π–π Aggregation in Metalloporphyrins: Causative Factors

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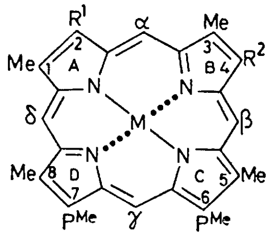
Summary The strength of aggregation in Pd^{II}, Ni^{II}, Zn^{II}, and Cd^{II} metalloporphyrins is shown by n.m.r. spectroscopy to depend upon interaction of the metal ion with the porphyrin π-system; within a selected series of 2,4-disubstituted deuteroporphyrin-IX dimethyl esters complexed with a constant metal ion the aggregation is further enhanced by the presence of electron-withdrawing substituents on the porphyrin periphery.

THE literature documents strong metal to side-chain interactions in the chlorophylls,[1] but only very weak π–π interactions in porphyrin free bases,[2] and in thallium(III)[3] or nickel(II)[4] complexes. Zinc(II) methyl phaeophorbide-*a* has been shown[5] to exhibit 'significant coordination and π-π aggregation' whereas the Ni^{II} and Cu^{II} analogues did not.[6] More recently, a 'tight dimer' in iron(III) protoporphyrin-IX has been described.[7] The foregoing communication[8] delineated two types of aggregation phenomena in metalloporphyrins, specifically a very strong aggregation in zinc(II) protoporphyrin-IX dimethyl ester (**1**) (Figure). We outline here the factors which are responsible for the formation of strong π–π complexes, both with respect to the central metal ion and the nature of the porphyrin ligand. Thus we are able to demonstrate that the degree of π–π aggregation in metalloporphyrins is predictable and an important fundamental property of the electronic structure.



(**1**) $M = Zn, R^1 = R^2 = V$
(**2**) $M = 2H, R^1 = R^2 = Et$
(**3**) $M = Zn, R^1 = R^2 = Et$
(**4**) $M = Zn, R^1 = R^2 = P^{Me}$
(**5**) $M = Zn, R^1 = R^2 = H$
(**6**) $M = Zn, R^1 = CHO, R^2 = V$
$V = CH{:}CH_2$
$P^{Me} = CH_2CH_2CO_2Me$

We have measured the ^1H n.m.r. spectra of the Pd^{II}, Ni^{II}, Zn^{II}, and Cd^{II} complexes of mesoporphyrin-IX dimethyl ester (**2**). Since the fine structure in the spectra is similar it follows that the aggregates formed have similar structures,† and therefore that the strengths of the interactions can be estimated directly from the aggregation shifts in the n.m.r. spectra under standard conditions.‡

TABLE 1. Aggregation shifts ($\Delta\delta$)[a] for mesoporphyrin-IX dimethyl ester (**2**) and metal complexes, and oxidation potential differences ($\Delta E_{\frac{1}{2}}$).[b]

	(**2**)	Pd^{II} complex	Ni^{II} complex	Zn^{II} complex	Cd^{II} complex
$\Delta\delta$/p.p.m.	0·05	0·05	0·09	0·61	1·31
$\Delta E_{\frac{1}{2}}$/V	0·00	−0·01	0·08	0·18	0·26

[a] See footnote ‡. Calculated by taking centre of gravity of *meso*-proton resonances in *ca.* 0·015 M solution in $CDCl_3$. Measured on a Varian XL-100 spectrometer. [b] See footnote ¶.

Table 1 shows the aggregation shifts ($\Delta\delta$) for the *meso*-protons of the porphyrins investigated here. If, as we suggest, these are characteristic of all divalent metalloporphyrins, one would expect a correlation between these shifts and a quantity characteristic of the metal-to-porphyrin interaction. We have chosen§ the *difference* ($\Delta E_{\frac{1}{2}}$) between the electrochemical first oxidation potential of the free porphyrin and that of the corresponding metal complex,¶ which can crudely be regarded as a measure of the extent of polarisation (positive–negative between metal–porphyrin) induced by the presence of the particular metal ion. These data show a striking correlation with the aggregation shifts (Table 1).

TABLE 2. Aggregation shifts ($\Delta\delta$)[a] of zinc(II) porphyrins and pK_3 values of corresponding metal-free porphyrins

	(**3**)	(**4**)	(**5**)	(**1**)	(**6**)
$\Delta\delta$/p.p.m.	0·50	0·54	0·70	1·16	1·62[b]
pK_3 of metal-free porphyrin	5·85	5·58	5·50	4·80	3·75

[a] The downfield shift of the centre of gravity of the *meso*-protons before and after addition of pyrrolidine to a 0·0065 M solution in $CDCl_3$. Spectra were obtained at 300 MHz. [b] Spectrum obtained at 100 MHz on a Varian XL-100 spectrometer.

Polarisation between metal ion and porphyrin can also be varied by introduction of electron-releasing or electron-withdrawing substituents into the ligand. Thus, we have

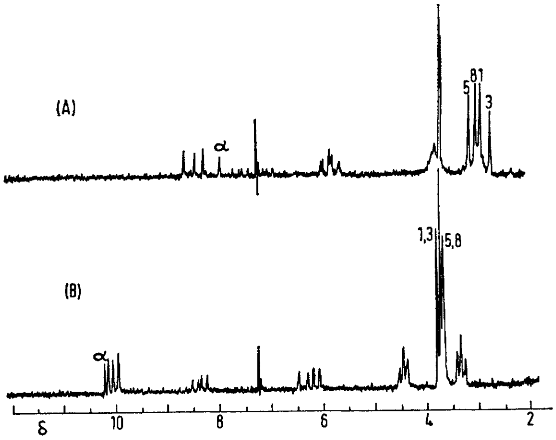


FIGURE. ^1H N.m.r. spectra of (**1**) (0·096 M) in (A) $CDCl_3$ alone, and (B) $CDCl_3$ containing a slight excess [with respect to (**1**)] of pyrrolidine. Spectra were measured on a Varian HA-100 instrument. Greek letters and numbers over resonances indicate assignments as given in the structural formula; methyl assignments were made using regiospecifically deuteriated samples of protoporphyrin-IX (*cf.* J. A. S. Cavaleiro, A. M. d'A Rocha Gonsalves, G. W. Kenner, and K. M. Smith, *J.C.S. Perkin I*, **1974**, **1771**).

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† A full analysis of the geometry of these aggregates will be presented elsewhere.

‡ The aggregation shift is the quantity $\delta_s - \delta_{(\text{inf. diln.})}$. The most convenient method for evaluation of this is to obtain the shifts before and after addition of pyrrolidine (ref. 9) and then to add to this the infinite dilution shift of the free base, which for mesoporphrin-IX dimethyl ester is 0·05 p.p.m. (ref. 4). Since Ni^{II} porphyrins become paramagnetic upon addition of bases, we have used $\delta_s - \delta_\infty$ for Ni^{II} mesoporphyrin-IX dimethyl ester from ref. 4. The free-base dilution shift is only *ca.* 0·02 p.p.m. for the more dilute solutions reported in Table 2, and has been ignored.

§ The relative susceptibilities of the metalloporphyrins to electrophilic substitution (*cf.* ref. 10) might just as easily be used. Work on this correlation is in hand.

¶ Electrochemical data for the full mesoporphyrin-IX series is not available in the literature; we have therefore used the oxidation potentials (ref. 11) for the metal complexes in the octaethylporphyrin series. The $\Delta E_{\frac{1}{2}}$ value for magnesium(II) octaethylporphyrin (0·27 V) indicates that in the absence of donor side-chains, suitably substituted magnesium(II) porphyrins should form π–π aggregates.

measured the ^{1}H n.m.r. spectra of a series of 2,4-disubstituted deuteroporphyrin-IX dimethyl ester zinc(II) complexes. In Table 2 the *meso* proton aggregation shifts for the series of zinc(II) complexes [(**3**), (**4**), (**5**), (**1**), and (**6**) respectively] of methyl esters of mesoporphyrin-IX, coproporphyrin-III, deuteroporphyrin-IX, protoporphyrin-IX, and chlorocruoroporphyrin are correlated with the pK_3 of the corresponding free porphyrin;[12] again, aggregation is enhanced by increasing the electrostatic polarisation between metal ion and porphyrin. The intramolecular polarisation or electrostatic imbalance is therefore reflected in increased intermolecular aggregation, with the strength of the latter depending upon the extent of the former.

From the assignments given in the Figure it can be seen that disaggregation with pyrrolidine causes the largest shifts for the α-*meso* proton and the 1- and 3-methyl groups. Preliminary studies† show that, in the aggregate, rings A and B lie over rings C and D (with some displacement along a diagonal). Significantly, rings A and B in (**1**) might be regarded as electron-deficient, and C and D as electron-rich; this electronic imbalance could be an important factor in determining the geometry of the aggregates in porphyrins bearing electronically dissimilar rings. A donor–acceptor argument for dissimilar rings has been advanced by LaMar and Viscio,[7] while Janson and Katz[2b] have deduced that rings A and B lie above rings C and D in aggregates obtained in metal-free protoporphyrin-IX diester. In the absence of electronically dissimilar rings (*e.g.* coproporphyrins[2a]) then steric factors will be the major influence.

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