The Effect of 1,3,5-Trinitrobenzene on ^1H Nuclear Magnetic Resonance and Electron Paramagnetic Resonance Spectra of Some Cobalt(II) Porphyrins

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The e.p.r. spectra of Co^{II} mesoporphyrin IX dimethyl ester and Co^{II} aetioporphyrin I, as frozen solutions in chloroform, are weak and suggest extensive association of the Co^{II} porphyrins. The presence in solution of 1,3,5-trinitrobenzene gives rise to much more intense resonances, with different g- and A-values-the ^1H n.m.r. spectra at 299 K of the Co^{II} porphyrins are assigned and it is found that the chemical shifts are increased by the addition of trinitrobenzene, presumably owing to the formation of the Co^{II} porphyrin-trinitrobenzene molecular complexes and the concomitant reduction in Co^{II} porphyrin association. The paramagnetic shifts are assumed to be due mainly to the dipolar contribution and the shifts calculated by use of parameters derived from the e.p.r. spectra agree well with those observed.

PREVIOUS investigations of the magnetic resonance properties of cobalt(II) porphyrins have been principally concerned [1] with the e.p.r. spectra of their complexes with nitrogenous bases. Some workers have described [2] the e.p.r. of cobalt(II) porphyrins in non-polar solvents, and it is obvious that, as with many other porphyrins,[3] considerable association occurs at the concentrations normally used in these experiments. Our studies on the use of porphyrins as ' shift reagents ' have shown [4,5] that this association is broken up on molecular complex formation with non-co-ordinating planar molecules, and this paper describes the magnetic resonance properties of the monomeric cobalt(II) porphyrins.

EXPERIMENTAL

E.p.r. spectra were recorded on a JEOL JES-3BSX spectrometer at *ca.* 9·15 GHz in a 3 mm quartz tube fitted with a Thunberg head. The sharp resonance of 1,1-diphenyl-2-picrylhydrazyl was used as an external standard, and a dilute sample of manganese oxide was used for field calibration.

N.m.r. spectra were recorded on a JEOL-JNM-C-60HL spectrometer at 60 MHz. $CDCl_3$ was degassed and saturated with N_2 before use and appreciable ($>2\%$ as indicated by a shoulder at 411 nm) oxidation of Co^{II} to Co^{III} was avoided. Co^{II} and Ni^{II} porphyrins were prepared by standard methods,[6,7] and most experiments were carried out on the crystalline product isolated from the reaction mixture. This was thoroughly washed with glacial acetic acid, methanol, and a little peroxide-free ether and dried at 393 K and then *in vacuo*. The purity, determined by absorption spectroscopy by use of the known extinction coefficient at 552 nm in benzene,[6] was $>99\%$.

The following were prepared: *cobalt*(II) *mesoporphyrin IX dimethyl ester* (Found: C, 66·6; N, 8·45; H, 6·1. Calc. for $C_{36}H_{40}CoN_4O_4$: C, 66·4; N, 6·8; H, 6·2%), *cobalt*(II) *aetioporphyrin I* (Found: C, 72·5; N, 10·7; H, 7·3. Calc. for $C_{32}H_{36}CoN_4$: C, 71·9; N, 10·5; H, 6·8%), *nickel*(II) *mesoporphyrin IX dimethyl ester* (Found: C, 66·65; N, 84·; H, 6·3. Calc. for $C_{36}H_{40}NiN_4O_4$: C, 66·4; N, 8·6; H, 6·2%), and *nickel*(II) *aetioporphyrin I* (Found: C, 71·2; N, 10·4; H, 6·6. Calc. for $C_{32}H_{36}NiN_4$: C, 71·8; N, 10·45; H, 6·8%).

1,3,5-Trinitrobenzene (B.D.H.) was twice recrystallized from ethanol. All solvents were AnalaR grade.

RESULTS AND DISCUSSION

The e.p.r. spectrum of Co^{II} mesoporphyrin IX dimethyl ester (Ia) as a frozen solution in $CHCl_3$ *in vacuo* at 133 K is shown in Figure 1. At both 5×10^{-3}M and 10^{-2}M the signals were comparatively weak and high recorder gains were necessary to record the spectra. It is likely that the loss of signal intensity is caused by partial pairing of unpaired spins through porphyrin dimerization. E.p.r. work on the dimerization of Cu^{II} porphyrins has pointed out [8,9] that the metal ion does not play a major role in the association phenomenon. However, in the presence of 2,4,7-trinitrofluorenone,[4] 1,3,5-trinitrobenzene, and various steroids [5] the signal intensities increased so that lower gains could be employed. The spectrum shown in Figure 2 is that of the fully-formed

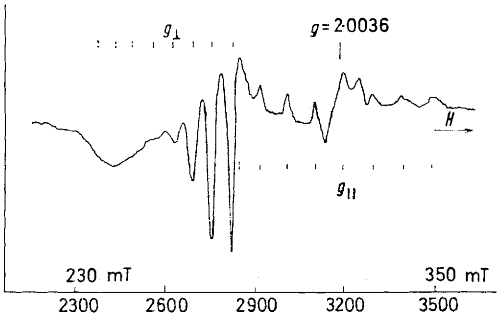

FIGURE 1 E.p.r. spectrum of Co^{II} mesoporphyrin IX dimethyl ester (10^{-2}M) in $CHCl_3$ at 133 K at 9154 MHz

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Co^{II} porphyrin–trinitrobenzene complex. Increasing the relative concentration of the acceptor component had no effect on the spectrum. These spectra show features which are typical of those normally found for low-spin Co^{II} porphyrins [1,2] and phthalocyanines.[10–14]

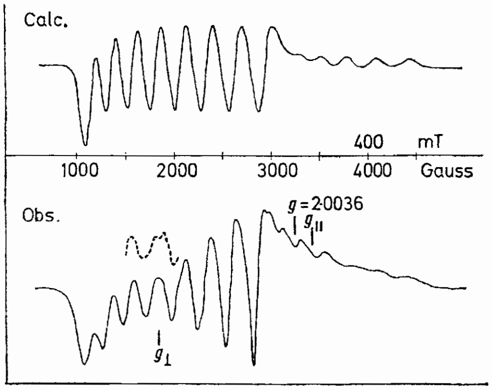
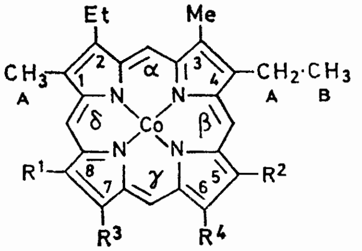


FIGURE 2 E.p.r. spectrum of Co^{II} mesoporphyrin IX dimethyl ester (10^{-2}M) in the presence of trinitrobenzene (0·1M) in $CHCl_3$ at 133 K and 9168 MHz

The general shape of the e.p.r. spectrum of a complex with axial symmetry has been described by Kneubühl.[15] The detailed description requires a consideration of the



(Ia) Co^{II} mesoporphyrin IX dimethyl ester; $R^1 = R^2 =$ Me, $R^3 = R^4 = CH_2(A)CH_2(B)CO_2Me(D)$: I(b) Co^{II} aetioporphyrin I; $R^1 = R^4 =$ Et, $R^2 = R^3 =$ Me

spin Hamiltonian introduced by Abragam and Pryce.[16] The total energy of the system is expressed as the sum of the component interactions and a perturbation treatment applied. For an axially symmetric transition metal complex with electron spin $S = \frac{1}{2}$ and nuclear spin $I > \frac{1}{2}$ the spin Hamiltonian is (1) where β and β_N are the

$$\mathscr{H} = \beta[g_\parallel H_zS_z + g_\perp(H_xS_x + H_yS_z)] + AS_zI_z + B(S_xI_x + S_yI_y) + Q[I_z^2 - \tfrac{1}{3}I(I+1)] - g_N\beta_N H . I \quad (1)$$

Bohr and nuclear magneton, $g_\parallel$ and $g_\perp$ denote the g-values parallel and perpendicular to the symmetry axis (z axis) of the molecule, and $H_{x,y,z}$ are the components of the magnetic field vector. S_z and I denote the electron and nuclear spin angular momentum vectors. The nuclear hyperfine coupling constants parallel and perpendicular to the symmetry axis are given by A and B respectively, and Q is the nuclear electric quadrupole coupling constant.

In powders or frozen glasses the molecular axes are randomly oriented and the fraction with angles between θ and $\theta + d\theta$ is $\frac{1}{2} \sin \theta \, d\theta$,[17] where θ is the angle between the molecular symmetry axis and the applied field. The number of absorbing molecules will thus vary with θ, reaching a maximum at $\theta = 90°$, the perpendicular region. The eight derivative absorptions seen to low field in Figure 2 are components of $g_\perp$. These are less well-resolved in cobalt porphyrin itself. Similarly most of the eight lines of $g_\parallel$ can be discerned at high field, although there is some overlap in the middle of the spectrum.

Bleaney has calculated [14,18] the resonance field for $\Delta m_I = 0$ transitions. To first order the peaks of $g_\parallel$ and $g_\perp$ should be equally spaced but unequal spacings arise through second-order contributions to the parallel components, and both second-order and quadrupole contributions to the perpendicular components. A computer simulation of the Co^{II} porphyrin–trinitrobenzene spectrum, following Bleaney's treatment, was carried out, a Gaussian line-shape function being assumed. The calculated g values and hyperfine coupling constants for the fit, shown in Figure 2, are recorded in Table 1. The g-values at the mid-point between the fourth and fifth hyperfine peaks and the average hyperfine spacings for both observed spectra are also given in Table 1.

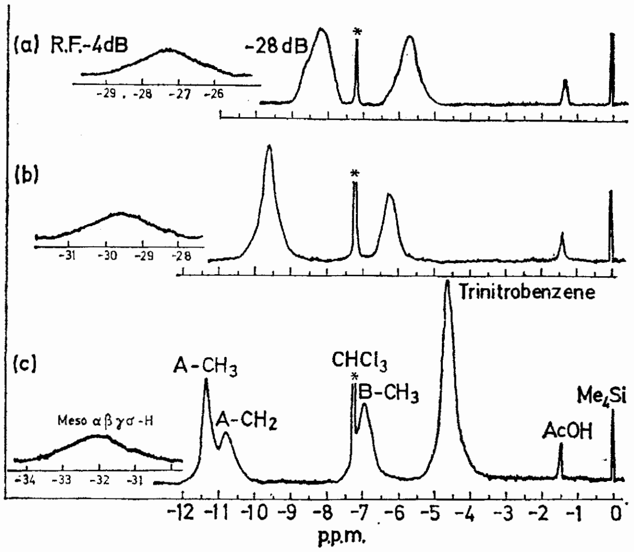


FIGURE 3 ^{1}H N.m.r. spectrum at 60 MHz of Co^{II} aetioporphyrin I (0·01M) in $CDCl_3$ in the presence of various amounts of trinitrobenzene at 299 K; (a), 0·0M; (b), 0·020M; (c), 0·082M

The g-values for low-spin complexes are dependent on the tetragonal splitting; [19] ($g_\perp - g_\parallel$) increases as the

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tetragonal splitting increases, and are still consistent with a $^2A_1$ ground state in the present case.[19,20]

The 60 MHz spectrum of cobalt(II) aetioporphyrin I (Ib) as a 0·01M solution in deuteriochloroform is shown in Figure 3. The chloroform was degassed and saturated with nitrogen before use. The spectrum was reproducible during several hours. There were three weak, broad bands and by addition of acetic acid the small peak at −1·4 p.p.m. was identified. The intensities of the bands, except those of $CHCl_3$ and tetramethylsilane, were increased by high radiofrequency powers without saturation. The very weak band at −27 p.p.m. was particularly difficult to locate and it was unnecessary to spin the sample. This band appeared to move to low field by 1 p.p.m. when the porphyrin concentration was decreased to 0·003M, although no other shift could be detected.

TABLE 1

E.p.r. parameters for cobalt(II) mesoporphyrin IX dimethyl ester (10^{-2}M in $CHCl_3$) at 133 K at 9154 MHz

	Co^{II} porphyrin	Co^{II} porphyrin–trinitrobenzene	
	estimated	estimated	calculated
$g_{\parallel}$	2·047	1·891	1·70
$g_{\perp}$	2·510	3·611	3·20
A	97×10^{-4} cm^{-1}	179×10^{-4} cm^{-1}	160×10^{-4} cm^{-1}
	(10·2 mT) [a]	(20·3 mT) [b]	(20·2 mT)
B	81×10^{-4} cm^{-1}	426×10^{-4} cm^{-1}	380×10^{-4} cm^{-1}
	(6·9 mT) [b]	(25·3 mT) [c]	(25·4 mT)

The calculation assumed Q = 0·4 mT and half-peak-to-peak width of the derivative of a single component line at a particular angle = 6·5 mT.

[Trinitrobenzene] = 0·1M. [a] Average 6 spacings. [b] Average 4 spacings. [c] Average 7 spacings.

Solid 1,3,5-trinitrobenzene was added to the tube, which was reweighed to determine the concentration. At a trinitrobenzene concentration of 0·02M its single peak, equivalent to 3 protons, was 3·55 p.p.m. to the high-field side of Me_4Si. As the trinitrobenzene concentration was increased the porphyrin band at *ca.* −11 p.p.m. resolved into peaks, and all resonances shifted to low field as shown in Figure 4. There are at least four sets of non-equivalent protons in Co^{II} aetioporphyrin I: meso α, β, γ, δ-H (4 protons), A-CH_2 (8 protons), A-CH_3 (12 protons) and B-CH_3 (12 protons). The least intense peak at *ca.* −33 p.p.m. in the trinitrobenzene complex can be assigned to the meso protons, whilst the integration of the other 3 peaks gave the ratios 12 : 8 : 12. Thus the peak at −11 p.p.m. can be assigned to the A-CH_2 protons. The spectrum of Co^{II} mesoporphyrin was also investigated, and this made further assignments possible.

The 60 MHz ^{1}H n.m.r. spectrum of Co^{II} mesoporphyrin IX dimethyl ester as a 0·01M solution in deuteriochloroform is shown in Figure 5. Only a single trinitrobenzene peak was again observed when the solid was added to the tube, indicating a fast exchange between complexed and uncomplexed forms. At 0·013M this peak was 3·72 p.p.m. to high field of tetramethylsilane. The correspondence between the peak positions for the two cobalt porphyrins can be seen in Figure 4. If the sharp peak at −4·5 p.p.m. is assigned to the D-CH_3 groups of the ester side chains the doublet at −6·5 p.p.m. is equivalent to 6 protons. The peak in aetioporphyrin was equivalent to 12 protons and this can therefore be assigned to the B-CH_3 protons, since there are still 12 A-CH_3 protons in mesoporphyrin. The latter must be assigned therefore to the most intense peak at *ca.* −11 p.p.m.

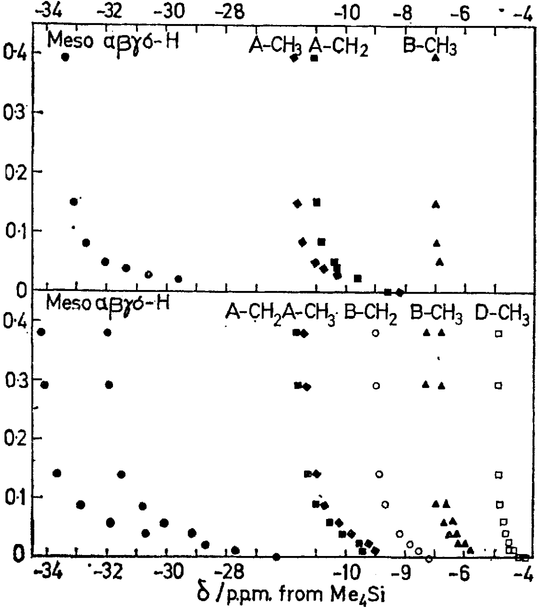

FIGURE 4 The effect of trinitrobenzene on the chemical shifts of protons in Co^{II} aetioporphyrin I (upper) and Co^{II} mesoporphyrin IX dimethyl ester (lower)

The spectrum of a 4×10^{-2}M solution of Co^{II} mesoporphyrin IX dimethyl ester was also recorded. Dimerization, which occurs with the Ni^{II} porphyrin,[3] could be important at this concentration, since the meso peak had shifted to high field by 2 p.p.m., the D-CH_3 peak by 0·1 p.p.m., and the other peaks by 0·5 p.p.m. Over the temperature range −47 to +51 °C the general features of

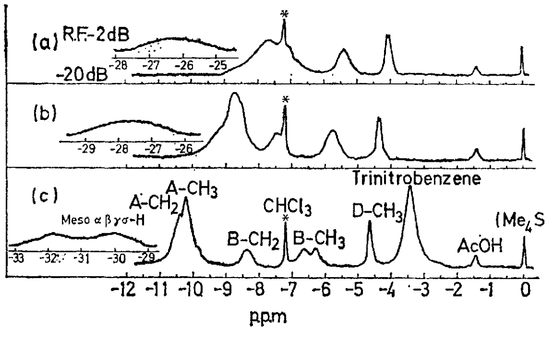

FIGURE 5 ^{1}H N.m.r. spectrum at 60 MHz of Co^{II} mesoporphyrin IX dimethyl ester (0·01M) in $CDCl_3$ in the presence of various amounts of trinitrobenzene at 299 K; (a), 0·0M; (b), 0·013M; (c), 0·056M

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[20] H. A. O. Hill, J. P. Jesson, and P. Meakins, unpublished work.

the spectrum remained the same. At −47 °C all peaks broadened and the largest shift was by 1 p.p.m. to high field by the band at *ca.* −7·4 p.p.m. At +51 °C this peak shifted by 0·3 p.p.m. to low field. [Peaks from this porphyrin (4×10^{-3}M) in the presence of trinitrobenzene (3×10^{-2}M) were sharp and clearly resolved at 220 MHz. There were 4 peaks at −10·5 p.p.m., a doublet at −8·7 p.p.m., two peaks at −6·5 and −6·9 p.p.m., and a doublet at −4·8 p.p.m. No search was made for the meso protons. It is possible that the A-CH_2 protons are resolved into a doublet at this frequency and that the A-CH_2 protons of the ester side chains can be distinguished from the other A-CH_2 protons.]

The 1 : 1 doublets of the meso and B-CH_3 protons at 60 MHz (Figure 5) are curious. There may be two or more types of trinitrobenzene complex with Co^{II} mesoporphyrin in solution. Indeed, the approach of trinitrobenzene from above and below the mesoporphyrin could give rise to a pair of optical isomers, whereas the two complexes would be equivalent for cobalt aetioporphyrin. It is also possible that the non-equivalences are associated with a deformation of the porphyrin skeleton caused by interaction of the propionic ester side chains. Flexibility of the skeleton is well known in the solid state,[21] and has also been suspected in solution.[22] Alternatively, a small rhombic component of the g-tensor of this unsymmetrical porphyrin may render the meso hydrogens magnetically inequivalent.

TABLE 2

Observed and calculated paramagnetic shifts of Co^{II} porphyrins (ratios with respect to the shifts of the meso protons are given in parentheses)

	meso-H	A-CH_3	A-CH_2	B-CH_3	B-CH_2	D-CH_3
(i)	−17·57(100)	−4·73(27)	−4·66(27)	−3·92(22)	—	—
(ii)	−16·62(100)	−4·35(26)	−4·4(26)	−3·67(22)	−3·90(23)	−0·32(2)
(iii)	−4·95(100)	−1·74(35)	−1·74(35)	−0·97(20)	−0·97(20)	−0·43(9)
(iv)	−23·46(100)	−7·43(32)	−7·59(32)	−5·04(21)	—	—
(v)	−24·70(100)	−8·05(33)	−7·62(31)	−5·67(23)	−5·79(23)	−1·22(5)
	−22·30(100)	(36)	(34)	(23)	(26)	(5)
(vi)	−16·78(100)	−5·91(35)	−5·91(35)	−3·29(20)	−3·29(20)	−1·44(9)

Key: (i) Cobalt(II) aetioporphyrin I. (ii) Cobalt (II) mesoporphyrin IX dimethyl ester. (iii) Calculated (see text). (iv) Cobalt(II) aetioporphyrin–trinitrobenzene. (v) Cobalt(II) mesoporphyrin–trinitrobenzene. (vi) Calculated (see text).

Paramagnetic Shifts.—The origin of the paramagnetic (Knight) shift in metal complexes may lie in both the contact and/or the dipolar (pseudo-contact) term. Previous investigations of Fe^{III} porphyrins have shown [23,24] that the contact interaction makes a major contribution to the shift of the porphyrin resonances mainly by interaction with the π-orbitals of the ring. If the single unpaired electron in low-spin Co^{II} porphyrins is well described by d_{z^2} then a similar mechanism of spin transfer is not applicable and any delocalization of spin must take place through the σ-framework. The large anisotropy in the g-tensor in the monomeric Co^{II} porphyrins means that the dipolar contribution may be the most significant, and the equation describing this has been given by Jesson [25] (his case *a*) for a g-tensor with tetragonal symmetry and a ground state well-separated from excited states [equation (2)], where Ω is the angle

$$\frac{\Delta\nu_d}{\nu_0} = -\frac{\beta^2 S(S+1)}{3kT}\cdot\frac{g_\parallel^2 - g_\perp^2}{3}\cdot\frac{(3\cos^2\Omega - 1)}{r^3} \qquad (2)$$

between the main symmetry axis and the metal–nucleus vector. Taking $g_\parallel = 1{\cdot}9$ and $g_\perp = 3{\cdot}6$ and distances (r) from the metal to protons of meso 4·59; A, 6·5; B, 7·9; D, 10·4 Å (though in solution the rotation about single bonds introduces considerable difficulty in choosing appropriate values of r), we calculate the dipolar shifts given in Table 2(vi). The experimental values given in Table 2 were obtained by referencing the limiting chemical shifts of Figure 4 with respect to analogous peaks in solutions containing the analogous Ni^{II} porphyrin.

The sign and size of the shifts of the protons in the Co^{II} porphyrins–trinitrobenzene molecular complexes are reasonably well described by the dipolar term, the largest discrepancy being for the meso protons. This may arise from the approximations involved in equation (2) or may reflect a small contact contribution which would be expected to be most significant for these protons. Though the paramagnetic shifts of the Co^{II} porphyrins (Table 2,i,ii) are smaller than those of the analogous molecular complexes (Table 2,iv,v) they are still larger than those calculated by use of $g_\parallel = 2{\cdot}0$ and $g_\perp = 2{\cdot}6$ which might be considered those most appropriate. However, this draws attention to the consequences of using data obtained from e.p.r. spectra measured at low temperature (on account of the short electronic relaxation time) to interpret room-temperature parmagnetic shifts. We may assume that association of the Co^{II} porphyrins is favoured by lowering the temperature; consequently the g-values obtained at this temperature are those of the *associated* Co^{II} porphyrins whereas at room temperature the n.m.r. spectra reflect presumably the average of an increased concentration of monomer (with paramagnetic shifts not very different from those of the Co^{II} porphyrin molecular complex), and the associated porphyrin (with paramagnetic shifts close to those calculated by use of $g_\parallel = 2{\cdot}0$ and $g_\perp = 2{\cdot}6$).

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[25] J. P. Jesson, *J. Chem. Phys.*, 1967, **47**, 579.

We note also that the reversed sign of the paramagnetic shift for protons of the porphyrin compared with those in the other component of the molecular complex, *e.g.*, trinitrobenzene or trinitrofluorenone [4] which are positioned over and 'above' the macrocycle, is in accordance with the change in sign of the angular term $(3\cos^2\Omega - 1)/r^3$.

In conclusion we see that the properties of *monomeric* Co^{II} porphyrins are semiquantitatively interpretable in terms of the known electronic structure of the cobalt and illustrate the potential of n.m.r. spectroscopy as a probe for structure in solution.

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