Nuclear Magnetic Resonance Study of Metal Complexes of the ' Capped ' Porphyrins

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The cobalt(II) derivatives of the ' capped ' porphyrins CP2, CP3, and CP2(N) were studied by ^1H n.m.r. spectroscopy. From an analysis of the paramagnetic shifts in the n.m.r. spectrum the cap–porphyrin separations were deduced and the overall conformation examined. It was found that the cavity size, as implied by the cap–porphyrin separation, increased in the order CoCP3, CoCP2, then CoCP2(N). The cap proton resonance linewidths were consistent with this ordering. This order correlates with the observed O_2 affinity of the iron(II) capped porphyrins. A comparison of the solvent effects on the n.m.r. spectrum of CoCP2 and CoCP3 indicates binding of solvent on the cavity side in CoCP3. We also report a comparison of CP2(N) and its zinc derivative with CP2 and ZnCP2 which shows close similarity in their behaviour.

Iron(II) ' capped ' porphyrin complexes are able to bind oxygen reversibly.[1] This property seems to be dependent on the cavity between the porphyrin plane and the capping benzenoid ring. The capped porphyrins CP2 and CP3 (see Figure 1) form an interesting contrast since the iron(II) complex of CP3 has a lower oxygen affinity than the complex of CP2.[2] This is in spite of the presence of an additional methylene group in the aliphatic chain between the cap and the porphyrin, which should allow CP3 to have a larger cavity and so reduce steric interactions between the cap and bound oxygen. Previous n.m.r. studies of the diamagnetic zinc complexes,[3] ZnCP2 and ZnCP3, were unable to show clearly any difference in the cavity size. In these complexes the cap–porphyrin separation was deduced from the size of the porphyrin ring-current shift on the capping benzenoid proton. A precise comparison was complicated by the presence of additional perturbations on the chemical shift of the cap proton, such as the magnetic anisotropy and electric-field shifts from the adjacent ester groups, which could not be properly determined. In order to examine the capped porphyrins further we studied the cobalt(II) complexes, CoCP, of CP2 and CP3, making use of the paramagnetic shift and relaxation effects observed in these complexes to obtain structural information. In addition we studied the capped porphyrins CP2(N), ZnCP2(N), and CoCP2(N), which differ from CP2 in having naphthyl rather than phenyl *meso*-substituents (Figure 1).

Experimental

The free base and metal-substituted capped porphyrins were prepared following procedures published elsewhere.[4] The deuteriated solvents were obtained from Merck, Sharp, and Dohme Ltd. and used directly. Approximately 0.005M solutions of the porphyrin in the appropriate deuteriated solvent were used. N.m.r. spectra were acquired at 270 and 300 MHz using Bruker spectrometers with Oxford Instrument Company superconducting magnets. Typical acquisition conditions for the CoCP were: a sweep width of 12 kHz over 16 K data points collecting 256 transients. Tetramethylsilane was used as an internal n.m.r. standard.

Results

A spectrum of CP2(N) in [^{2}H]chloroform at 27 °C indicating the resonance assignments is shown in Figure 2. The assignments were based on spin-decoupling and NOE experiments.

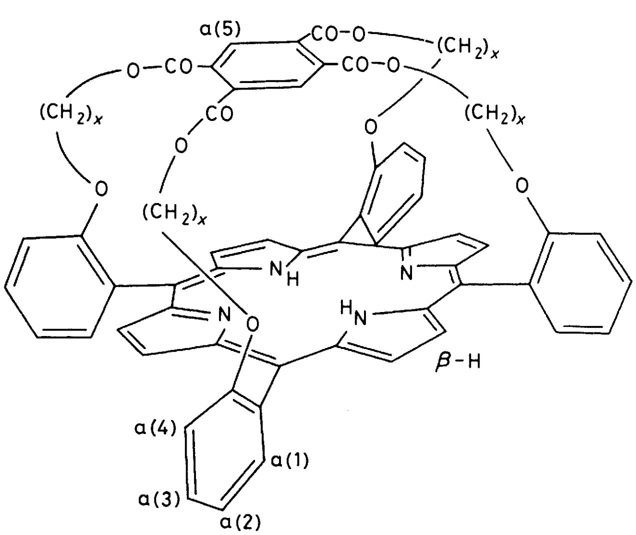

Figure 1. Capped porphyrin molecule and labelling scheme: (a) CP2, $x = 2$; (b) CP3, $x = 3$; (c) CP2(N), $x = 2$, *meso*-phenyl group replaced by a naphthyl group. $(CH_2)_x$ denoted by w(*i*)

The solvent dependence of the assigned resonances in CP2(N) and ZnCP2(N) is shown in Table 1. A comparison of the solvent shifts, defined as $\delta_{CDCl_3} - \delta_{solvent}$, for CP2 and CP2(N), together with those for ZnCP2 and ZnCP2(N), is given in Table 2.

A spectrum of CoCP2 in [^{2}H]chloroform at 27 °C is shown in Figure 3. The resolution of the aromatic resonances, labelled a(2)—a(4), was sufficient to see the *J* coupling. Resonance assignments were based on spin-decoupling experiments and the resonance linewidths. We took the chemical shifts of the resonances in the zinc-substituted capped porphyrins [3] as the diamagnetic reference in order to derive the paramagnetic shifts shown in Tables 3—5 for CoCP2, CoCP2(N), and CoCP3 respectively. Resonance linewidths for CoCP2 and CoCP3 are presented in Table 6.

Discussion

CP2(N) and ZnCP2(N).—The spectra of CP2(N) and ZnCP2(N) are similar to those of CP2 and ZnCP2 (compare

Table 1. Solvent dependence of the chemical shifts in CP2(N) and ZnCP2(N)

	$CDCl_3$			$C_6D_5CD_3$			[$^2H_6$]DMSO		
Proton	CP2(N)	ZnCP2(N)	D	CP2(N)	ZnCP2(N)	D	CP2(N)	ZnCP2(N)	D
β-H(1)	8.45	8.56	0.11	8.36	8.53	0.17	8.33	8.24	−0.09
β-H(2)	8.36	8.49	0.13	8.29	8.45	0.16	8.24	8.21	−0.03
a	7.82	7.86	0.04	7.35	7.36	0.01	8.10	8.06	−0.04
b	8.26	8.27	0.01	7.95	7.99	0.04	8.41	8.34	−0.07
c	7.96	7.97	0.01	7.74	7.79	0.05	8.07	8.02	−0.05
d	7.26	7.24	−0.02				7.26	7.24	−0.02
e	6.74	6.72	−0.02	6.51	6.58	0.07	6.82	6.79	−0.03
f	6.22	6.07	−0.15	6.35	6.47	0.12	6.03	6.12	0.09
a(5)	5.75	5.66	−0.09	5.95	5.93	−0.02	5.82	5.81	−0.01
(1)	4.62	4.66	0.04	4.12	4.08	−0.04	4.60	4.56	−0.04
(2)	4.48	4.54	0.06				4.45	4.42	−0.03
(3)		4.49	0.01	3.91	3.87	−0.04	4.27	4.24	−0.03
(4)	4.03	4.04	0.01	3.54	3.55	0.01	4.06	4.03	−0.03
[NH]	−2.75			−2.24			−2.78		

Table 2. Solvent shifts for the free-base and zinc-substituted ' capped ' porphyrins

	[$^2H_6$]DMSO		[$^2H_8$]Toluene		[$^2H_6$]DMSO		[$^2H_8$]Toluene	
Proton	CP2	CP2(N)	CP2	CP2(N)	ZnCP2	ZnCP2(N)	ZnCP2	ZnCP2(N)
β-H(1)	0.11	0.12	0.01	0.09	0.29	0.32	−0.04	0.03
β-H(2)	0.10	0.12	−0.05	0.07	0.29	0.29	−0.07	0.04
a(4),a	−0.19	−0.28	0.44	0.47	−0.12	−0.20	0.45	0.49
a(3),b	−0.08	−0.15	0.28	0.31	0.01	−0.07	0.27	0.28
a(5)	−0.09	−0.06	−0.26	−0.21	−0.10	−0.16	−0.28	−0.28
w(1)	0.06	0.02	0.54	0.50	0.10	0.10	0.53	0.58
w(4)	0.01	−0.02	0.49	0.49	0.01	0.01	0.46	0.49
NH	0.06	0.04	−0.43	−0.50				

Table 3. Paramagnetic shifts in CoCP2 (0.005M in $CDCl_3$) at 27 °C

Resonance	δ(CoCP2) (p.p.m.)	Δ_p (p.p.m.)	Observed $\Delta_p{}^i/\Delta_p{}^{a(1)}$	Calculated $\Delta_{pc}{}^i/\Delta_{pc}{}^{a(1)}$	Δ_p(Co-*o*-CH_3TPP) (p.p.m.)
β-H(1)	17.03	−8.15	1.45	1.88	−7.00
β-H(2)	16.28	−7.44	1.32	1.88	
a(1)	13.44	−5.64	1.00	1.00	−5.00
a(2)	9.82	−2.44	0.43	0.46	−2.15
a(3)	10.14	−2.35	0.42	0.41	−2.03
a(4)	10.44	−2.88	0.51	0.46	−2.15
a(5)	−14.34	19.76			

Table 4. Paramagnetic shifts in CoCP2(N) (0.005M in $CDCl_3$) at 27 °C

Resonance	δ[CoCP2(N)] (p.p.m.)	Δ_p (p.p.m.)	Observed $\Delta_p{}^i/\Delta_p{}^b$	Calculated $\Delta_{pc}{}^i/\Delta_{pc}{}^b$
β-H(1)	16.66	−8.10	3.33	4.60
β-H(2)	15.53	−7.04	2.90	
a	10.55	−2.70	1.11	1.13
b	10.70	−2.43	1.00	1.00
c	9.41	−1.44	0.39	0.71
d	7.38	−0.14	0.06	0.20
e	4.29	2.43	−1.00	−0.33
f	9.41	−3.34	1.37	1.21
a(5)	−13.74	19.40		

Table 5. Paramagnetic shifts in CoCP3 (0.005M in $CDCl_3$) at 27 °C

Resonance	δ(CoCP3) (p.p.m.)	Δ_p (p.p.m.)	Observed $\Delta_p{}^i/\Delta_p{}^{a(1)}$	Calculated $\Delta_{pc}{}^i/\Delta_{pc}{}^{a(1)}$
β-H(1)	17.38	−8.46	2.02	1.88
β-H(2)	15.32	−6.59	1.58	
a(1)	11.79	−4.18	1.00	1.00
a(2)	9.09	−1.82	0.44	0.46
a(3)	9.75	−2.05	0.49	0.41
a(4)	10.20	−2.76	0.66	0.46
a(5)	−16.35	21.90		
w(5)	2.12	−0.20		
w(6)	1.33	0.51		

Table 1 with Table 1 of ref. 3), and, as with CP2, the addition of Zn only produces small perturbations to resonance chemical shifts.

Three effects can give rise to a metallation shift. First, the binding of zinc will alter the electronic structure and hence the shielding properties of the porphyrin ring. Second, a conformational change may be induced on binding zinc. Third, the presence of the zinc might alter the solvation of the porphyrin and thus the solvent contribution to the chemical shift. Since zinc is a σ-acceptor, it will tend to reduce the magnitude of the ring current by indirectly reducing the π-electron density in the porphyrin. On the other hand metal complexation enhances the symmetry of the porphyrin, which increases the ring current. Empirically it is found that zinc-substituted porphyrins have a reduced ring-current shift.[5] The

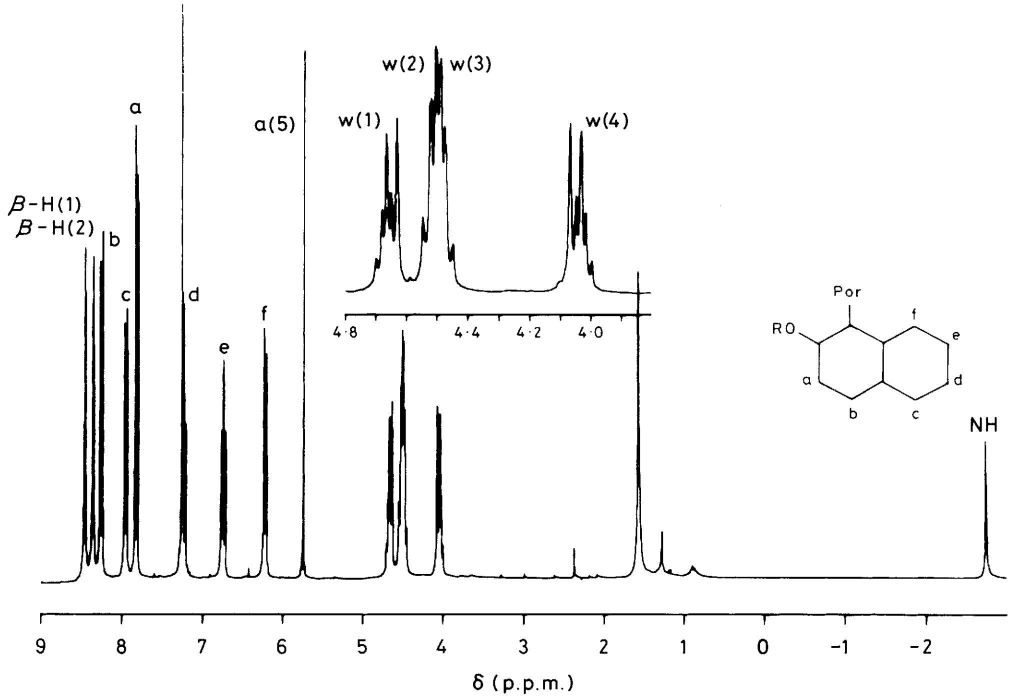

Figure 2. 300 MHz ^{1}H n.m.r. spectrum of CP2(N) (0.005M in CDCl$_3$) at 27 °C indicating the resonance assignments

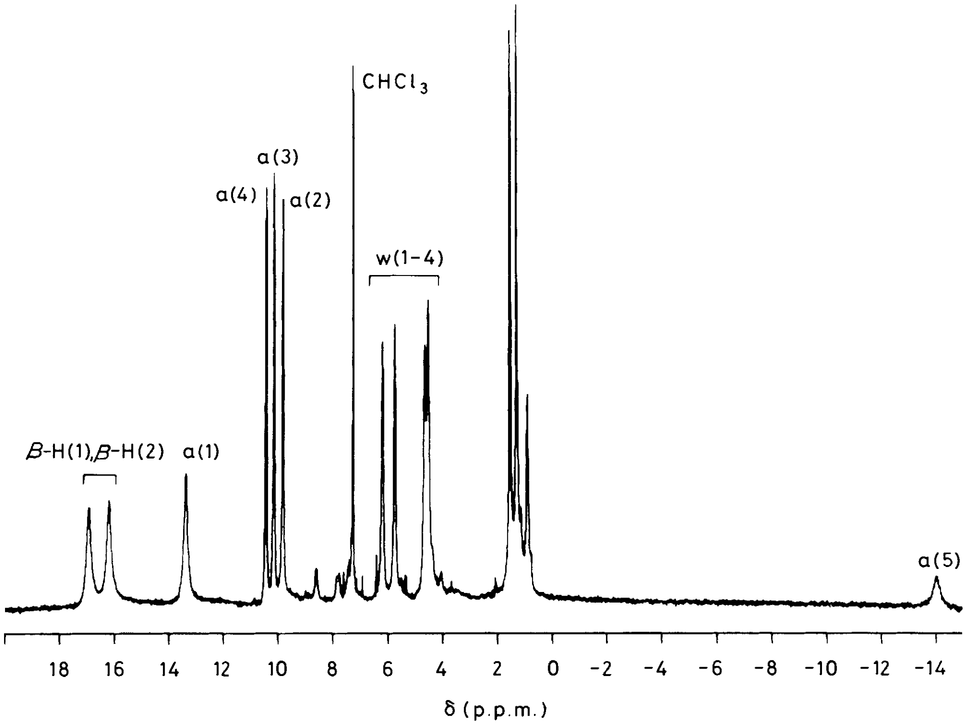

Figure 3. 300 MHz ^{1}H n.m.r. spectrum of CoCP2 (0.005M in CDCl$_3$) at 27 °C indicating the resonance assignments

crystal structure of CP2 at −150 °C shows a puckered porphyrin plane [6a] while zinc-substituted porphyrins, which are normally pentaco-ordinate, have an out-of-plane zinc in a tetrahedral environment.[7] Thus, although we might expect some averaging at room temperature of the puckering observed at low temperature, it seems likely that the binding of zinc could cause a substantial change in the porphinato core which in turn would be propagated to the rest of the molecule, as is seen in the crystal structure of Fe^{III} CP2Cl.[6b] As can be seen in the spectrum of ZnCP2(N) a trace of water is present in the [^{2}H]chloroform solution providing a ligand to give a pentaco-ordinate zinc while in [^{2}H$_6$]DMSO the DMSO itself is a ligand. The precise co-ordination of the zinc in [^{2}H$_8$]-toluene is uncertain.

Table 6. Resonance linewidths for CoCP2 and CoCP3 (0.005M in $CDCl_3$) at 27 °C

Resonance	CoCP2	CoCP3
β-H	62.3 Hz	66.9 Hz
a(5)	90.2 Hz (1.448) [a]	138.0 Hz (2.063) [a]
a(1)	50.0 Hz (0.80) [a]	77.0 Hz (1.15) [a]
Cap-porphyrin separation	4.3 Å	3.95 Å

[a] Linewidth ratio with respect to the β-H.

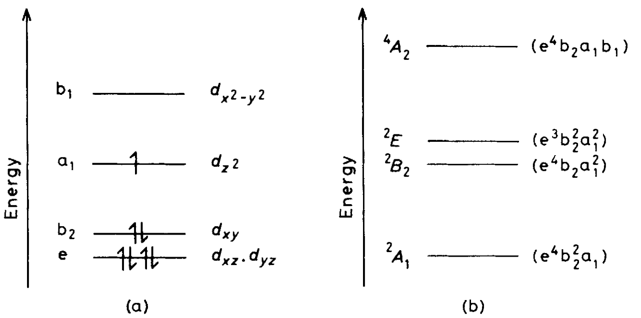

Figure 4. Energy diagrams for planar low-spin cobalt(II) with C_{4v} symmetry: (a) orbital energies; (b) state energies

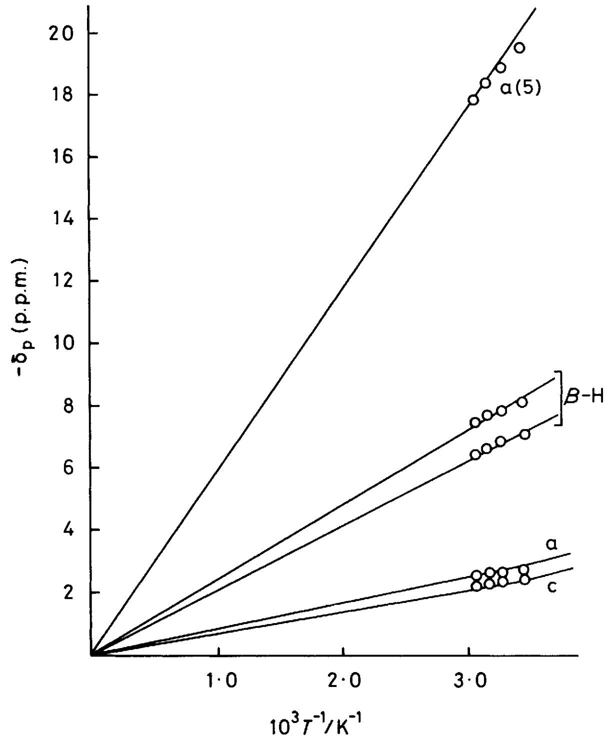

Figure 5. Curie plot for the paramagnetic shifts in the ^1H n.m.r. spectrum of CoCP2(N) in $CDCl_3$. For a(5), δ_p has been plotted

It can be seen from Table 1 that all the metallation shifts are small. Furthermore, the actual shifts are closely similar to those seen for CP2. The similar metallation shifts in [^2H]-chloroform and [$^2H_8$]toluene would suggest that changes in the solvent shift are unimportant. In addition the small magnitude of the metallation shifts implies that no conformational changes occur. The small shifts seen in [^2H]chloroform and [$^2H_8$]toluene are consistent with an increased ring-current magnitude. From this we infer a slightly greater distortion, and thus lower symmetry, in the free base than in the metallated complexes. However, in contrast to these solvents the metallation shifts in [$^2H_6$]DMSO are inconsistent with this simple view since the β-H and a(5) resonance shifts imply opposite changes in the magnitude of the ring current in this solvent. This is probably because of a specific solvent effect. However, the point to be stressed is that the changes in the n.m.r. spectrum caused by the co-ordination of zinc are minor. Thus despite the large changes in structure one might expect on binding zinc, none is observed with CP2(N).

An inspection of the solvent shifts in Table 2 reinforces the impression of the similarity between CP2 and CP2(N). Indeed the solvent shifts for the free base and zinc-substituted capped porphyrins are almost identical within experimental error. It is thus clear that the increased steric restraint to rotation about the *meso*-substituent–porphyrin bond, due to replacement of phenyl by naphthyl, has little effect.

CoCP.—Paradoxically, in view of their complexity, n.m.r. spectra of the cobalt(II) complexes of the capped porphyrins are easier to analyse quantitatively than are the spectra of the diamagnetic free base and zinc-substituted porphyrins. This is because the paramagnetic effect dominates the n.m.r. spectrum and can be readily analysed, provided that diamagnetic controls are available, as they are in the present case.

Paramagnetic Shifts.—Paramagnetic shifts result from the nuclear–electron spin interaction.[8] They can be separated into two terms, the pseudocontact or dipolar shift, and the Fermi contact term. These terms correspond to a through-space and through-bond mechanism respectively. Geometrical information can be derived from the pseudocontact shift, while the Fermi contact shift can be used to investigate the metal–ligand bonding. Cobalt(II), d^7, is low spin in its porphyrin complexes.[9] To a first approximation the capped porphyrins have C_{4v} symmetry; the appropriate orbital and state energies [10] are shown in Figure 4. The electronic ground state is $^2A_1$ corresponding to the unpaired electron in the d_{z^2} orbital. Since we expect the d_{z^2} orbital to be only weakly interacting with the porphyrin orbitals the paramagnetic shift will be largely pseudocontact in character. This was found to be the case for the cobalt(II) porphyrins Co(o-CH_3TPP) and Co(p-CH_3-TPP) [10] and was shown to be the case here for the CoCP complexes by the linear nature and zero intercepts of the Curie plot (Figure 5). In the case of axial symmetry the pseudocontact shift may be calculated using equation (1). The conditions under which this expression is valid have been detailed.[11]

$$\Delta pc = \frac{\beta^2S(S+1)}{9kT} \cdot (g_{\parallel}{}^2 - g_{\perp}{}^2) \cdot \frac{(1 - 3\cos^2\theta)}{R^3} \quad (1)$$

$g_{\parallel}$ and $g_{\perp}$ are the g value parallel and perpendicular to the symmetry axis, R is the distance between the proton and the metal, and θ is the angle the metal–proton vector makes with the symmetry axis. E.s.r. can be used to characterise the cobalt(II) electronic state and to determine the g-tensor anisotropy. Although frozen chloroform solutions of CoCP2 and CoCP3 have similar e.s.r. spectra at 77 K these were quite different from that of Co^{II}TPP and we were unable to analyse them directly. In view of this the pseudocontact shifts were calculated using a g-tensor anisotropy derived from the paramagnetic shift on the *para*-proton of the *meso*-phenyl substituent. This is equivalent to expressing the results in terms of pseudocontact shift ratios on two protons *i* and *j* [equation (2)].

$$\frac{\Delta_{pc}^{\,i}}{\Delta_{pc}^{\,j}} = \left[\frac{3\cos^2\theta_i - 1}{3\cos^2\theta_j - 1}\right]\left(\frac{r_j}{r_i}\right)^3 \qquad (2)$$

The magnitude of the *g*-tensor anisotropy (and the resonance linewidths as determined by the electronic relaxation time, T_{1e}) can be related to the difference in energy [10] between the $^2A_1$ and ^2E energy states. This energy difference in turn can be related to axial solvation of the cobalt(II), and to low-symmetry perturbations on the cobalt(II) environment. Thus as the energy difference increases the magnetic anisotropy, $g_{\parallel}^2 - g_{\perp}^2$, decreases leading to smaller pseudocontact shifts, and at the same time the electronic relaxation becomes less efficient, T_{1e} increases, and the resonance linewidth gets larger. Calculated pseudocontact shift ratios for the CoCP complexes are given in Tables 3—5. The geometric factors used to calculate the shift ratios, and paramagnetic shifts given for Co(*o*-CH_3TPP), were taken from refs. 10 and 12.

Initially we consider the paramagnetic shifts for CoCP2 and CoCP2(N) on the basis of the known structure of CP2 because earlier studies with zinc have shown that metal complexation does not greatly perturb the porphyrins from their free-base structure, implying a degree of structural rigidity. It can be seen from Table 3 that the observed and calculated shift ratios are in good agreement for the *meso*-phenyl protons in CoCP2. We can interpret the non-equivalence of the paramagnetic shift on a(2) and a(4) in terms of a slight displacement of the cobalt from the plane passing through a(3). This is supported by the mean shift being within 2% of the calculated value. A comparison of the *meso*-phenyl shifts in CoCP2 and Co(*o*-CH_3TPP) reveals: (i) a greater magnetic anisotropy in CoCP2 and (ii) a greater contact shift on the pyrrole β-H in CoCP2 with a differential effect on β-H(1) and β-H(2).

From the paramagnetic shift of the *meso*-phenyl protons we can estimate the magnetic anisotropy to be −9.3 for CoCP2 given it is −8.2 for Co(*o*-CH_3TPP).[10] A straightforward use of the magnetic anisotropy ($g_{\parallel}^2 - g_{\perp}^2$) of −9.3 in the pseudocontact shift, equation (1), and the observed paramagnetic shift on the cap proton a(5), gives a geometric factor of 1.23×10^{28} which corresponds to a cap–porphyrin separation of 3.65 Å. The increase in magnetic anisotropy for CoCP2 is supported by the following analysis based on the procedure of McGarvey.[13] An increase in the magnetic anisotropy requires a decrease in the energy separation between ^2E and $^2A_1$ and thereby $g_{\perp}$ increases and $g_{\parallel}$ decreases. In order to lower the energy of the ^2E state relative to $^2A_1$ it is necessary that a low-symmetry perturbation be present, C_{2v} or lower, so that the d_{z^2} and the $d_{x^2-y^2}$ orbitals belong to the same irreducible representation allowing mixing and thus a lowering of the energy of $a_1(d_{z^2})$. The presence of such a low-symmetry perturbation is supported by the upfield contact shifts seen on the pyrrole β-H. We obtain the contact shifts on these resonances by subtracting the calculated pseudocontact shift found using the above magnetic anisotropy from the observed paramagnetic shift. This gives β-H(1)Δ_c +2.4 p.p.m. and β-H(2)Δ_c +3.2 p.p.m. With a true $^2A_1$ ground state only σ-delocalisation is possible and thus a downfield shift is expected. On the other hand a pertubation of C_{2v} symmetry causes the non-bonding porphyrin π-orbitals (a_{2u}, b_{2u}, in D_{4h}) to transform to a_1 allowing unpaired electron spin density localised in the cobalt d_{z^2} orbital to be delocalised onto a ligand π-orbital. Positive spin density would then give an upfield shift.

Turning to the paramagnetic shifts in CoCP2(N) given in Table 4, we calculate the magnetic anisotropy to be −9.8 based on the shift for b and its geometric factor of 1.48×10^{27}. This implies a cap–porphyrin separation of 3.85 Å. The contact shifts on the pyrrole β-H resonances are β-H(1), Δ_c +3.0 p.p.m., and β-H(2), Δ_c +4.1 p.p.m. We observe both a larger contact shift on β-H and a greater differential effect. Furthermore the magnetic anisotropy in CoCP2(N) is bigger than in CoCP2. All these observations are consistent with the naphthyl substituent causing a stronger low symmetry perturbation than the phenyl group. Although, on the whole, the observed and calculated shift ratios agree, a notable exception is the resonance e. An inspection of a Dreiding model shows this proton to be close to the edge of the cobalt dipole shielding cone and it is plausible that a small displacement of the cobalt or the proton could account for the discrepancy. It is therefore likely that disagreement between the calculated and observed pseudocontact shifts reflect small deviations in the true geometry from the idealised values used.

In contrast to CoCP2 and CoCP2(N) the paramagnetic shifts in CoCP3 are somewhat anomalous (Table 5). The ratio for a(3) is rather high. This in turn implies that the actual geometric factor for a(1) is smaller than the one given in ref. 12; that is, the phenyl group is restricted to being perpendicular to the porphyrin plane with only minor torsional oscillations. However, again we observe that the paramagnetic shifts on a(2) and a(4) are not the same while their mean value is close to that seen for the *meta*-proton in Co(*o*-CH_3TPP), implying a smaller magnetic anisotropy than in CoCP2, yet the differential paramagnetic shift on the pyrrole β-H at 1.9 p.p.m. is the largest of the three capped porphyrins. Above, we noted this correlated with a larger magnetic anisotropy. The behaviour of CoCP3, therefore, does not appear to follow that of the other capped porphyrins. This may be due to the greater flexibility seen for CP3, one consequence of which may be that the zinc-substituted porphyrin is not a good diamagnetic reference for the cobalt complex. The resonance a(3) will be the least affected by any differences in structure which may exist between CoCP3 and ZnCP3. Its magnetic anisotropy of *ca.* −8.5 gives a cap–porphyrin separation of only 3.4 Å. Despite the uncertainty in the size of the magnetic anisotropy, and hence in the cap–porphyrin separation, a clear indication of the aliphatic chain conformation is given by the paramagnetic shifts on the central methylene protons. It is observed that these protons have paramagnetic shifts of opposite sign. This suggests the chain is turned in towards the cavity thereby restricting its size.

Resonance Linewidths.—An additional check on the distances in the CoCP complexes can be made using the resonance linewidths. Providing we have extreme narrowing conditions the dominant contribution to the nuclear spin relaxation will usually be the paramagnetic interaction between the nuclear and electron spin. Under these conditions, and assuming that the dipolar term dominates the nuclear–electron spin interaction together with an axially symmetric *g*-tensor anisotropy, the linewidth, $\Delta\nu_{\frac{1}{2}}$, will be proportional to the inverse sixth power of the proton–electron distance.[11] Consequently, the ratio of the linewidths can be used to gain an indication of the relative distances.

The resonance linewidths provide clearer evidence that the cap–porphyrin separation is smaller in CoCP3 than CoCP2. In order to derive the cap–porphyrin separation we assume the linewidth is determined predominantly *via* relaxation induced by the nuclear–electron spin interaction. Knowing the cobalt–pyrrole β-H distance, 5.3 Å, we can use expression (3)

$$\Delta\nu_{\frac{1}{2}}^{\,i}/\Delta\nu_{\frac{1}{2}}^{\,j} = (r^j/r^i)^6 \qquad (3)$$

to obtain the separations. These are given in Table 6. It can be seen the cap is indeed closer to the porphyrin in CoCP3.

Neglecting the contact contribution to the relaxation overestimates the cap–porphyrin separation, since part of the linewidth will be due to this interaction. Thus if the greater differential contact shift in CoCP3 does reflect a greater contact contribution to the nuclear–electron spin interaction then we would find an even smaller cap–porphyrin separation, accentuating the smaller cavity in CoCP3 than in CoCP2. The anomalous behaviour of CoCP3 is again apparent from the large linewidth of the resonance a(1) which would suggest the phenyl ring is buckled under the porphyrin to give a shorter distance between a(1) and the cobalt. This is not necessarily inconsistent with a smaller geometric factor for a(1) noted above since a buckling deformation will decrease the angular term at the same time as increasing the r^{-3} term. The nett effect on the geometric factor will depend on the precise form of the distortion.

Solvent Effects.—We have observed that ZnCP3 coordinates DMSO leading to an increase in the cap–porphyrin separation while ZnCP2 does not.[3] The solvent dependence of the paramagnetic shifts in the Co^{II} capped porphyrins confirms this. Axial solvation of cobalt(II) [10] will give rise to an interaction between $a_1(d_{z^2})$ and the appropriate solvent molecular orbital thereby raising the energy of a_1. As a consequence the energy separation between the $^2A_1$ and ^2E states increases and $g_\perp$ approaches the spin-only value causing the magnetic anisotropy to decrease. The increased separation between the $^2A_1$ and ^2E states will make electron spin relaxation less efficient, increasing T_{1e}, and so the resonances will broaden. It is observed that for the pyrrole β-H in CoCP3 in [$^2H_6$]-DMSO at 380 K and 270 MHz $\Delta\nu_{\frac{1}{2}}$ was *ca.* 300 Hz while for CoCP2 under similar conditions it is *ca.* 90 Hz. Furthermore, the observed chemical shift of the pyrrole β-H in CoCP2 at 300 K in [$^2H_6$]DMSO was 12.3 p.p.m., significantly upfield of their positions in [^2H]chloroform. Similarly the magnetic anisotropy of CoCP3 is smaller in [$^2H_6$]DMSO than in [^2H]-chloroform. It is also smaller than that of CoCP2 in [$^2H_6$]-DMSO.

These observations are consistent with the axial solvation outlined above. The differing extent to which the resonances are broadened for CoCP2 and CoCP3 reflects the degree of the interaction between the d_{z^2} orbital and the solvent orbital. It is reasonable to suppose that solvent–cobalt interactions will be similar on the non-cap side for both capped porphyrins, since π–π interactions between the cap and porphyrin will have a negligible effect on the non-cap-side solvation. Therefore, the significantly greater broadening of the resonances in CoCP3 is due to cap-side interactions indicating that the cavity size is sufficiently flexible to allow a DMSO molecule at least partial entry into the cavity to allow co-ordination to the cobalt.

Size of Cavity in Capped Porphyrins.—The separation between the proton of the capping benzene ring and the porphyrin plane is taken to be a measure of the relative size of the porphyrin cavity. Previous n.m.r. studies of diamagnetic capped porphyrins were unable to calculate precise values for the cavity size. The data presented in this paper show conclusively that the cavity of CoCP3 is smaller than the cavity of CoCP2.

The distances calculated from the two paramagnetic probe effects are for CoCP2, 4.3 and 3.65 Å, and for CoCP3, 3.95 and 3.4 Å. The differences of 0.65 Å for CoCP2 and 0.55 Å for CoCP3 appear large by crystallographic standards. However, they are distances obtained by analysis from first principles of spectroscopic data and as such the agreement is good. In the crystallographic studies of CP2 and Fe^{III} CP2Cl at −150 °C similar separations of *ca.* 3.9 Å were obtained.[6] The crystal structure for CP3 has not been obtained yet. In any event, it is the relative order of distance that is most useful. According to this the cavity size varies in the order CoCP2(N) > CoCP2 > CoCP3. Exactly the same order as the decrease in the O_2 binding affinity of the Fe^{II} porphyrins. Thus a direct correlation between size of cavity and O_2 affinity is established. A note of caution should be given here. The n.m.r. measurements in this and an earlier report [3] stress the extreme solvent dependency of CoCP3, and to a lesser extent CoCP2. In particular, toluene was found to produce particularly anomalous solvation effects. These have yet to be adequately explained. Measurements of O_2 binding affinities have all been done in toluene at 0 °C.

The increase in aliphatic chain size from $(CH_2)_2$ to $(CH_2)_3$ results in a decrease in cavity size for the reasons suggested earlier; the additional methylene groups fold into the cavity and ' pull ' the capping benzene and porphyrin together. The cavity of CoCP2(N) is apparently slightly larger than that of CoCP2, although the difference is close to the limit of error of the technique. It is encouraging that such agreement follows for two different porphyrins when the magnetic anisotropies and consequently n.m.r. chemical shifts, are so different. The similarity in cavity size for complexes of CP2 and CP2(N) is also suggested by the n.m.r. data for the diamagnetic free base and zinc-substituted complexes.

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