and the propionate carbonyl group in another; in contradistinction, the similarly strong aggregation observed for the first time in zinc(II) porphyrins [*e.g.* (**2**)] is shown to be independent of a metal to side-chain interaction.

Aggregation in solutions of chlorophylls and porphyrins has been widely studied.[1] Two types of complex have been identified, namely a strong interaction in the chlorophylls involving a specific complex between metal atom and side-chain carbonyl, and a much weaker π–π interaction in metal-free porphyrins.† We now show that the strong aggregation exhibited by the chlorophylls can be duplicated in magnesium(II) porphyrins. Moreover, we describe a novel aggregation of zinc(II) porphyrins which is of similar magnitude to that found in the chlorophylls but wherein a side-chain to metal interaction is not imperative.

Comparison of the ^{1}H n.m.r. spectra of magnesium(II) mesoporphyrin-IX dimethyl ester (**1**) in $CDCl_3$ alone (Figure, A) with that of the same solution containing a slight excess of pyrrolidine‡ (Figure, B) shows substantial upfield shifts of the resonances due to the γ-*meso* proton, the propionic ester methyl groups the methylene groups adjacent to the ester carbonyl, and to a lesser extent the propionate methylene groups adjacent to the macrocycle and the 5- and 8-methyl groups. This demonstrates that the predominant interaction involves the magnesium atom and the propionic ester carbonyl function; thus, given the presence



(**1**) M = Mg, R^1 = Et, R^2 = $CH_2CH_2CO_2Me$.
(**2**) M = Zn, R^1 = $CH{=}CH_2$, R^2 = $CH_2CH_2CO_2Me$.
(**3**) M = Zn, R^1 = $CH{=}CH_2$, R^2 = CH_2CH_2Me.

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† These types of aggregation can be differentiated by the fact that the former is removed by addition of donor molecules (*e.g.* methanol, pyrrolidine).

‡ Aggregates of zinc(II) porphyrins are broken up by addition of a slight excess of pyrrolidine (ref. 2).

of side-chain carbonyl groups,§ the strong aggregation effect found in chlorophylls, and upon which the phenomenon of photosynthesis depends, is largely a consequence of the presence of the magnesium, rather than a unique feature of the substituent arrays present in 'chlorophylls.' The shifts are not markedly diminished upon dilution (to *ca.* 0·0016M), and this emphasises the strength of the aggregation.

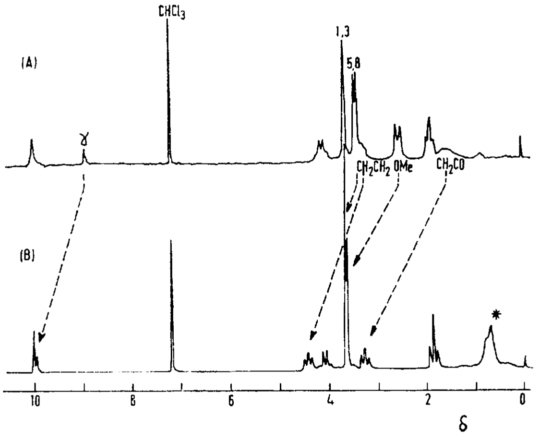

FIGURE. ^{1}H N.m.r. spectra of magnesium(II) mesoporphyrin-IX dimethyl ester (**1**) (0·016 M) in (A) $CDCl_3$ alone, and (B) $CDCl_3$ containing a slight excess, with respect to (**1**), of pyrrolidine. The peak marked with an asterisk in (B) is due to pyrrolidine. Spectra were measured on a Varian XL-100 spectrometer using Fourier transform.

The ^{1}H n.m.r. spectrum of zinc(II) protoporphyrin-IX dimethyl ester (**2**)¶ also shows a previously unobserved strong aggregation, the strength of which is comparable with that found in chlorophylls, and in (**1**). However, the pattern of the shifts, combined with the observation that the side-chain methoxy-resonances¶ show no shifts whatsoever, indicated that the mechanism responsible for the aggregation of zinc(II) porphyrins is entirely different from that in the magnesium series. All peaks (with the exception of the methoxy-resonances) showed downfield shifts upon disaggregation with pyrrolidine.

The ^{13}C n.m.r. spectra of (**1**) and (**2**) confirmed these results. For example, the ^{13}C (and ^{1}H) aggregation shifts for the 1-, 3-, 5-, and 8-methyl groups in (**2**) are 0·97 (0·98), 1·20 (1·25), 0·61 (0·66), and 0·75 (0·81) p.p.m. respectively. The ^{13}C studies also confirmed our assignments, *e.g.* of the CO_2Me in (**1**), the assignment of which is trivial in ^{13}C n.m.r. studies, but rather more of a problem in ^{1}H n.m.r. studies. Absolute confirmation was obtained using the the di(trideuteriomethyl) ester analogue.

In order to investigate further the interactions responsible for the aggregation in zinc(II) protoporphyrin-IX dimethyl ester (**2**), we synthesised** zinc(II) 1,3,5,8-tetramethyl-6,7-dipropyl-2,4-divinylporphin (**3**); the ^{1}H n.m.r. spectrum of this compound in $CDCl_3$ alone is typical of a strongly aggregated metalloporphyrin with large upfield shifts. Upon addition of pyrrolidine the resonances experience downfield shifts to afford the spectrum of the disaggregated monomer, *clearly demonstrating that a side-chain to metal interaction is not a prerequisite for this aggregation.*

Thus, aggregation of zinc(II) porphyrins must take place through a mechanism involving π–π interaction; the factors which determine the strength of this type of aggregation in divalent diamagnetic metalloporphyrins are considered in the following communication.[3]

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§ Similar effects were observed in magnesium(II) protoporphyrin-IX dimethyl ester. We cannot exclude the participation of water molecules as is the case in the chlorophyll series. The unique feature of magnesium seems to be its *preferential* attraction for the carbonyl function, and this does not imply that the novel π–π interaction (ref. 3) does not occur with magnesium complexes.

¶ See Figure in the accompanying communication (ref. 3).

** Protoporphyrin-IX dimethyl ester was reduced with lithium aluminium hydride and the resulting diol, after complexation with zinc(II), was treated with methanesulphonyl chloride. Further reduction with lithium aluminium hydride gave the 6,7-dipropyl compound (**3**). All new compounds gave satisfactory elemental analyses and spectroscopic data.

[1] For a review see H. Scheer and J. J. Katz in 'Porphyrins and Metalloporphyrins,' ed. K. M. Smith, Elsevier, Amsterdam, 1975, p. 399.

[2] R. J. Abraham, H. Pearson, and K. M. Smith, *J. Amer. Chem. Soc.*, 1976, **98**, 1604.

[3] R. J. Abraham, F. Eivazi, H. Pearson, and K. M. Smith, following communication.