Electron Spin Resonance Study of the Oxygenation of Cobalt(II) Tetraphenylporphyrintetrasulphonate

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E.s.r. spectroscopy has been used to show that the addition of *NN*-dimethylformamide or dimethyl sulphoxide to aqueous solutions of cobalt(II) tetraphenylporphyrintetrasulphonate, [Co^{II}(tpps)], results in a disaggregation of the metalloporphyrin and provides conditions for its oxygenation by molecular oxygen. Larger additions of ethanol lead to formation of a monomeric six-co-ordinate cobalt(II) porphyrin which does not undergo a reaction with molecular oxygen to any great extent. On long storage in air, [Co^{II}(tpps)] in the solid state forms a complex with molecular oxygen. The magnetic parameters associated with the e.s.r. spectra of the monomeric forms of the metalloporphyrin and its complex with molecular oxygen have been determined. The oxygenated complex is believed to involve a Co–O–O bond angle of 105°, intermediate between the two models proposed previously for oxyhaemoglobin.

THE reaction of molecular oxygen with cobalt(II) porphyrins proceeds by attachment of the oxygen molecule to the cobalt(II) porphyrin, with a base occupying the other out-of-plane position.[1-4] E.s.r. measurements provide a convenient method for the detection of the cobalt porphyrin–oxygen complex which possesses a characteristic e.s.r. spectrum. The salient features of the oxygenation reaction of cobalt(II) porphyrins in solutions containing an aliphatic or aromatic amine which have emerged from e.s.r., as well as kinetic and thermodynamic studies of this reaction, may be summarised as follows.[1-4] (*i*) The formation of the five-co-ordinate complex of the cobalt(II) porphyrin results in displacement of the cobalt atom out of the plane of the porphyrin. (*ii*) The cobalt(II) atom is more sensitive to electronic effects within the porphyrin ring than it is to the basicity of the amines. However, the ease of formation of the oxygen adduct is a function of amine basicity. (*iii*) The 1 : 1 oxygen complex is rapidly formed at low temperatures and the reaction is reversible. If the temperature is allowed to rise, the e.s.r. signal is slowly lost presumably due to formation of binuclear oxygen-bridged species.

A particular advantage of the previous oxygenation studies is that they were carried out in non-polar organic solvents where the cobalt(II) porphyrins used are monomeric. The role played by the addition of nitrogen bases to such solutions is one which results in axial interactions of the metalloporphyrin, and hence allows the attachment of the oxygen molecule. In the case of water-soluble porphyrins it is necessary to consider the role played by their polymeric forms. Studies with copper(II) tetraphenylporphyrintetrasulphonate (tpps) show that disaggregation of copper(II) water-soluble porphyrins is strongly influenced by the solvent composition.[5] Thus the addition of polar organic solvents, *e.g.* alcohols, *NN*-dimethylformamide (dmf), or dimethyl sulphoxide (dmso), favours the formation of monomeric species. It may be anticipated that the addition of polar organic solvents to the aqueous solutions of [Co^{II}(tpps)] may result not only in the disaggregation of the polymeric species, but also in participation of these solvent molecules into the axial interactions which are thought to play an essential role in the oxygenation process. The degree of axial interaction involved may be monitored by the spectra observed. These are different depending on whether Co^{II} is five-co-ordinate (type A), six-co-ordinate (type B), or has no specific axial interactions (type C). The first two types are those most commonly encountered, but all three species may be present simultaneously and in comparable amounts. The possible presence of these types of signal, together with the signal arising from the oxygenated complex, may lead to quite complicated spectra.

As regards the structure of the cobalt–oxygen complex, it is now generally agreed that the system can be written as $[Co^{III}(O_2)]^{2+}$ (see, for example, refs. 6—10),

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[1] F. A. Walker, *J. Amer. Chem. Soc.*, 1970, **92**, 4235.
[2] F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **95**, 1150.
[3] F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **95**, 1154.
[4] D. V. Stynes, A. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, 1973, **95**, 1142.
[5] J. A. De Bolfo, T. D. Smith, J. F. Boas, and J. R. Pilbrow, *J.C.S. Dalton*, 1975, 1523.
[6] B. S. Tovrog and R. S. Drago, *J. Amer. Chem. Soc.*, 1975, **97**, 673.
[7] B. M. Hoffman, T. Szymanski, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 673.
[8] D. Getz, E. Melamud, B. L. Silver, and Z. Dori, *J. Amer. Chem. Soc.*, 1975, **97**, 3846.
[9] J. B. Raynor, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 867.
[10] A. Dedieu and A. Veillard, *Theor. Chim. Acta*, 1975, **36**, 231.

although much of the discussion does not take into account the possibility of a Co–O–O angle <180°. This is despite the *X*-ray results of Rodley and Robinson [11] on [Co(acacen)(O_2)] where the Co–O–O angle was found to be 126° [acacen = *NN'*-ethylenebis(acetylacetoniminato)]. If the bond is bent, it may be expected that the e.s.r. spectra of these oxygenated complexes will show effects arising from non-coincidence of the g and A tensors. Apart from the work of Chien and Dickinson,[12] none of the previous e.s.r. studies (*e.g.* ref. 13) have allowed for this possibility. The present paper examines the relation between g and A tensors in the cobalt porphyrin–oxygen complex. A very valuable discussion of the issues surrounding oxygenation and the degree of delocalisation of the unpaired electron in oxygenated complexes is given by Ochiai [14] who draws attention to the misuse of simplified molecular-orbital pictures in relation to electron delocalisation. We go further and suggest that any models of oxygen binding which have no provision for a bent-bond arrangement are likely to be of very little value in improving our understanding.

EXPERIMENTAL

Tetraphenylporphyrin (tpp) and its tetrasulphonated derivative (tpps) were prepared by a modification of the methods described in the literature.[15] In the present investigation [Co^{II}(tpps)] was prepared as follows. An aqueous solution of the porphyrin (1.0 g) was converted into the tetrasodium salt form by addition of sodium hydroxide. To this solution was added an aqueous solution of cobalt(II) acetate (0.3 g) and the reaction mixture was heated for 1 h. Most of the water was removed to allow precipitation of the cobalt(II) chelate which was purified by recrystallisation from ethanol–water (Found: C, 42.8; H, 3.5; N, 5.45; S, 10.3. Calc. for $C_{44}H_{28}CoN_4Na_4O_{12}S_4\cdot 8H_2O$: C, 43.05; H, 3.25; N, 5.55; S, 10.4%).

X-Band e.s.r. measurements were made at room temperature and 77 K using a Varian E12 e.s.r. spectrometer.

RESULTS AND DISCUSSION

Solutions of Co^{II} and tpps (tetrasodium salt) in pure water did not give rise to an e.s.r. signal at room temperature or 77 K. However, the progressive addition of *NN*-dimethylformamide (dmf) to the solution prior to freezing resulted in the e.s.r. signals shown in Figure 1. The spectra are due to both the monomeric form of the cobalt(II) porphyrin and to its complex with molecular oxygen. Prolonged exposure to air prior to freezing resulted in a diminution of the signals due to the monomeric forms of the cobalt(II) porphyrins. The signals from the oxygenated complex are the group of closely spaced lines between 0.305 and 0.332 T. The other lines observed arise from the monomeric form of [Co^{II}(tpps)].

Monomeric [Co^{II}(tpps)].—The e.s.r. spectrum due to monomeric [Co^{II}(tpps)] may be interpreted on the basis of the usual spin Hamiltonian (1) for axial symmetry, where $S = \frac{1}{2}$ and $I = \frac{7}{2}$.

$$\mathscr{H} = \beta[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (1)$$

Computer-simulated spectra were obtained using the methods referred to previously [16] and the spin-Hamiltonian parameters determined by comparison between experiment and theory are listed in Table 1. In order to obtain a satisfactory fit in the perpendicular or low-field region, it was necessary to introduce the variation (2) of the linewidth

$$\sigma = a + bm \qquad (2)$$

in the xy plane where, typically, $a = 1.5$ mT and $b = 0.3$ mT, and m is the nuclear quantum number ($I, I - 1 \ldots -I$). Such dependence of σ on m is usually attributed to motional effects.

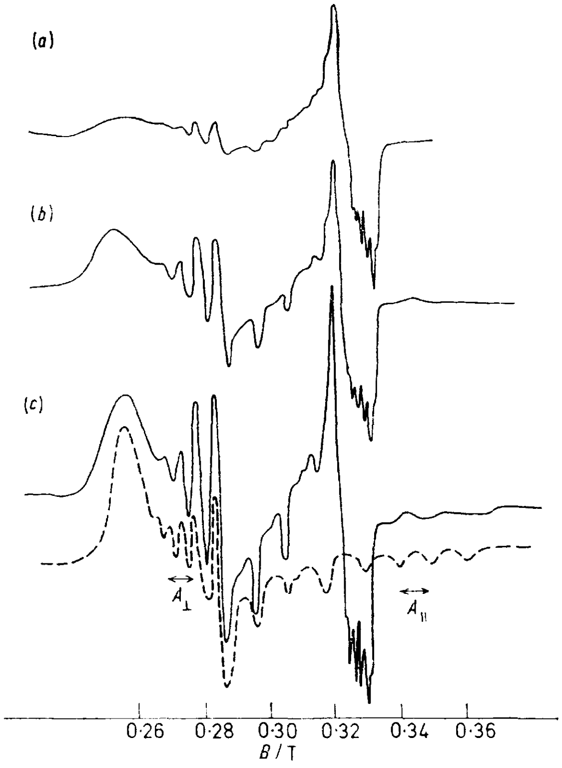

FIGURE 1 E.s.r. spectra at 77 K of aqueous solutions of [Co^{II}(tpps)] prepared in air and containing various amounts of dmf: (*a*) 12, (*b*) 25, and (*c*) 75% v/v. The broken line is the computer-simulated spectrum of the non-oxygenated complex with the parameters given in Table 1. Microwave frequency, 9 080 MHz. The signals at *ca.* 0.325 T are due to oxygenated complexes

The spectrum of the monomeric form of [Co^{II}(tpps)] observed here is described as type B and is thought to

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[11] G. A. Rodley and W. T. Robinson, *Nature*, 1972, **235**, 438.

[12] J. C. W. Chien and L. C. Dickinson, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 2783.

[13] B. M. Hoffman, D. L. Liemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.

[14] Ei. Ochiai, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3375.

[15] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.

[16] J. A. De Bolfo, T. D. Smith, J. F. Boas, and J. R. Pilbrow, *J.C.S. Faraday II*, 1976, 481.

arise from a six-co-ordinate state.[16] Oxygenation probably occurs according to reaction (3). The effect

$$[\mathrm{Co^{II}(tpps)}]\cdot2\mathrm{dmf} + \mathrm{O_2} \rightleftharpoons [\mathrm{Co^{III}(tpps)}]\cdot\mathrm{dmf}\cdot\mathrm{O_2}^- + \mathrm{dmf} \quad (3)$$

of various additions of dimethyl sulphoxide (dmso) on the e.s.r. spectra of an aqueous solution of $[\mathrm{Co^{II}(tpps)}]$ at 77 K is shown in Figure 2. Here, in contrast to the results in Figure 1, the relative intensity of the signal due to the oxygen complex is smaller than that due to the monomeric form of the metalloporphyrin which is characterised in this case by a type A e.s.r. spectrum.[16] The appropriate magnetic parameters are listed in Table 1. There is, in addition, a sharp signal at dmso concentrations of *ca.* 5% which appears to be similar to the line at $g = 1.984$ reported by Rollman and Chan,[17] and which may be due to an intermediate species which disappears on further oxygenation. There is insufficient evidence to enable further characterisation of this spectrum. Oxygenation in dmso solutions may be represented as in equation (4).

TABLE 1

E.s.r. data (10^{-4} cm^{-1}) for monomeric $[\mathrm{Co^{II}(tpps)}]$

System	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$
dmf	2.040 ±0.002	2.410 ±0.002	95 ± 2	43 ± 2
dmso	2.05 ±0.02	2.31 ±0.03	95 ± 2	0 ± 2
EtOH	2.05 ±0.01	2.36 ±0.01	90 ± 5	45 ± 5
dmf + pyridine		2.225 ±0.005		52 ± 2
dmf + imidazole	2.04 ±0.01	2.30 ±0.01	⩽80	<10

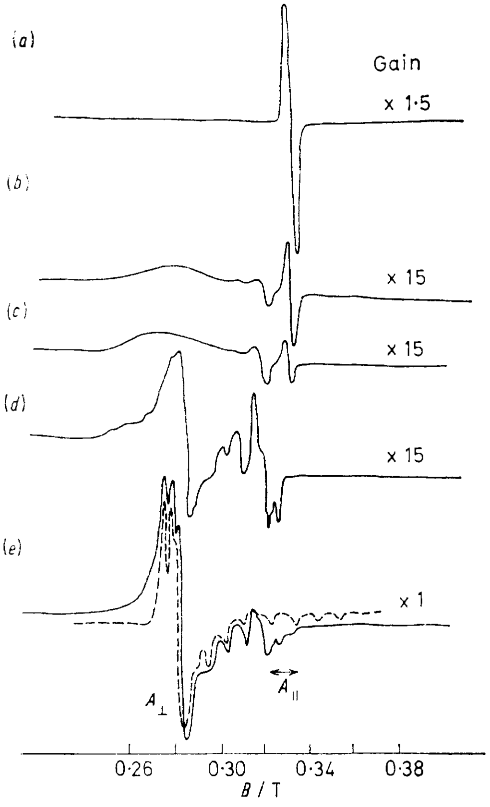

FIGURE 2 E.s.r. spectra at 77 K of aqueous solutions of $[\mathrm{Co^{II}}$-(tpps)] prepared in air and containing various amounts of dmso: (*a*) 5, (*b*) 10, (*c*) 25, (*d*) 50, and (*e*) 75% v/v. For other details see Figure 1

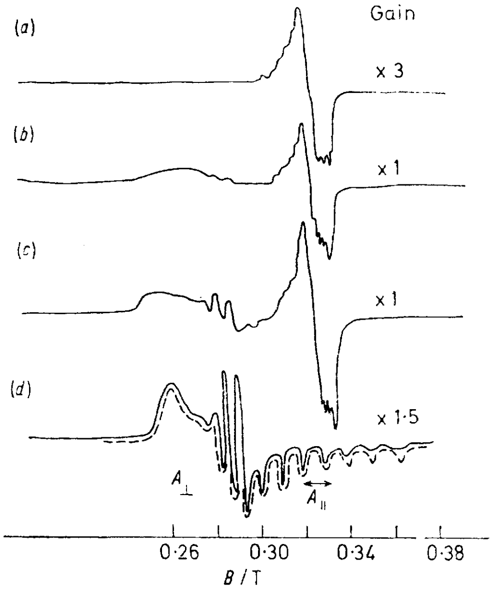

FIGURE 3 E.s.r. spectra at 77 K of aqueous solutions of $[\mathrm{Co^{II}(tpps)}]$ prepared in air and containing various amounts of ethanol: (*a*) 10, (*b*) 25, (*c*) 30, and (*d*) 50%. For other details see Figure 1

$$[\mathrm{Co^{II}(tpps)}]\cdot\mathrm{dmso} + \mathrm{O_2} \rightleftharpoons [\mathrm{Co^{III}(tpps)}]\cdot\mathrm{O_2}^- + \mathrm{dmso} \quad (4)$$

E.s.r. spectra of aqueous solutions of $[\mathrm{Co^{II}(tpps)}]$ containing various amounts of ethanol are shown in Figure 3. Thus when 10% v/v ethanol was present a relatively weak signal due to the cobalt(II)–tpps–oxygen complex was observed. On addition of larger amounts of ethanol a type B e.s.r. signal due to the monomeric form of the metalloporphyrin was observed, and at 50% v/v ethanol this was the only signal present. The appropriate magnetic parameters are listed in Table 1.

When acetone or acetonitrile was added to the aqueous solutions of $[\mathrm{Co^{II}(tpps)}]$ prior to freezing, only relatively weak signals due to monomeric $[\mathrm{Co^{II}(tpps)}]$ (a type B spectrum) and to the metalloporphyrin–oxygen complex were observed even when the amounts of these solvents were as high as 50% v/v. However, the e.s.r. spectrum of the oxygen complex is the same as that observed in the other solvent systems. The addition of these two solvents does not effect a disaggregation of the metalloporphyrin to any great extent, so that oxygenation of the chelate complex is limited.

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[17] L. D. Rollman and S. I. Chan, *Inorg. Chem.*, 1971, **10**, 1973.

The addition of 2,4,7-trinitrofluorenone, which has been shown to influence the e.s.r. spectrum of cobalt(II) mesoporphyrin IX dimethyl ester,[18] had little effect on the e.s.r. spectra at 77 K of [Co^{II}(tpps)] dissolved in pure water or water–ethanol mixtures. The addition of organic bases which are capable of co-ordination to the out-of-plane positions influenced the e.s.r. spectrum of monomeric [Co^{III}(tpps)]. Clear evidence for such co-ordination of the organic base is shown by the e.s.r. spectrum at 77 K obtained after addition of 5% v/v of pyridine to an aqueous solution containing 75% v/v of dmf (Figure 4). Thus the perpendicular region of the spectrum due to [Co^{II}(tpps)] was changed markedly, although the signal due to the oxygen complex was still the same as that in the absence of pyridine. On standing in air the signal due to [Co^{II}(tpps)] and that due to its complex diminished in intensity. Figure 4 shows that the addition of imidazole to a dmf solution of [Co^{II}(tpps)] containing 25% v/v of water caused a marked change in the e.s.r. spectrum at 77 K. In Figure 4(*a*), because of overlap with the oxygen signal, only the perpendicular part of the non-oxygenated cobalt spectrum is simulated. This signal may be described as type A.[16] The signal due to the oxygenated form was unaltered. The spectra in Figure 4 were not changed by further additions of pyridine or imidazole.

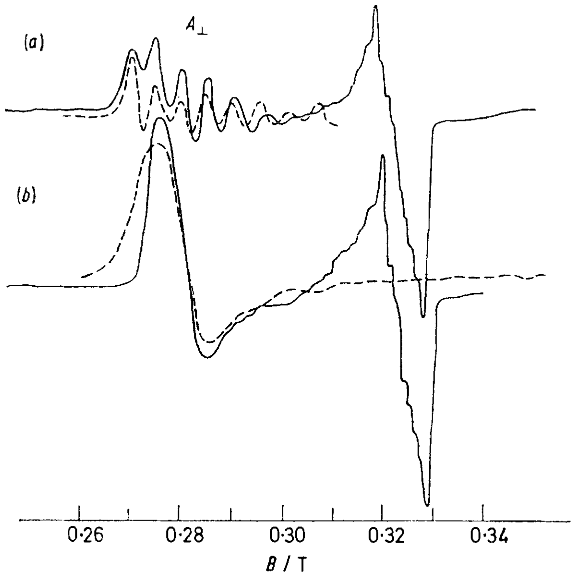

FIGURE 4 E.s.r. spectra at 77 K of aqueous solutions of [Co^{II}(tpps)] prepared in air and containing (*a*) 75% v/v dmf and 5% v/v pyridine, (*b*) 75% v/v dmf and 0.1 mol dm^{-3} with respect to imidazole. For other details see Figure 1

During the course of the investigation it was noticed that the e.s.r. signal due to the oxygenated form of the cobalt porphyrin became relatively more intense when the samples of metalloporphyrin had been stored for some time. Indeed a sample of solid [Co^{II}(tpps)] which had been stored for *ca.* 6 months and was subsequently dissolved in water containing 50% v/v of dmso gave an e.s.r. signal at 77 K exclusively due to the molecular oxygen complex of the metalloporphyrin. The same e.s.r. spectrum at 77 K was obtained by dissolving the same sample in water containing only 5% v/v of dmso (Figure 5). Dissolving the solid in water containing 50% v/v of dmf again gave the e.s.r. spectrum of only the cobalt(II)–tpps–oxygen complex, the intensity of which was diminished by prolonged passage of nitrogen. However, when the solid metalloporphyrin was dissolved in ethanol, only a weak signal due to monomeric [Co^{II}(tpps)] was observed, suggesting that the [Co^{II}(tpps)]–oxygen complex reacts with this solvent to give some cobalt(III) tpps species. It is concluded therefore that storage in air results in complete conversion of [Co^{II}(tpps)] into its molecular oxygen complex in the solid state. The e.s.r. signal due to the solid itself, although similar, was less well resolved and was also consistent with this view. Pumping the solid for 24 h at a reduced pressure of 10^{-6} mmHg did not affect the signal due to the oxygenated form of the metalloporphyrin in the solid state.*

Detailed discussion of the g and A values for the various types of non-oxygenated cobalt(II) complexes has been given elsewhere.[16,19,20] It should, however, be remarked in passing that a scrutiny of the expressions given by Pilbrow and Winfield [20] for $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$ for the low-spin cobalt(II) ion in a complex such as the cobalt(II) porphyrin indicates that simple relations do

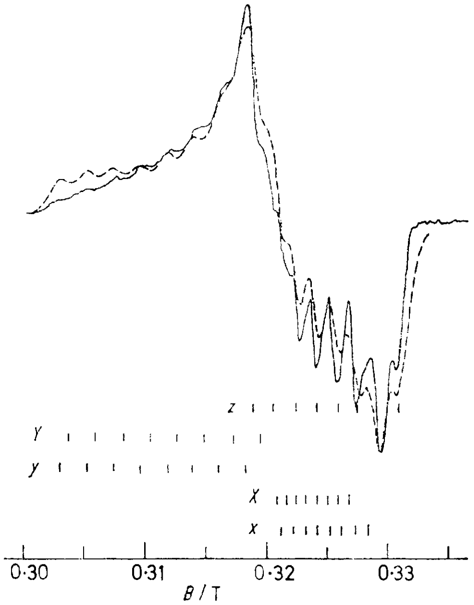

FIGURE 5 E.s.r. spectra at 77 K of the oxygenated form of [Co^{II}(tpps)]: (——) in an aqueous solution containing 75% v/v dmf at 77 K; (— — —) computer-simulated spectrum using the parameters given in Table 2. Stick spectra are labelled according to Figure 6. Microwave frequency, 9 143 MHz

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[18] H. A. O. Hill, P. J. Sadler, and R. J. P. Williams, *J.C.S. Dalton*, 1973, 1663.

[19] L. M. Englehardt and M. Green, *J.C.S. Dalton*, 1972, 724.

[20] J. R. Pilbrow and M. E. Winfield, *Mol. Phys.*, 1973, **25**, 1073.

not exist between the *s*-electron density on the cobalt nucleus (as expressed by the core-polarisation contribution to the hyperfine interaction), the covalency of the complex, and the measured values of $A_{\parallel}$ and $A_{\perp}$. It is evident that the contributions from the excited states are significant and cannot be determined from the e.s.r. data alone.

Oxygenated [Co^{II}(tpps)].—First, attempts were made to simulate the spectra of the cobalt(II)–tpps–oxygen complex assuming that both g and A tensors had rhombic symmetry and coincident axes. Although a general agreement between computed and experimental spectra was achieved, detailed agreement was not achieved in the regions between 0.320 and 0.324 T and in the region between 0.3295 and 0.3320 T. Since the results of Chien and Dickinson [12] for single crystals of oxygenated cobalt myoglobin provided evidence for a non-coincidence between the g axes for O_2^- and the hyperfine axes for its interaction with the cobalt nucleus, we then allowed for such an effect in the case of [Co^{II}(tpps)]. Thus the spin Hamiltonian, which allows for a complex with monoclinic local symmetry, and where the z axis is chosen to be the common two-fold axis, is [20] (5). A non-coincidence of $\alpha°$ between the g and A axes is allowed for in the xy plane (Figure 6).

$$\mathscr{H} = \beta[g_xS_xB_x + g_yS_yB_y + g_zS_zB_z] + A_XS_XI_X + A_YS_YI_Y + A_ZS_ZI_Z \quad (5)$$

With this monoclinic model, more satisfactory agreement was obtained between experimental and computer-simulated spectra with $\alpha = 15 \pm 2°$ than with the orthorhombic model referred to above. The results (Table 2) can be interpreted in terms of two different models of oxygen binding (Figure 7). Figure 7(*a*) shows a model with a Co–O–O angle of 105° while that in 7(*b*) has an angle of 165°. Both models are plausible in terms of the e.s.r. results and involve exactly the same spin Hamiltonian but whose axes are differently arranged in the molecule. The choice of axes is not altogether unique. We can, for instance, interchange the values of g_x and g_y, reverse the direction of the z axis, and put $\alpha = 75°$. Such a rearrangement leads, as it must, to identical computed spectra and identical models.

TABLE 2

Spin-Hamiltonian parameters for oxygenated [Co^{II}(tpps)]

$g_x = 1.998 \pm 0.002$
$g_y = 2.088 \pm 0.002$
$g_z = 1.997 \pm 0.002$
$A_X = (8.0 \pm 0.5) \times 10^{-4}\ cm^{-1}$
$A_Y = (22.0 \pm 0.5) \times 10^{-4}\ cm^{-1}$
$A_Z = (16.0 \pm 0.5) \times 10^{-4}\ cm^{-1}$
$\alpha = 15 \pm 2°$
Linewidths $\sigma_x = 1.2$ mT
$\sigma_y = 1.2$ mT
$\sigma_z = 1.0$ mT

The spin-Hamiltonian axes within the molecule cannot be defined uniquely without recourse to a single-crystal study, which is not feasible in this case. It is not possible to determine whether the Co–O–O plane contains one opposite pair of N atoms in the porphyrin plane, or whether it bisects N–Co–N bonds. It should be noted that, although the parameters given in Table 2 produced the best fit to the experimental spectrum, certain features were not completely accurately reproduced. These occur in just the troublesome areas noted above in relation to an attempt to fit the spectrum with an orthorhombic model, although the earlier model gave a far worse fit. It is possible that the z and Z

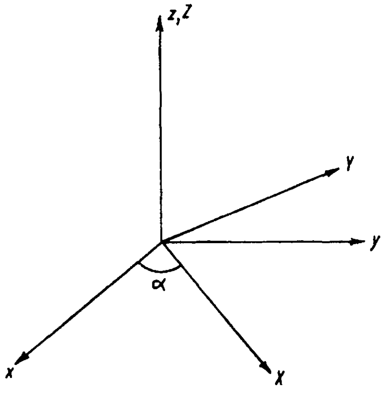

FIGURE 6 Principal axes for g and A values in monoclinic symmetry

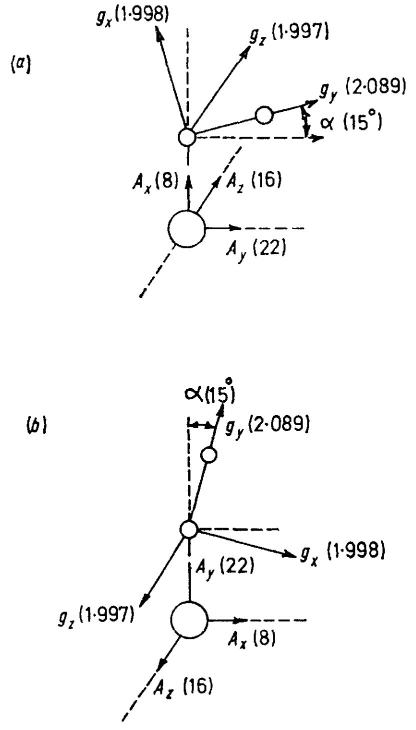

FIGURE 7 Arrangement of principal axes for two possible models of the cobalt(II)–tpps–oxygen complex: (*a*) Co–O–O angle 105°, YZ plane is the porphyrin plane; (*b*) Co–O–O angle 165°, XZ plane is the porphyrin plane. A values are in 10^{-4} cm^{-1}; the orientation of the in-plane axes in relation to the four atoms is not known

axes, assumed parallel here, do not coincide exactly, and that the overall magnetic symmetry is actually triclinic. Existing computer programs are limited to a monoclinic model and one non-coincidence angle so that we cannot test this point further. Small changes of linewidth in the xy plane had a marked effect on the resolution of the spectra arising from the x orientation.

In the next sections we shall consider the implication of these results for molecular arrangements in the oxygenated complex and review the results of other workers.

Models for the Cobalt(II)*-tpps-Oxygen Complex.*—It is generally accepted that the oxygenated complex may be considered as $[Co^{III}(tpps)]\cdot O_2^-$, where the electron has been largely transferred from a d_{z^2} orbital of Co^{II} to the oxygen which becomes essentially O_2^-. Unless the structure of the oxygenated complex is known, very little can be said about the character of the orbital containing the unpaired electron or about the degree of localisation on the oxygen.

In considering possible molecular models for the cobalt–oxygen complex, it is reasonable to suppose that the g values will be determined by spin–orbit coupling of the ground state of O_2^- to its excited states, and that the principal g axes will lie along and perpendicular to the O–O bond.[12,21] The similarity to O_2^- trapped in alkali halides is incomplete because the g shifts in that case are much larger than in typical oxygenated complexes.[21] With respect to the hyperfine interaction, we have been guided by the results of Chien and Dickinson [12] which showed that the cobalt hyperfine axes lie in the heme plane and normal to it. Thus we assume that the corresponding axes lie in the porphyrin plane and normal to it. Since the Co–O–O angle is likely to be $< 180°$, a non-coincidence between the g and A axes should be expected.

Conclusions.—The e.s.r. spectra of $[Co^{II}(tpps)]$ show similar characteristics to other cobalt systems such as phthalocyanines.[16] Oxygenation produces characteristic e.s.r. spectra which are explained in terms of an unpaired electron localised on the oxygen and a bent-bond model. In view of the results of Rodley and Robinson [11] and Chien and Dickinson,[12] we conclude that a possible model for our results is that shown in Figure 7(*a*) where the Co–O–O angle is 105°. This is intermediate between the two models proposed by Griffith.[22] Because the theoretical position is somewhat unclear, we await better calculations before attempting to define our model more completely. Above all, a combination of both *X*-ray and e.s.r. on oxygenated crystals will be needed to provide the essential information to clarify the position.

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[21] W. Kanzig and M. H. Cohen, *Phys. Rev. Letters*, 1959, **3**, 509.

[22] J. S. Griffith, *Proc. Roy. Soc.*, 1956, **A235**, 23.