Electron Spin Resonance Study of Dimers of Copper(II) Octaethylporphyrin, *meso*-Nitro-octaethylporphyrin, and *meso*-Dinitro-octaethylporphyrin in Solution

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The dimer e.s.r. spectra of copper(II) *meso*-nitro-octaethylporphyrin (1), copper(II) α,β-*meso*-dinitro-octaethylporphyrin (2), copper(II) α,γ-*meso*-dinitro-octaethylporphyrin (3), and copper(II) octaethylporphyrin (4) observed in a frozen toluene solution at 77 K are described. The equilibrium constants (*K*) for dimer formation have been obtained by fitting the observed monomer intensity as a function of the total concentration to a simple monomer–dimer scheme. For (1) and (2) the *K* values are (in 10^4 dm^3 mol^{-1}) 27 and 18, respectively, and there is an indication of a higher-order association, while the data for (3) and (4) can be explained only by dimer formation with smaller *K* values (0.15 × 10^4 and 0.68 × 10^4 dm^3 mol^{-1}, respectively). A structural analysis based on the point-dipole approximation shows that the Cu–Cu distance (4.16—4.19 Å) and the lateral shift angle (13—19°) are roughly the same in (1), (3), and (4). Complex (2) is unique in having a large angle (40°) and shorter interplane distance (3.2 Å). The effect of the electron-withdrawing nitro-group on dimerization is clearly demonstrated.

THE dimerization and polymerization of porphyrins and metalloporphyrins have been extensively studied by various spectroscopic techniques and are well documented.[1-11] Information pertaining to the geometrical structure of the dimeric species has been obtained mostly by n.m.r. measurements.[1-3] In paramagnetic complexes, however, except when the electron-spin relaxation time is sufficiently short, the method is difficult due to severe line broadening. Copper(II) porphyrins are a case in point, and have been studied, instead, by e.s.r. techniques. The first identification of the dimer (and polymers) was made by Blumberg and Peisach[8] for copper(II) uroporphyrin III in various aqueous media. Similar studies were later made of other copper(II) porphyrins by Boas *et al.*[9] and Boyd *et al.*[10] In most of these cases, because of insufficient spectral resolution of the $\Delta M = \pm 1$ transitions, an extensive spectral simulation of the half-field spectra ($\Delta M = 2$ transition) was required to extract structural information.

We present here the results of an e.s.r. study of copper(II) *meso*-nitro-octaethylporphyrin (1), and the corresponding α,β-*meso*-dinitro- (2) and α,γ-*meso*-dinitro-octaethylporphyrin complexes (3) as compared with copper(II) octaethylporphyrin (4). Our $\Delta M = \pm 1$ spectra of the dimeric species are very well resolved and yield sufficiently accurate structural information without making elaborate spectral simulations. The comparison of these complexes is considered particularly relevant to a determination of the effect on dimerization of simple modifications to the porphyrin π network. The results indicate clearly that the substitution of electron-withdrawing NO_2 groups enhances the metal–porphyrin electronic polarization, thereby promoting the dimerization. The structure of the dimeric species obtained in the present work is approximately in agreement with that derived by n.m.r. studies.[2]

EXPERIMENTAL

meso-Nitro-octaethylporphyrin was prepared by treatment of its zinc(II) complex (OEP) with thallium(III) nitrate trihydrate.[12] Complex (1) was obtained by treatment of a CH_2Cl_2 solution with copper(II) acetate monohydrate in MeOH, followed by crystallization from CH_2Cl_2–MeOH. Complexes (2) and (3) were prepared similarly from *meso*-dinitro-octaethylporphyrin.[13] Complex (4) was prepared by refluxing $Cu[O_2CMe]_2 \cdot H_2O$ and octaethylporphyrin in propionic acid, chromatography on alumina in $CHCl_3$, and recrystallized from $CHCl_3$–MeOH. The toluene used for e.s.r. measurements was carefully dried by refluxing over CaH_2.

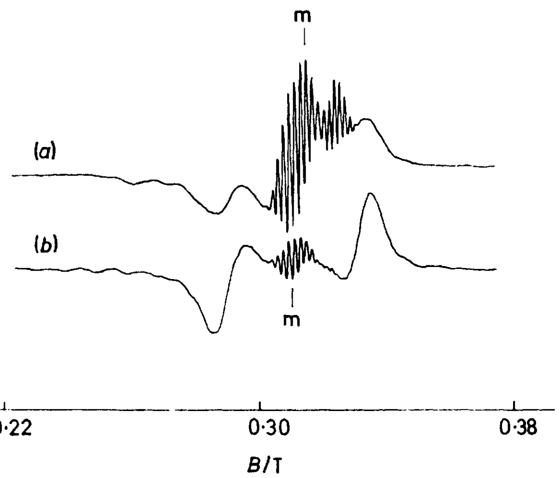

FIGURE 1 E.s.r. spectra of (*a*) complex (4) and (*b*) complex (1) at 77 K in toluene. Concentration = 5 × 10^{-4} mol dm^{-3}

E.s.r. measurements were made in solution at room temperature or in a frozen glass (77 K) of toluene, using a Varian E-9 *X*-band spectrometer with a 9-in magnet. The microwave frequency was measured by a cavity wavemeter calibrated against the signal of diphenylpicrylhydrazyl (dpph) (*g* 2.003 6); the magnetic field was measured by using a ^1H n.m.r. probe.

RESULTS AND DISCUSSION

The observed e.s.r. spectra of (1) and (4) in a frozen toluene solution at 77 K are shown in Figure 1. Considerable enhancement of dimer formation in (1), as compared with (4),* was clearly demonstrated by the relative intensities of the broad dimer absorptions and the well resolved monomer peaks marked ' m.' The spectroscopic designations for the dimer are indicated in Figure 2, in which A values indicate the hyperfine splittings, D the zero-field splittings, and g values are at the midpoints as indicated. Even at a concentration of 5×10^{-4} mol dm^{-3} the dimer formation is almost complete for (1). It is to be noted that (1) is more soluble than (4) in toluene, yet (1) forms a dimer much more readily under the same conditions. This is in contrast to β-diketone or Schiff-base complexes of Cu^{II}, where less dimerization takes place when the solubility of the complex is higher,[14-16] and indicates some distinction in the molecular mechanism of dimer formation.

In Figure 3 are shown the e.s.r. spectra of (2) and (3) observed under the same conditions. The dimer absorption of (3) appears quite similar to those of (1) and (4) in Figure 1, except for the different relative intensities. In contrast, it is evident that there is an increased amount of dimer for (2) and also the spectral characteristics are different from the other three complexes. Using the designations defined in Figure 2, the dimer spectrum of (2) is characterized by smaller D_1 and D_2 than of the other complexes, and a g_2 value which is significantly smaller than $g_{\parallel}$ of the corresponding monomer. In addition, there is a resolved hyperfine structure in the 0.25—0.3T region, which appears to be a superimposition of a normal parallel pattern and an extra hyperfine structure due to some rhombic distortion. These facts strongly suggest a dimeric structure of (2) in which the angle between $g_{\parallel}$ and the Cu–Cu axes may be larger and the Cu–Cu distance longer than in the other complexes. The monomeric part of the spectrum of (1) is obscured by the intense dimer absorptions, making it difficult to obtain accurate spectral characteristics of monomeric (1), especially g and A which are needed for estimating the structural parameters of the dimer. Use of a reagent such as pyrrolidine to prevent association of (4) caused changes in the e.s.r. parameters as shown in the Table, and, therefore, is also considered inadequate for the purpose of obtaining the parameters of monomeric (1). The e.s.r. characteristics are listed in the Table.

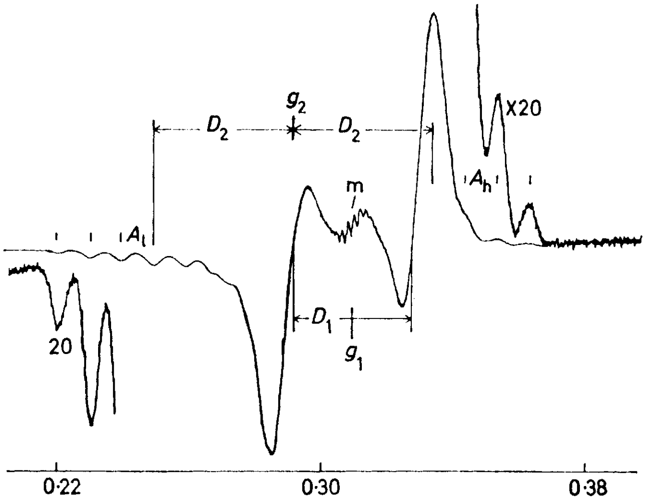

FIGURE 2 E.s.r. parameters for the dimer of (1). The spectrum recorded in toluene solution at 77 K; concentration = 6×10^{-4} mol dm^{-3}. D_1 is the fine-structure splitting of perpendicular transitions, measured as the distance between the crossing points. D_2 is half the distance between the centres of the parallel absorptions. A centre is located as the midpoint of seven hyperfine components due to the combined copper nuclear spin (I = 3). When a part of the hyperfine structure is hidden under the perpendicular signal the centre was located by extrapolation. Thus, detection of the edge of the hyperfine structure is critically important. The expressions for the parameters are given in the text

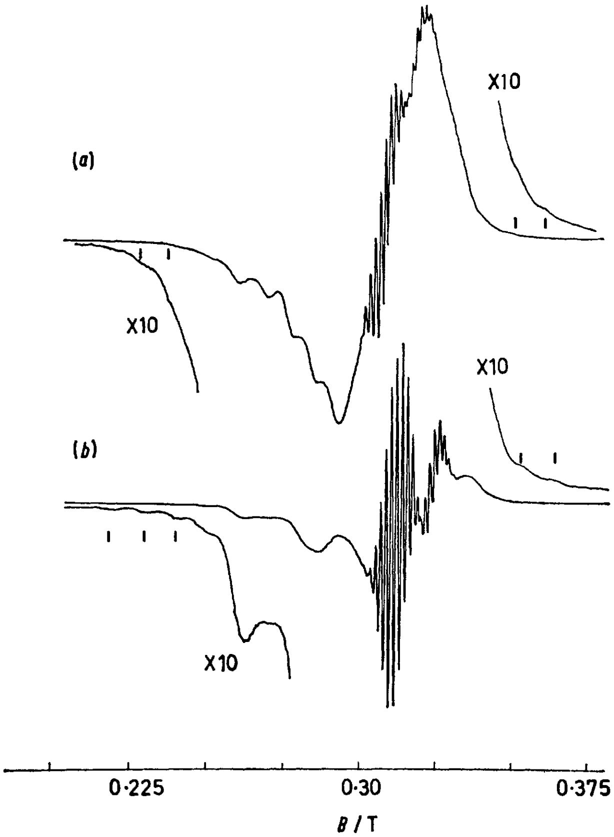

FIGURE 3 E.s.r. spectra of (a) complex (2) (1.75×10^{-3} mol dm^{-3}) and (b) complex (3) (1.56×10^{-3} mol dm^{-3}) at 77 K in toluene. The end parts of the hyperfine structure are indicated by short vertical bars. They were determined by repeated careful examination of the spectra with instrument settings for high sensitivity

Dimerization Equilibrium.—In order to obtain a semiquantitative measure for dimerization, the concentration dependence of the e.s.r. intensity was studied. Assuming a monomer(M)–dimer(D) equilibrium, 2M $\rightleftharpoons$ D, the

$$I_m = c[\mathrm{M}] = (c/K)[(8KC_0 + 1)^{\frac{1}{2}} - 1] \qquad (1)$$

normalized peak height (I_m) of the monomer e.s.r. signal is expressed as in (1) where c is a proportionality constant and C_0 the total concentration. Observations

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* An e.s.r. spectrum of a dimer of (4) has been reported (H. Yokoi and M. Iwaizumi, 16th E.s.r. Symposium, Sendai, Japan, October 1977).

were made by first equilibrating a toluene solution at the temperature of solid carbon dioxide, then quickly freezing in liquid nitrogen. The equilibrium constants obtained, therefore, are considered to relate to a temperature somewhere between 178 and 195 K. A plot of I_m against C_0 is shown in Figure 4. The data were fitted to equation (1) to determine c and the equilibrium constant K. Convergence in the least-squares fitting for complex (1) was slow and yielded a c value which is unacceptable. This result, as well as inspection of the observed data points, indicates that for complex (1) there may be some additional process(es) which consumes the monomer, and which takes place at high concentration ($>1.5 \times 10^{-4}$ mol dm^{-3}). Therefore, only ten points at lower concentrations were used for the curve fitting. A similar, but less drastic, situation occurs with complex (2), for which the converged K varies from 1.3×10^5 to 3.2×10^5 depending on the number of data points included in the fitting. Attempts to fit the whole data set of (1) and (2) to an equation which takes account of trimer or tetramer formation have been unsuccessful. Consequently, the equilibrium constant for complexes (1) and (2) may be an overestimation and correct only in its order of magnitude. In contrast, the fitting for (3) and (4) using the complete data set converged rapidly, giving reasonable c values. The equilibrium constants are listed in the Table. Thus the tendency for dimerization is in the order: (1), (2) $\gg$ (4) $>$ (3). In previous n.m.r. studies of zinc(II) complexes[2] the equilibrium constant for the analogue of (1) was estimated to be *ca.* 3 dm^3 mol^{-1}, and no dimerization was detected for the complexes corresponding to (3) and (4). The differences from the present results may be explained by the different temperature and solvent used in the n.m.r. and e.s.r. experiments.

TABLE

Comparison of e.s.r. characteristics, structural parameters, and equilibrium constants. For designations see Figure 2. ξ is the angle between the Cu–Cu direction and the normal to the porphyrin plane, A and D are in 10^{-4} cm^{-1}, distances in Å, and K in units of 10^4 dm^3 mol^{-1}. $g_\perp$ and $A_\perp$ were calculated from g_0 and A_0, respectively

	Complex			
	(1)	(2)	(3)	(4)
(*a*) Monomer				
$g_\parallel$		2.192	2.194	2.186 (2.220) *
$g_\perp$		2.063	2.062	2.053
g_0	2.104	2.106	2.106	2.097
$\lvert A_\parallel \rvert$		204	209	207 (189) *
$\lvert A_\perp \rvert$		27.6	27.7	26.4
A_0	87.7	86.4	88.1	86.6
(*b*) Dimer				
g_1	2.053			
g_2	2.179	2.132	2.185	2.170
D_1	346			
D_2	430	390	429	418
$\lvert A_l \rvert$	100	100	101	99
$\lvert A_h \rvert$	95	85	95	97
Cu–Cu distance	4.16	4.24	4.17	4.19
ξ	>19	40	13	19
K	27	18	0.15	0.68

* With added pyrrolidine.

Structure of the Dimeric Species.—Assuming that the porphyrin planes are parallel in a dimer, and that the principal axes of the g and A tensors coincide, various spin interactions in the dimer system are described to a good approximation by the spin Hamiltonian (2) where

$$\mathscr{H} = \beta S . g . H + (1/2) S . A . I - J S_1 . S_2 + \mathscr{H}_d \quad (2)$$

$S = S_1 + S_2$, $I = I_1 + I_2$, and g and A are the g matrix and the hyperfine tensor, respectively, appropriate for the monomer. Since the isotropic spin-exchange energy J in various copper(II) dimers is known to be <10 cm^{-1},[17] the anisotropic part of the spin exchange which originates from the interplay of the spin–orbit interaction and the J term is neglected. Thus the only anisotropic part

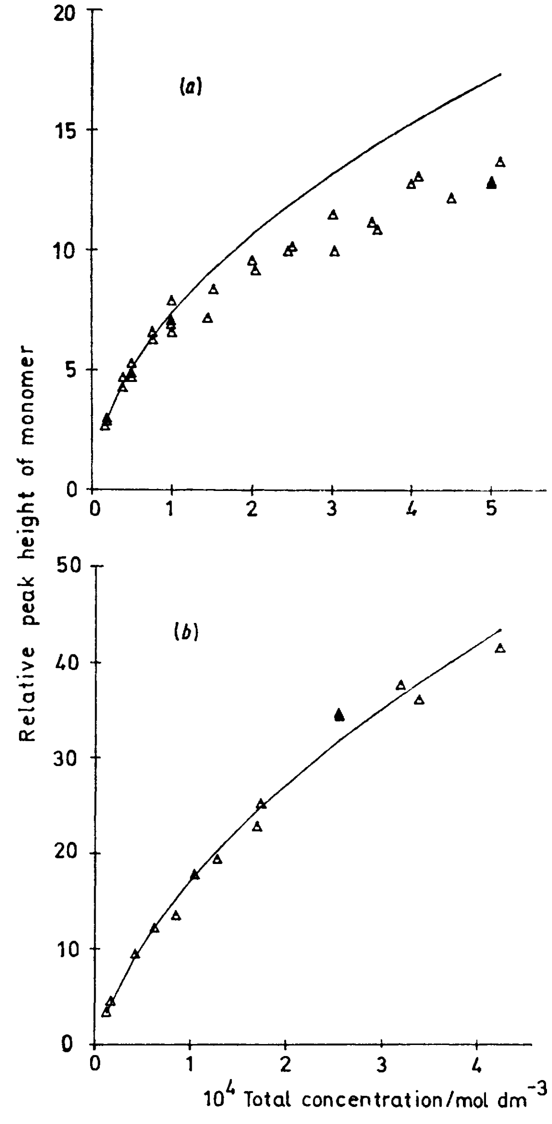

FIGURE 4 Plots of relative peak height against total concentration (in 10^{-4} mol dm^{-3}) for (*a*) complex (1) and (*b*) complex (4). (△) Experimental; (——) calculated

of the spin–spin interaction is dipolar [equation (3)]. When the g matrix is axially symmetric and the $g_{\parallel}$ axis

$$\mathscr{H}_{\mathrm{d}} = (\beta^2/r^3)[(gS_1)\cdot(gS_2) - (3/r^2)(gS_1\cdot r)(gS_2\cdot r)] \quad (3)$$

is parallel to the vector joining the copper(II) ions, $\mathscr{H}_{\mathrm{d}}$ can be rewritten [18] in the form (4) where $D = (3/4)g_{\parallel}^2\beta^2$,

$$\mathscr{H}_{\mathrm{d}} = D[S_z^2 - (1/3)S(S+1)] \quad (4)$$

$\langle(1 - 3\cos^2\theta)/r^3\rangle_{\mathrm{max.}} = 0.65\ g_{\parallel}^2/r^3$ and θ is the angle between the directions of $g_{\parallel}$ and H. When $g_{\parallel}$ and the Cu–Cu directions do not coincide, the expression for D is modified [19] to (5) where r is in Å and D_2 in cm^{-1}.

$$D_2 = 0.65g_2^2/r^3 \quad (5)$$

Using (5), the Cu–Cu distances for complexes (1) and (4) are found to be 4.16 and 4.19 Å respectively. The angle ξ between the $g_{\parallel}$ axis and the Cu–Cu direction is related to g_2 by (6). Thus ξ for (4) is calculated to be

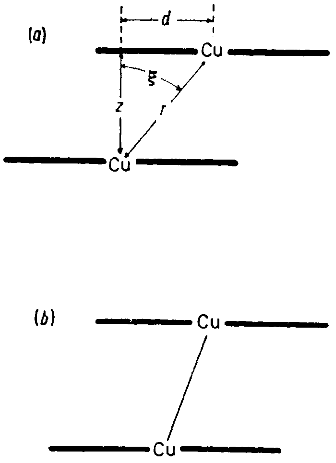

FIGURE 5 Schematic diagram of dimeric species: (a) α,β-*meso*-dinitro-complex; (b) an average of the other three complexes, indicating the shift angle (ξ), lateral shift (*d*), interplane distance (*z*), and the Cu–Cu distance (*r*)

$$g_2^2 = g_{\parallel}^2\cos^2\xi + g_{\perp}^2\sin^2\xi \quad (6)$$

ca. 19°. Due to the lack of accurate g values for the monomer it is difficult to estimate ξ for (1). However, it has been shown [19] that the difference $|A_1| - |A_{\mathrm{h}}|$ increases with the angle ξ in the range $0 < \xi < 50°$. Judging from the fact that $|A_1| - |A_{\mathrm{h}}|$ in the dimer of (1) is slightly larger than the corresponding value in (4), the angle ξ may be somewhat larger than 19° in the dimer of (1).

The structural parameters for (2) and (3) were determined similarly and are summarized in the Table. It is immediately evident that the structures of the dimers of (1), (3), and (4) have similar values for the Cu–Cu distance and the shift angle ξ. They are also approximately in agreement with the structure obtained previously by n.m.r. study of the zinc(II) analogues:[2] *cf.* the interplane distance of *ca.* 4.5 Å obtained by n.m.r. and the 3.9—4.0 Å in the present case, and the lateral shift of *ca.* 1 Å by n.m.r. and the 1.4 Å in this analysis [except in (3), see below]. The agreement appears to be excellent, considering the assumptions inherent in each method of analysis, and the differences in the temperatures of measurement and in the solvents used. However, it is known [20] that the point-dipole approximation with the magnetic moment localized on the metal tends to yield a larger metal–metal separation and a smaller shift angle ξ than those calculated by the distributed-dipole approximation which is thought to be a more realistic model. Thus the difference between the structures obtained by n.m.r. and e.s.r. spectroscopy may be somewhat larger than is apparent. It is conceivable that in the frozen state (77 K) for the e.s.r. observations the dimer molecules are closely ' packed ' together, while in solutions in which n.m.r. measurements are made the observed result is an average over vibrationally excited states such that the more ' loosely bound ' structure may have a substantial weight.

The structure of (2) is unique in that the shift angle is much greater than in the other complexes with a relatively small increase in Cu–Cu distance, thus resulting in almost twice as large a lateral shift (2.7 Å) and a closer packing of the two porphyrin planes (3.2 Å). This is especially in contrast to (3) (α,γ-dinitro-) in which the dimer has an interplane distance of 4 Å and a small lateral shift (0.9 Å). Such a remarkable distinction undoubtedly has its origin in the magnitude of the electronic polarization due to the two *meso*-nitro-substituents and in the location of the poles in the porphyrin plane. Assuming that steric hindrance is not an important factor in determining the relative orientation of two of the present molecules, the α,β-*meso*-dinitro-substituents appear to have an effect of shifting the electron-rich region towards the periphery in an opposite way to the symmetric α,γ-*meso*-dinitro-substituents. It is noted that there is a substantial lateral shift even in (4), which has no strongly electron-withdrawing substituent, and which formally has tetragonal symmetry. These results all indicate a significant role of the electronic polarization in the formation of dimers of metalloporpyrins. The results of a complete CNDO calculation, if available, would provide further insight into the details of the formation mechanism.

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