Electron Spin Resonance Evidence for Dimer Formation in High Spin Iron(III)-octaethylporphyrin and Iron(III)-*meso*-Nitro-octaethylporphyrin in Solution

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Summary E.s.r. signals representing a dimeric species and another form of aggregation in high-spin Fe^{III}Cl-*meso*-nitro-octaethylporphyrin (OEP) (**1**) are presented, and a spectral assignment is made for the dimer signal to a transition within the lowest triplet levels.

The dimerization of Fe^{III}-porphyrins in solution has been studied by n.m.r., c.d., o.r.d., or u.v.–visible spectroscopy.[1] However, application of e.s.r. spectroscopy to this problem has not been reported so far. We report here e.s.r. evidence for a dimer formation by Fe^{III}Cl-*meso*-nitro-octaethylporphyrin (OEP) (**1**) in solution.

The e.s.r. spectrum (Figure ii) of (**1**) in a frozen toluene solution at a concentration of $1{\cdot}87 \times 10^{-3}$ M shows a pair of satellites with different intensities around the well known $g = 6$ peak belonging to the high-spin Fe^{III}-porphyrin. The intensity ratio of the satellites to the $g = 6$ (or 2) peak is undetectably low at a lower initial concentration C_0 (Figure i). When C_0 is varied over the range 10^{-5}—10^{-4} M, the ratio changes systematically, increasing toward the higher C_0 values. The relative heights of peaks L and D also depend upon C_0, L diminishing more than D when C_0 is decreased. This observation suggests that the extra e.s.r. signals may be due to some type of association process, and the fact that the signal D on the high field side remains visible to lower concentrations indicates that D is due to a dimer and L probably represents some higher order association. Similar spectra were observed for the bromide analogue as well as for unsubstituted Fe^{III}Cl(OEP).

Previous n.m.r.[2] and e.s.r.[3] studies of the corresponding Zn^{II}- and Cu^{II}-(OEP) and *meso*-nitro-derivatives have established that dimer formation occurs in these complexes, and that the extent of dimerization is enhanced by *meso*-nitro-substitutions. This is explained by increased electronic polarization in the porphyrin plane due to the strongly electron withdrawing $-NO_2$ group(s). The formation constants for Cu^{II} complexes, obtained by the e.s.r. method, are *ca.* $10^3\,M^{-1}$ for Cu^{II}(OEP) and $10^5\,M^{-1}$ for the corresponding *meso*-nitro-derivatives. An analogous situation exists in Fe^{III} complexes; *i.e.* the e.s.r. intensity ratio of signal D to the monomer signal in (**1**) is approximately twice that of the unsubstituted complex at the same concentrations, a fact which lends support to the view that the signal D is indeed due to the dimer formation.

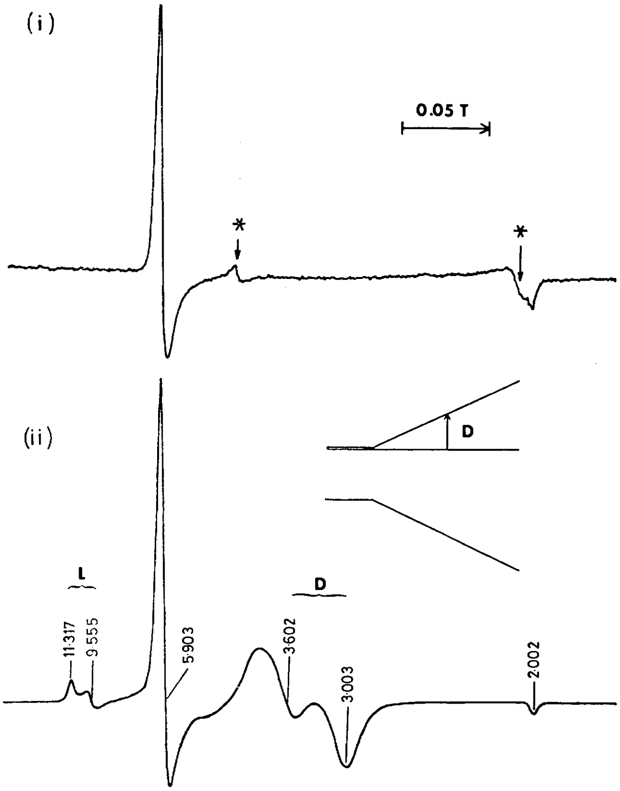

FIGURE. E.s.r. spectra of (**1**) in toluene at 14 K. Concentrations: (i), $5{\cdot}8 \times 10^{-6}$ M; (ii) $1{\cdot}87 \times 10^{-3}$ M. The peaks marked * in (i) are due to impurities. D corresponds to a transition between the two higher spin levels; the insert is shown for the perpendicular case in which the magnetic field is in the porphyrin plane. The gain setting in (i) is 25 times higher than that in (ii).

Other spectral features can also be explained on the basis of dimerization, by using the spin Hamiltonian relationship (1) for an $S = 5/2$ pair assuming that the porphyrin planes are parallel to each other, where the first term is the

$$H = D(S^2_{1z} + S^2_{2z}) - JS_1S_2 + H_{zeeman} + H_{dipolar} \qquad (1)$$

zero-field splitting of the monomer, while the second is the isotropic spin exchange interaction. An appropriate basis set consists of all combinations of $|I,J>$, in which $I,J = \pm 5/2, \pm 3/2$, or $\pm 1/2$. Using only the three lowest symmetric combinations of $|\pm 1/2>$, for simplicity, the observed e.s.r. signal D is assigned to the transition within the triplet levels as shown in the Figure. The assignment is based upon the fact that there is only one observable transition, on the high field side of the monomer signal. Even in this crude approximation the position of the observed signal can be explained semi-quantitatively by adjusting the parameters in the spin Hamiltonian relationship. The splitting in the signal D (g = 3·602, 3·003) can be reproduced in the spectral simulation by assuming a small anisotropy in zero-field splitting in the porphyrin plane. Perhaps one crucial, if not absolute, test of this assignment is that the calculated powder spectrum for the transition D should be confined to a narrow region of the magnetic field (*ca.* 0·04 T), as is indeed the case in the observed spectrum. The nature of the transition associated with the signal L is unknown at this point. At this order of approximation, the sign of J cannot be determined. In the energy level diagram depicted in the Figure, J was arbitrarily taken to be negative. It is noted that J must be of the same order of magnitude or less than the Zeeman as well as the dipolar term in order that there be at least one transition observed near the $g = 6$ peak. This fact, and the large number of the higher states to be included, make the perturbation treatment quite cumbersome, and, therefore, the entire matrix for the spin Hamiltonian relationship must be diagonalized to include the effect of the higher states. Also, to obtain accurate information for the structure of the dimer, it is necessary to carry out a precise spectral simulation.

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