A Study of Substituent and Base Effects on the Electron Spin Resonance Spectra of the Molecular Oxygen Adducts of Cobalt(II) Porphyrin Chelates

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A detailed e.s.r. study of low-spin cobalt(II) porphyrins with formula [CoLL'(O_2)] has shown that the spin-Hamiltonian parameters are hardly sensitive to changes in L (*meso*-substituted porphyrin) and L' (nitrogenous base). Only where L is protoporphyrin IX dimethyl ester are clearly discerned effects observed upon changing substituents on L'.

Since the iron(II) chelate of protoporphyrin IX† plays a fundamental role in dioxygen binding by the oxygen-transport and storage proteins in mammalian physiology, studies of the oxygenation of iron(II) porphyrins have acquired a particular importance. For investigating certain factors which influence the addition of molecular oxygen to the metal centre of the porphyrin chelate it is advantageous to study the corresponding cobalt(II) chelate. This is particularly true when e.s.r. spectroscopy is being used, since the odd-electron system with its hyperfine interactions is helpful in deducing electronic and structural features of the oxygen adduct.

A number of aspects in the oxygenation of cobalt(II) porphyrins such as axial-ligand interactions,[1] stereochemistry of low-spin porphyrins,[2-4] e.s.r. and spectroscopic properties of the molecular oxygen adducts,[5-7] thermodynamics,[8,9] and kinetics [10] of oxygen binding to cobalt(II) porphyrins have recently been reviewed.[11] Generally, the 1 : 1 complexes of the form [CoLL'(O_2)] (L = *meso*-substituted porphyrin, L' = nitrogenous base) are stable at low temperatures and are formed rapidly. The formation constants of the adducts in polar aprotic solvents are much higher than in toluene solution. Molecular oxygen adduct formation by the cobalt(II) chelate of protoporphyrin IX dimethyl ester in the presence of 2-(methylthio)ethanol or mercaptoethanol in toluene has been described,[12] while more recently the e.s.r. spectra of the corresponding adduct of 5,10,15,20-tetraphenylporphyrinatocobalt(II) in the presence of thiophen has been reported.[13] In the present investigation, the effect has been studied of varying the substituent group, particularly at the methene carbon position of the porphyrin ring, and the obligatory base on the parameters associated with the e.s.r. spectra of the molecular oxygen adduct of cobalt(II) porphyrin chelates. Such variations enable one to see how the electronic structure of the cobalt–dioxygen centre may be affected by changes in the cyclic structure and axial ligand bonding to the central cobalt atom.

RESULTS AND DISCUSSION

Dry molecular oxygen was passed into toluene solutions containing pyridine (1% v/v) and the porphyrin complex {5,10,15,20-tetraphenylporphyrinatocobalt(II), [Co(tpp)]; -tetra(*p*-methoxyphenyl)porphyrinatocobalt(II), [Co(tmopp)]; -tetra(*p*-tolyl)porphyrinatocobalt(II), [Co(ttp)]; -tetra(*p*-fluorophenyl)porphyrinatocobalt(II), [Co(tfpp)]; -tetra(*p*-chlorophenyl)porphyrinatocobalt(II), [Co(tcpp)]; -tetra(*p*-cyanophenyl)-porphyrinatocobalt(II), [Co(tcypp)]; -tetra(*p*-nitrophenyl)porphyrinatocobalt(II), [Co(tnpp)]; -tetra(*p*-carboxyphenyl)porphyrinatocobalt(II), [Co(tcopp)]; or -tetra(*p*-methoxycarbonylphenyl)porphyrinatocobalt(II), [Co(tmcpp)]} and the e.s.r. spectra of the frozen solution recorded at 110 K. A typical result is shown in Figure 1.

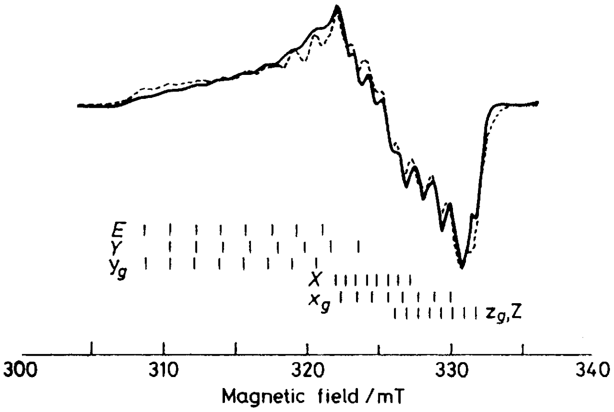

Figure 1 E.s.r. spectrum (——) at 110 K and 9.149 GHz due to the dioxygen adduct of [Co(tmopp)] in toluene solution containing pyridine (1% v/v). Computer-simulated spectrum (— — —) is based on parameters given by first entry in Table 1. Stick spectra labelled according to Figure 2 except for *E* which is spectrum due to orientation corresponding to slight angular anomaly at low field

To determine the effect of the solvent on the e.s.r. spectra of the molecular oxygen adducts, spectra of chloroform solutions containing pyridine (1% v/v) and one of [Co(tmopp)], [Co(tpp)], [Co(tfpp)], [Co(tcpp)], and [Co(tcypp)] were recorded. A similar set of chloroform solutions was prepared but containing picoline (4-methylpyridine) (1% v/v) to observe the effect on the e.s.r. spectra of a change in the base. The effects of a wider variation of base on the e.s.r. spectra of the molecular oxygen adduct of [Co(tpp)] in chloroform solution were evaluated by the introduction of 1% (v/v) amounts of one of pyridine, 2-methylpyridine, 4-methylpyridine, 2,4-

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† Protoporphyrin IX = 3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropionic acid.

dimethylpyridine, 2,6-dimethylpyridine and 2,4,6-trimethylpyridine. The effects of a similar range of bases on the e.s.r. spectra of the corresponding adduct of the cobalt(II) chelate of protoporphyrin IX dimethyl ester in chloroform solution at 77 K were also observed.

In order to account for the features of the observed e.s.r. spectra due to oxygenated porphyrins it is necessary to consider a spin Hamiltonian[14] (1) which allows the g and A tensors to be non-coincident in the XY plane[14] (see also Figure 2). The effective spin $S = \frac{1}{2}$ while $I = \frac{7}{2}$ for the hyperfine interaction (h.f.i.) with the cobalt

$$\mathscr{H} = \beta \sum_{i = x_g, y_g, z_g} g_i B_i S_i + \sum_{I = X, Y, Z} A_I S_I I_I \qquad (1)$$

nucleus. It should be noted that we use x_g, y_g, and z_g to denote principal g axes, in contrast to previous papers,[15,16] so as to reserve use of x, y, and z for a co-ordinate system fixed at the cobalt site. We retain X, Y, Z for use with the computer simulation program where z_g and Z remain common.[14-18] In Tables 1—5, *e.g.* A_X is written as $A_z(X)$ since z and X are common. The symmetry model in Figure 2 corresponds ideally to C_s where the common two-fold magnetic axis for g and A is Z or x.

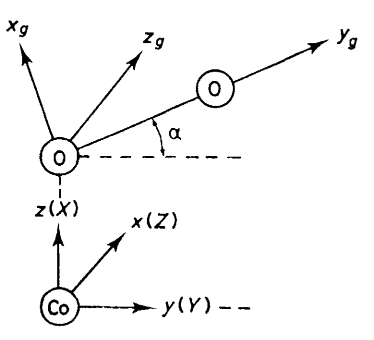

FIGURE 2 Simplified molecular structure of cobalt(II)–oxygen adducts; principal g axes are x_g, y_g, and z_g; principal A axes are $X(z)$, $Y(y)$, and $Z(x)$. Symmetry is C_s

Since the symmetry is lower than orthorhombic, h.f. constants cannot be directly read from the experimental spectrum of a powder or frozen solution. The reason is that A values do not maximise or minimise along g directions except where there is a common axis (Z or x). The essential results of the computer simulations of the experimental e.s.r. spectra are summarised in Tables 1—5.

Previous studies have shown that various substituents on the *meso*-phenyl groups[19-23] or on the pyrrole positions[24] affect a number of properties concerned with electron transfer from the metal centre. Porphyrin ^{15}N n.m.r. chemical shifts of complexes formed by 5,10,15,20-tetraphenylporphyrinatozinc(II) with substituted pyridines may be correlated with electron-donating ability of the pyridine substituent.[25] The present results, outlined in Tables 1—3, indicate that the change in the magnetic parameters associated with the dioxygen adducts of various cobalt(II) porphyrins in toluene or chloroform containing pyridine or 2-methylpyridine are little affected by in-plane substituents on the *meso*-phenyl group.

Variation in the nature of the nitrogenous base does not greatly affect the magnetic parameters, as can be seen from Table 4. However, as shown in Table 5, the spin-Hamiltonian parameters associated with the molecular oxygen adduct formed by cobalt(II) protoporphyrin IX in the presence of various bases are sensitive to the substituents on the axial base, such that the introduction of a methyl group into the 2- or 4-positions of the pyridine base causes a marked change in the value of α.

To explain the e.s.r. properties of Co–O_2 adducts, attention has been drawn to the possible formation of an O_2^- radical ion resulting from almost complete electron transfer from Co^{II} to molecular oxygen, or from spin pairing resulting in the formation of a σ bond. Participation of a cobalt d_{xz} orbital (Figure 2) through direct overlap with the unpaired electron in a π* orbital is considered most likely to be responsible for the occurrence of cobalt(II) hyperfine structure in the O_2^- model.[26] Spin-polarisation mechanisms which imply indirect polarisation of d-electron orbitals on cobalt by the unpaired electron on O_2 have been suggested as a result of a number of inconsistencies resulting from h.f. analyses based upon the O_2^- picture.[27-29] The implied spin pairing of an oxygen π* orbital and a cobalt d orbital to form a σ bond has been discussed in other contexts qualitatively[7,30] and is supported by molecular-orbital calculations.[31,32] A summary of a simple model which takes into account both direct and indirect contributions to hyperfine structure is given in the Appendix.

In Tables 1—5 it can be seen that, with a few exceptions, the values of $g + h$ all lie in the range *ca.* 12—14.5, implying that α''^2 is *ca.* 0.06—0.07. The $f + h$ values are positive, with one exception, for a range of porphyrins in toluene containing pyridine (Table 1), but otherwise largely negative. [For definitions of $(g + h)$, $(f + h)$, α''^2, *etc.* see Appendix.] The data in Table 1 suggest that the proposed model, with a judicious mixture of direct and indirect hyperfine coupling, accounts reasonably well for a range of porphyrins in toluene solution with 1% (v/v) pyridine. Within the limits of error, the $f + h$ values are all very similar. On the other hand, for some of the same porphyrins in chloroform solution, the values of $f + h$ are all negative, except in one case where it is barely positive (Table 2), and in chloroform containing 2-methylpyridine (1% v/v) the values are all either negative or zero. In these cases, one must conclude that the hyperfine coupling is due to direct interactions and the orbital ψ_2 must be supplemented, as allowed by the assumed C_s symmetry, with admixtures of d_{z^2} and d_{yz} orbitals. The base-variation results in Tables 4 and 5 show a more pronounced set of negative values of $f + h$, again consistent with more direct mixing into ψ_2.

In conclusion, we recognise that this simple analysis does not directly take into account specific involvement of ligands, bases, or substituent groups. A more com-

TABLE 1

Magnetic parameters for the dioxygen adducts of various cobalt(II) porphyrins in toluene solution containing pyridine (1% v/v) *

Cobalt(II) porphyrin	g_y	g_x	g_z	α/°	$A_y(Y)$	$A_z(X)$	$A_x(Z)$	a_x	a_y	a_z	$f+h$	$g+h$
					10^{-4} cm^{-1}							
[Co(tmopp)]	2.079	2.006	1.989	27	18.1	6.8	7.5	3.8	−6.8	3.0	0.9	12.4
[Co(ttp)]	2.079	2.008	1.991	27	18.2	6.7	7.7	3.7	−6.8	3.2	0.6	12.3
[Co(tpp)]	2.075	2.005	1.989	27	17.9	7.7	8.0	3.7	−6.2	2.5	1.4	11.6
[Co(tfpp)]	2.084	2.009	1.993	26	18.3	7.4	7.9	3.8	−6.6	2.8	1.2	12.2
[Co(tcpp)]	2.076	2.007	1.990	27	17.8	7.2	7.8	3.6	−6.4	2.7	1.1	11.7
[Co(tcypp)]	2.081	2.004	1.989	26	20.9	6.8	9.5	3.4	−8.0	4.6	−1.4	13.3
[Co(tnpp)]	2.077	2.007	1.990	27	18.0	7.0	7.7	3.7	−6.6	2.9	0.9	12.0
[Co(tcopp)]	2.076	2.007	1.990	27	17.8	7.3	7.6	3.8	−6.4	2.6	1.4	11.9
[Co(tmcpp)]	2.076	2.007	1.989	27	18.0	7.0	7.2	4.0	−6.8	2.7	1.5	12.6

* Fitting errors: in g values, $< \pm 0.001$; in A values, $\pm 0.5 \times 10^{-4}$ cm^{-1}; in α, ±1°.

TABLE 2

Magnetic parameters for the dioxygen adducts of various cobalt(II) porphyrins in chloroform solution containing pyridine (1% v/v) *

Cobalt(II) porphyrin	g_y	g_x	g_z	α/°	$A_y(Y)$	$A_z(X)$	$A_x(Z)$	a_x	a_y	a_z	$f+h$	$g+h$
					10^{-4} cm^{-1}							
[Co(tmopp)]	2.086	2.005	1.989	28	21.4	6.8	9.5	3.4	−7.9	4.6	−1.4	13.2
[Co(tpp)]	2.081	2.008	1.992	26	20.2	6.0	9.0	3.2	−8.0	4.7	−1.8	13.1
[Co(tfpp)]	2.082	2.009	1.993	26	18.7	6.8	7.9	3.7	−7.1	3.3	0.5	12.6
[Co(tcpp)]	2.081	2.003	1.989	26	21.1	7.3	10.3	2.9	−7.7	4.9	−2.3	12.4
[Co(tcypp)]	2.081	2.004	1.989	26	20.9	6.8	9.5	3.4	−7.9	4.6	−1.4	13.2

* Fitting errors as in Table 1.

TABLE 3

Magnetic parameters for the dioxygen adducts of cobalt(II) porphyrins in chloroform solution containing 2-methylpyridine (1% v/v) *

Cobalt(II) porphyrin	g_y	g_x	g_z	α/°	$A_y(Y)$	$A_z(X)$	$A_x(Z)$	a_x	a_y	a_z	$f+h$	$g+h$
					10^{-4} cm^{-1}							
[Co(tmopp)]	2.077	1.998	1.982	26	21.2	7.2	9.8	3.4	−8.0	4.5	−1.3	13.3
[Co(tpp)]	2.081	2.008	1.989	26	20.0	6.1	7.6	4.1	−8.3	4.1	0.0	14.5
[Co(tcpp)]	2.082	2.003	1.986	27	20.8	6.7	8.9	3.7	−8.2	4.4	−0.8	13.9
[Co(tcypp)]	2.075	1.997	1.982	26	19.9	7.3	9.4	3.3	−7.2	3.9	−0.7	12.3

* Fitting errors as in Table 1.

TABLE 4

Magnetic parameters of the molecular oxygen adduct of [Co(tpp)] in chloroform solution containing various bases (1% v/v) *

Base	g_x	g_y	g_z	α/°	$A_y(Y)$	$A_z(X)$	$A_x(Z)$	a_x	a_y	a_z	$f+h$	$g+h$
					10^{-4} cm^{-1}							
Pyridine	2.081	2.008	1.992	26	20.2	6.0	9.0	3.2	−8.0	4.7	−1.8	13.1
2-Methylpyridine	2.081	2.008	1.989	27	20.0	6.1	7.6	4.1	−8.3	4.1	0	14.5
4-Methylpyridine	2.081	2.008	1.989	27	20.0	6.1	7.6	4.1	−8.3	4.1	0	14.5
2,4-Dimethylpyridine	2.081	2.011	1.984	26	21.5	6.6	10.5	2.9	−8.1	5.3	−2.8	12.9
2,6-Dimethylpyridine	2.082	2.011	1.984	27	20.0	6.5	11.0	2.0	−7.0	5.0	−3.5	10.5
2,4,6-Trimethylpyridine	2.081	2.011	1.983	26	20.0	6.6	11.0	2.0	−7.0	4.9	−3.4	10.5

* Fitting errors as in Table 1.

TABLE 5

Magnetic parameters due to the molecular oxygen adduct of cobalt(II) protoporphyrin IX dimethyl ester in chloroform containing various bases (1% v/v) *

Base	g_y	g_x	g_z	α/°	$A_y(Y)$	$A_z(X)$	$A_x(Z)$	a_x	a_y	a_z	$f+h$	$g+h$
					10^{-4} cm^{-1}							
Pyridine	2.082	2.008	1.990	26	20.2	6.0	8.5	3.6	−8.1	4.6	−1.2	13.7
2-Methylpyridine	2.082	2.008	1.993	25	19.7	6.0	9.0	3.1	−7.6	4.6	−1.8	12.5
4-Methylpyridine	2.081	2.007	1.993	25	20.0	6.0	9.0	3.2	−8.0	4.7	−1.8	13.1
2,4-Dimethylpyridine	2.082	2.005	1.985	30	23.0	7.6	11.0	3.4	−8.6	5.3	−2.2	14.0
2,6-Dimethylpyridine	2.082	2.011	1.984	27	20.0	6.5	11.5	1.7	−6.8	5.2	−4.1	9.9
2,4,6-Trimethylpyridine	2.075	2.006	1.997	27	21.0	6.5	11.9	1.7	−7.4	5.6	−4.6	0.6

* Fitting errors as in Table 1.

prehensive theory which does not seem possible at present is required to take such effects into account.

EXPERIMENTAL

Samples of the *p*-substituted *meso*-tetraphenylporphyrins were prepared by the procedure of Adler *et al.*,[33] while the *p*-nitro- and *p*-carboxy-derivatives were prepared as outlined by Thomas and Martell.[34] Esterification of the tetra-*p*-carboxyphenyl was carried out as described in the literature.[35] Conversion into the cobalt(II) chelates was performed using methods outlined by Buchler.[36] Protoporphyrin IX was obtained from the Sigma Chemical Company and converted into the cobalt(II) chelates. E.s.r. spectra were obtained using a Varian E12 spectrometer operating at *ca.* 9.15 GHz. Low temperatures were achieved using a Varian liquid-nitrogen accessory.

APPENDIX

The hyperfine analysis was performed as follows. It is supposed that all the h.f. constants are negative and that they must first be corrected for the direct dipolar interaction. For this we use the values [27] given in (A1), based

$$A_{\text{dip.}}(O_2) = (\overset{x}{-0.5},\ \overset{y}{-0.5},\ \overset{z}{1.0}) \times 10^{-4}\ \text{cm}^{-1} \quad \text{(A1)}$$

upon co-ordinates for [Co(bzacacen)(O$_2$)][bzacacen = *N,N'*-ethylenebis(benzoylacetoneimine)] from an *X*-ray study.[37]

The electronic model is based, in simpler treatments, on a three-electron model according to the scheme shown in Figure 3, where ψ_1 and ψ_2 are given by equations (A2) and (A3). The antibonding orbital ψ_3 is not filled. Since d_{z^2} and d_{yz} transform according to the same representation of C_s (where x is normal to the mirror plane), then we cannot separate their individual contributions. Of course, under C_s symmetry, the *d*-orbital description in Figure 3 is only a first approximation. A good deal of orbital mixing must take place, *e.g.* $d_{x^2-y^2}$ might be involved in ψ_1. Tovrog *et al.*[27] in connection with their back-bonding argument argue that, in ψ_2, α'' should be small; ψ_2 is the orbital favoured by Hoffman *et al.*[26] in an O$_2^-$ picture. In equation (A3) $\pi^*(x_g)$ is the oxygen π^* orbital participating in σ-bond formation whereas π^* is the unpaired electron orbital; α', α'', γ, β, and ε are all as defined by Tovrog *et al.*[27] The parameter α''' is introduced by us to allow for d_{yz} mixing in ψ_1.

$$\psi_1 = \alpha' d_{z^2} + \alpha''' d_{yz} + \gamma 4s + \beta\pi^*\ (x_g) \quad \text{(A2)}$$

$$\psi_2 = \varepsilon\pi^* + \alpha'' d_{xz} \quad \text{(A3)}$$

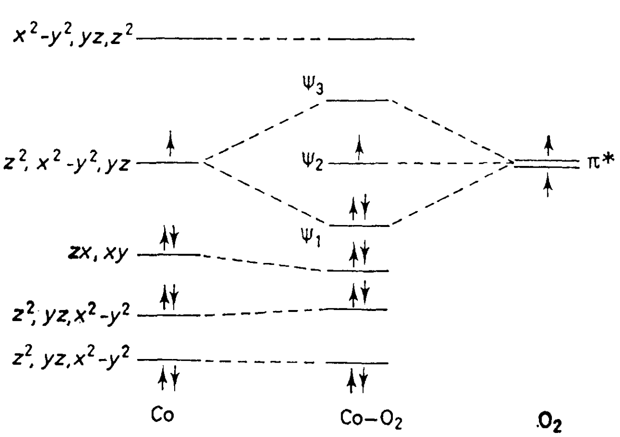

FIGURE 3 Simplified molecular-orbital diagram for Co–O$_2$ complexes. The low C_s symmetry will permit *d*-orbital mixing: $d_{x^2-y^2}$ mixing into ψ_1 is neglected and d_{xy} mixing into ψ_2 is not included. Spin polarisation of two electrons in ψ_1 arises from electrostatic repulsion (exchange effect) between them and the unpaired electron in ψ_2. The lowest pair of *d* orbitals cannot be degenerate under C_s symmetry

Indirect hyperfine coupling *via* spin polarisation is presumed to occur as a result of the polarisation of the spin-paired electrons in ψ_1 by the unpaired electron in ψ_2 by means of the electrostatic repulsion, e^2/r_{12}, in such a way that a net negative spin unpairing occurs at the cobalt. It is considered to be an indirect effect because it does not involve a direct overlap of ψ_1 and the *d* orbitals of ψ_2.[38] This does not, of itself, alter the spin density of the unpaired electron. Direct hyperfine coupling, as a result of the mixing of d_{xz} in equation (A3), can easily be understood.

To complete the analysis, equations (A4)—(A6) are needed. In this model, *f*, *g*, and *h* are all positive. Here,

$$\left.\begin{aligned} A_x - \langle A\rangle = a_x &= \tfrac{2}{7}(f + g + 2h) \\ A_y - \langle A\rangle = a_y &= \tfrac{2}{7}(f - 2g - h) \\ A_z - \langle A\rangle = a_z &= \tfrac{2}{7}(-2f + g - h) \end{aligned}\right\} \quad \text{(A4)}$$

$$\langle A\rangle = \tfrac{1}{3}(A_x + A_y + A_z) \quad \text{(A5)}$$

$$\begin{matrix} z & y & x \end{matrix}$$

$$\left.\begin{aligned} f &= P\rho_O U_{\text{Co-O}}\alpha'^2 \\ g &= P\alpha''^2 \\ h &= P\rho_O U_{\text{Co-O}}\alpha'''^2 \end{aligned}\right\} \quad \text{(A6)}$$

$P = 2\beta g_n\beta_n\langle r^{-3}\rangle_{3d} \approx 0.02$ cm^{-1} for cobalt(II) compounds, ρ_O is the spin density on the ' middle ' oxygen, and $U_{\text{Co-O}}$ is an empirical spin-polarisation constant. In equations (A6) *f* and *h* represent indirect interactions involving spin polarisation of d_{z^2} and d_{yx} respectively, while *g* represents the direct interaction due to d_{xz}. Tables 1—5 give not only the spin-Hamiltonian parameters but a_x, a_y, a_z, $f + h$, and $g + h$ where we have used the relations (A7).

$$\left.\begin{aligned} f + h &= \tfrac{7}{6}(a_x - a_z) \\ g + h &= \tfrac{7}{6}(a_x - a_y) \end{aligned}\right\} \quad \text{(A7)}$$

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