Synthesis of Iron(II) ' C_2-Capped Strapped ' † Porphyrin Complexes and their Reaction with Dioxygen

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The synthesis of potentially quinquedentate ligands based on a C_2-capped porphyrinate ligand, the ' C_2-capped strapped ' ligands, is described where the ' strapping ' groups contain a pyridine function. The iron(II) complexes of the ligands undergo reversible oxygenation at room temperature in toluene solution, and show good stability to autoxidation. Interestingly the products of decomposition are not μ-oxo dimers but are iron(III) species which can be directly reduced back to the active iron(II) form. The affinities of the complexes for dioxygen have been determined. The relatively low affinities of these new complexes are ascribed to inhibition of the motion of the iron(II), which must occur on the binding of O_2. This is due to the locking of the complex in a ' domed ' configuration, enhanced by the strapping group, and to unfavourable steric interactions of the strapping group with the parent porphyrin.

The study of transition metal complexes which will act as reversible carriers of dioxygen has long been a topic of great interest.[1] Work with complexes of iron(II) has been concerned primarily with the use of porphyrin ligands which incorporate some form of steric protection of the dioxygen binding site, such as our 'capped' porphyrin,[2] Collman's 'picket fence' porphyrin,[3] and Traylor's 'cyclophane hemes'.[4] Recently we have reported on the synthesis of some variations of the 'capped' porphyrinate ligand [5] and upon the reaction of the corresponding iron(II) complexes with dioxygen.[6] The steric protection is necessary to inhibit the series of facile irreversible reactions which result in formation of μ-oxo-iron(III) dimer complexes.

Most solution studies of the oxygenation reactions of iron(II) porphyrin complexes have involved the use of an added axial ligand, such as pyridine or 1-methylimidazole, which bind on the unprotected face of the complex. This is necessary to prevent the dimerisation reaction from occurring *via* this unprotected face. A more convenient system is where the axial ligand is covalently linked to the porphyrin superstructure and is thus an integral part of a potentially quinquedentate ligand. Since the axial ligand is held close to the metal ion, the five-co-ordinate complex is favoured and the need for an externally added axial base is removed. A number of complexes are known which employ this strategy, for example, 'tail base' or 'chelated heme',[7] where the base is linked by one covalent bond to the parent porphyrin ligand. More recently, complexes have been reported with bases which employ two covalent bonds, producing a more rigid linkage, such as Battersby's 'double strapped' system [8] or the 'hanging base' porphyrin complex.[9]

The subject of this paper is the preparation of modified 'C_2-capped' porphyrin complexes, which incorporate a nitrogenous base, namely pyridine, covalently bound to two opposite *meso*-aromatic positions of the parent 'C_2-capped' porphyrin (Figure 1). The behaviour of the iron(II) complexes of these 'C_2-capped strapped' porphyrinate ligands, in their reaction with dioxygen, is also described.

† We have adopted a trivial system of nomenclature in order to distinguish readily the different complexes: 'C_2-capped porphyrins' refers to compounds with two methylene units in each rib of the capping structure; 'C_n strapped' refers to a compound with n methylene units in each of the two side arms linking a pyridine group to the parent porphyrin ligand.

Non-S.I. unit employed: Torr ≈ 133 Pa.

Results and Discussion

Preparation of C_2-Capped Strapped Porphyrin Complexes.—To achieve a convergent synthesis of a 'C_2-capped strapped' porphyrin, it was decided to couple a base containing the 'strap' with a suitably difunctionalised capped porphyrin. The points of attachment of the strap are on two diametrically opposed *meso*-aromatic rings of the parent structure, and were selected in an attempt to minimise any unfavourable steric interaction between the strap and the porphyrin ring.

The reaction of choice in forming the strapped porphyrin is that between an activated acid derivative and an amine to produce the stable amide linkage. In capped porphyrin systems, the amino group is conveniently introduced in a latent form as the nitro group.[10] Since C_2-capped strapped derivatives formed from the primary aromatic amine (12) had problems associated with lack of solubility,[11] the amino group was first benzylated before use in the ' strapping' reaction. The synthesis of the bis(benzylamino) C_2-capped porphyrin (13) is outlined in Schemes 1 and 2.

Condensation of the hydroxyaldehyde (3) [5] with the dianhydride of benzene-1,2,4,5-tetracarboxylic acid, (4), in pyridine, yields a mixture of the desired 1,4-diacid diester (5) and the isomeric 1,5-diacid diester. Separation of the isomers is achieved by fractional crystallisation of the 1,4-diacid diester from glacial acetic acid. The dinitrotetra-aldehyde intermediate (9) is formed from condensation of the 1,4-diacid diester (5) with the nitrohydroxyaldehyde (8) in the presence of dicyclohexylcarbodi-imide (dcci) and 4-*NN*-dimethylaminopyridine (dmap).[12] The nitrohydroxyaldehyde (8) is produced from the reaction of the sodium salt of 5-nitrosalicylaldehyde (7) with 2-chloroethanol (6).

Condensation, at high dilution, of (9) with pyrrole (10), in refluxing propanoic acid gives the bis(nitro) C_2-capped porphyrin (11) as purple crystals. Initially, reduction of the nitro groups to the corresponding amine was complicated by competing reduction of the porphyrin ring and apparent cleavage of the capping unit but clean reaction is achieved using sodium tetrahydroborate and 10% palladium on charcoal in a propan-2-ol–dichloromethane (*ca.* 2 : 3 v/v) solvent system.

Reaction of the primary amine (12) with benzaldehyde, followed by reduction with sodium cyanotrihydroborate,[13] yields the desired bis(benzylamino) C_2-capped porphyrin (13).

The pyridine-containing straps are synthesised by the method outlined in Scheme 3. Pyridine-3,5-dicarbaldehyde (14) [14] is reacted with the phosphorus ylides (15a) and (15b) [15] and this is followed by catalytic reduction to yield the

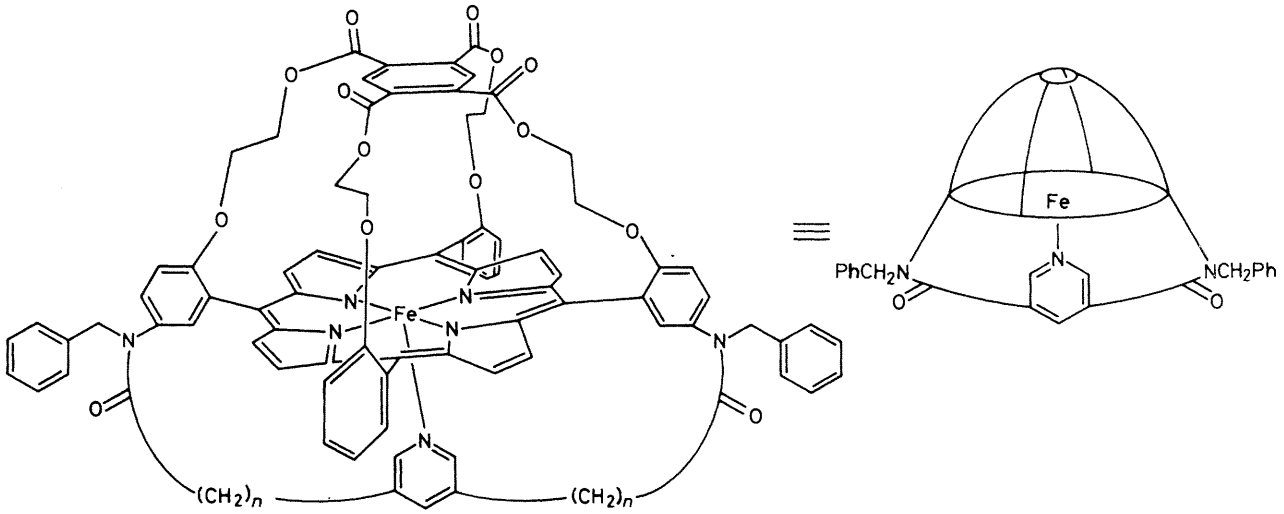
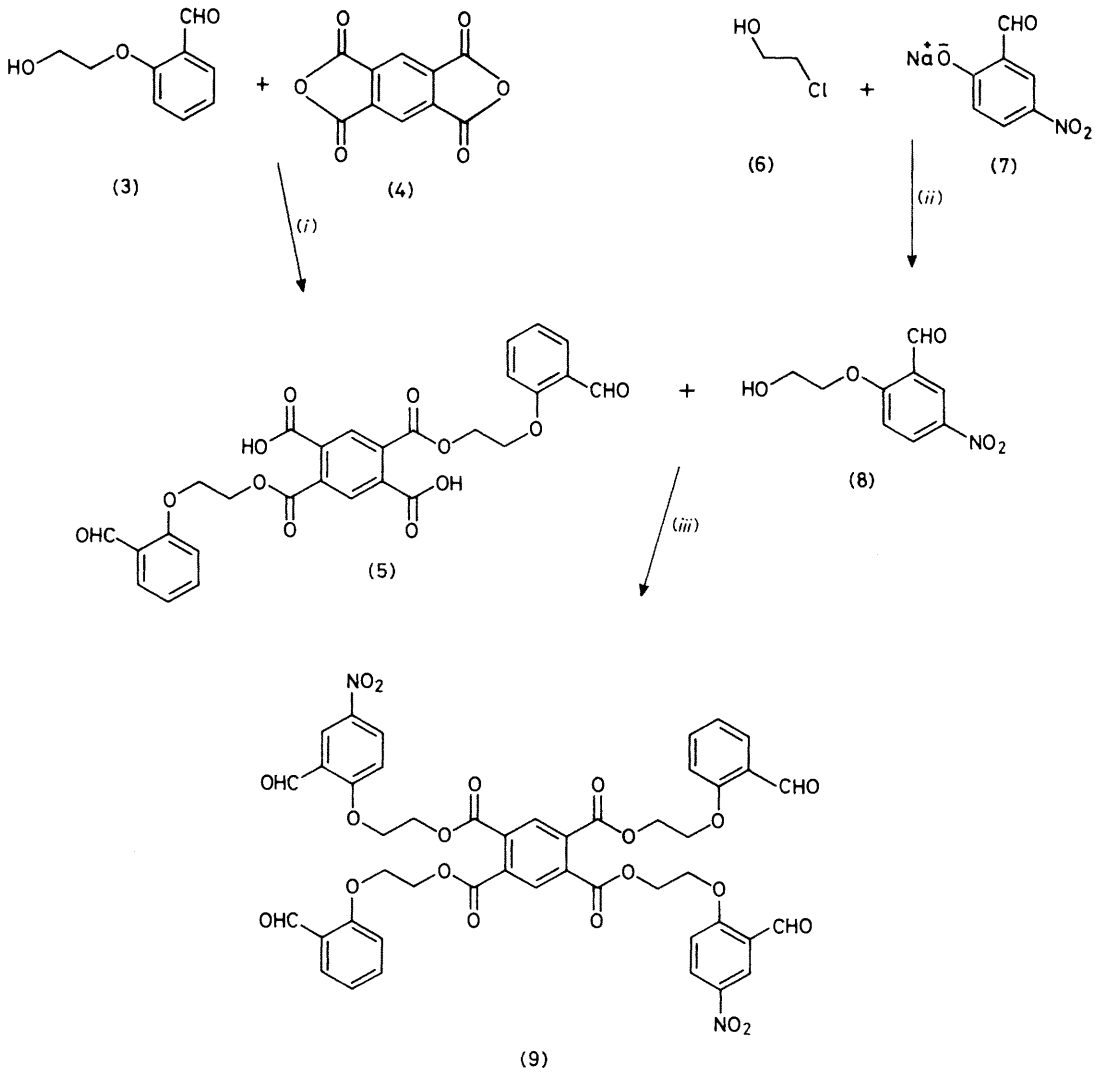
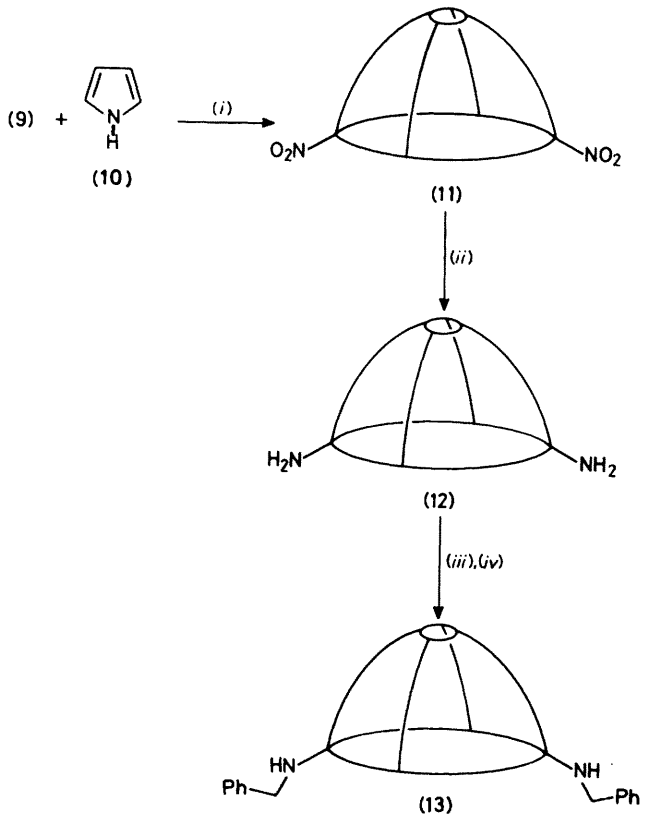


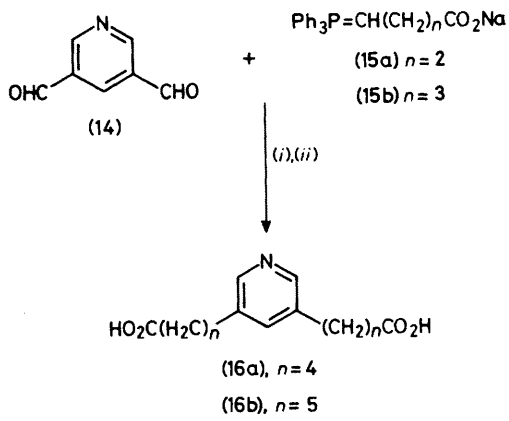
Figure 1. C_2-Capped strapped porphyrin complexes: (1a), $n = 4$; (1b), $n = 5$. For the neutral ligand, Fe is replaced by 2 H: (2a), $n = 4$; (2b), $n = 5$



Scheme 1. (*i*) pyridine, heat at reflux, 6 h; (*ii*) KI, H_2O, heat at reflux, 48 h; (*iii*) dmap, dcci, dmf, 17 h



Scheme 2. (*i*) propanoic acid, heat at reflux; (*ii*) 10% Pd/C, $NaBH_4$, Pr^iOH, CH_2Cl_2; (*iii*) PhCHO, thf, tsa; (*iv*) $Na(NCBH_3)$, NH_4O_2CMe, MeOH, $MeCO_2H$



Scheme 3. (*i*) NaH, dmso, dmf; (*ii*) 10% Pd/C, H_2, EtOH

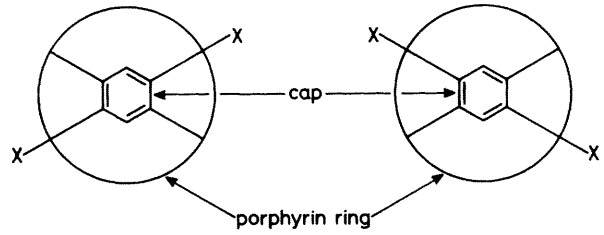


Figure 2. Schematic plan of a disubstituted C_2-capped porphyrin showing the chirality of the molecule; X represents a substituent on the *meso*-aromatic ring

required diacid compounds (16a) and (16b). The length of the alkyl side chains was chosen to give reasonable yields during the subsequent coupling reaction, based upon the results of model studies with long-chain alkyl diacids.

Coupling of the diacid compounds (16a) and (16b) with the bis(benzylamino) C_2-capped porphyrin is achieved using 2-chloro-*N*-methylpyridinium iodide and tri-n-butylamine [16] in dichloromethane solution. The yields of the quinquedentate ligands (2a) and (2b) reflect the ease with which the strap can span the face of the porphyrin group. For the 'C_4 strap' (16a) the yield of porphyrin (2a) was *ca.* 14% and for the 'C_5 strap' (16b) the yield of (2b) was 25%.

A useful method of characterising the 'capped strapped' porphyrins is ^1H n.m.r. spectroscopy. The resonances due to the methylene units and the substituted pyridine of the strap are shifted to higher field due to the shielding provided by the ring current of the porphyrin. A similar effect has been noted in the 'chelated heme' complexes.[7a] An interesting point from the ^1H n.m.r. spectrum is that the methylene units of the strap are diastereotopic in nature due to the chirality of the disubstituted C_2-capped porphyrin system (Figure 2).

Incorporation of iron into the free-base porphyrins (2a) and (2b) proceeds smoothly using standard methods, yielding the iron(III) chloro complexes. These iron(III) complexes are readily reduced by aqueous sodium dithionite solution to produce the desired iron(II) C_2-capped strapped complexes.

Confirmation of the nature of the iron(II) complex is provided by the carbon monoxide complex of (1b). The chemical shifts of the ^1H n.m.r. spectrum of this complex are indicative of a diamagnetic, low-spin iron(II) complex. Co-ordination of the pyridine to the metal ion in this complex is implied by the upfield shifts of the protons on the pyridine, due, again, to the porphyrin ring current. The α and γ protons of the pyridine are shifted by 6.7 and 2.7 p.p.m. respectively.

Reaction of the Iron(II) C_2*-Capped Strapped Complexes with Dioxygen.*—Both of the iron(II) C_2-capped strapped porphyrin complexes (1a) and (1b) exhibit reversible binding behaviour with dioxygen, at room temperature in toluene solution. They show good stability with respect to autoxidation reactions, as evidenced by sharp isosbestic points in the visible spectrum, during each oxygenation/deoxygenation cycle. Complex (1b), the C_5-strapped complex (*i.e.* $n = 5$ in the strapping unit), has a half-life of several days under pure oxygen, while complex (1a), the C_4-strapped complex, has a half-life of several months. This latter complex is extremely stable to autoxidation compared with other iron(II) porphyrin complexes in the literature.[1] It should be pointed out, however, that the observed stability to autoxidation is in part due to the low affinity of the iron(II) complex for dioxygen. Although a kinetic study has not been carried out for this complex, it seems likely that the rate of decomposition will be dependent upon the concentration of oxygen adduct. Since the affinity for O_2 is low, only a relatively small amount of Fe^{II}–O_2 complex will exist at room temperature. Any true assessment of the relative stability to autoxidation of the known iron(II) porphyrin complexes relies upon an accurate determination of the kinetics of the decomposition reaction.

An important feature of both complexes (1a) and (1b) is that the product of decomposition is not a μ-oxo dimer as is observed with other systems, but an iron(III) monomer complex which can be reduced back to the active iron(II) species in virtually quantitative yield by a further treatment with a solution of dithionite. The counter ion of the decomposition product is unknown but it may be hydroxide ion, produced from some residual moisture present in the reaction mixture.

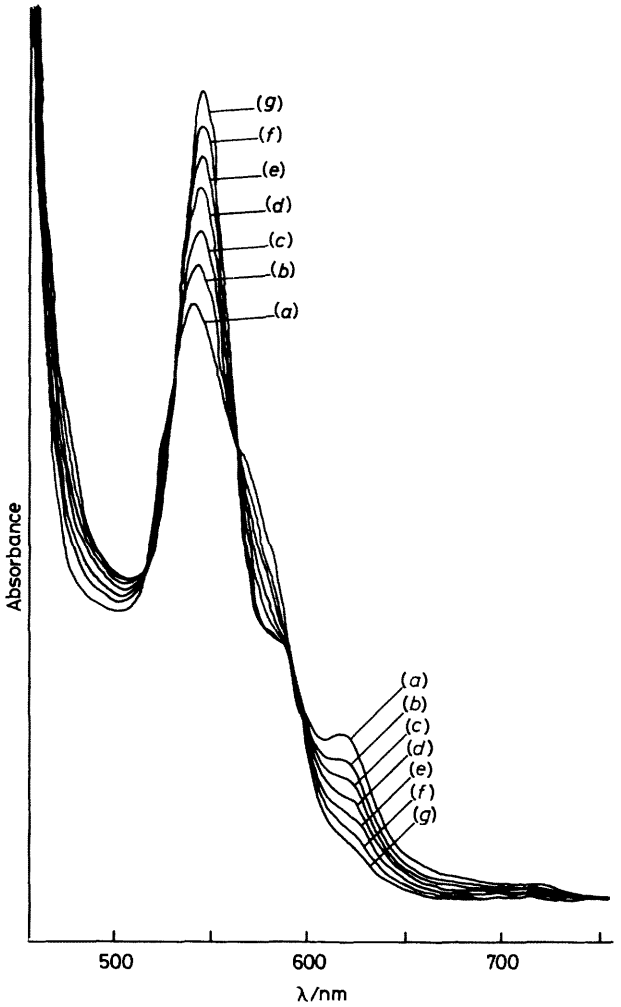


Figure 3. Absorption spectra of the Fe^{II} C_2-capped C_4-strapped porphyrin complex (1a) with the following pressures of oxygen: (*a*) 0, (*b*) 60.3, (*c*) 118.1, (*d*) 213.0, (*e*) 325.0, (*f*) 502.0, (*g*) 742.2 Torr, in toluene solution at −20 °C

Evidently, although a slow oxidation of iron(II) is occurring, the strapping groups are effective in preventing the dimerisation reactions from proceeding.

A typical series of spectra for complex (1a) as a function of oxygen pressure is shown in Figure 3. The five-co-ordinate species has $\lambda_{max.}$ 540, 562 (sh), and 616 nm and the O_2 adduct has $\lambda_{max.}$ 546 and 580 (sh) nm. There are isosbestic points at 562, 532, and 514 nm. For complex (1b), the spectra are very similar with the five-co-ordinate complex having $\lambda_{max.}$ 539, 560 (sh), and 612 nm and the O_2 adduct, $\lambda_{max.}$ 545 and 580 nm. The isosbestic points are at 561, 529, and 514 nm.

The binding constants of the complexes for dioxygen were determined using the method of Basolo and co-workers [17] and the data were treated according to the method of Collman *et al.*[18] The oxygen affinities, in terms of the $P_{\frac{1}{2}}$ value, are presented in the Table as a function of temperature. The $P_{\frac{1}{2}}$ value is defined as the pressure of oxygen, in Torr, necessary to bring about 50% oxygenation of the available iron(II) porphyrin complex. The $P_{\frac{1}{2}}$ value is thus the reciprocal of K_{O_2}, where K_{O_2} ($Torr^{-1}$) is defined as in equation (i) (P represents the quinquedentate porphyrinate ligand and p_{O_2} the pressure of oxygen in Torr).

$$K_{O_2} = \frac{[Fe(P)(O_2)]}{[Fe(P)][p_{O_2}]} \quad (i)$$

Table. Dioxygen affinities ($P_{\frac{1}{2}}$/Torr) [a] of iron(II) complexes in toluene solution

	θ_c/°C			
Porphyrin ligand	0	−10	−20	−30
C_2-Capped [b]	26			
C_2-Capped C_5-strapped	110	60	36	17
C_2-Capped C_4-strapped	1 080	540	311	129

[a] Values are reproducible to within 10%. [b] In the presence of 10% (v/v) of pyridine.

From the Table it is seen that the introduction of the strapping group has the effect of decreasing the affinity of the complex for dioxygen. The dioxygen affinity of the unstrapped complex, with an externally added excess of pyridine as the axial ligand, is four times that of the C_5-strapped material (1b). The effect is even more dramatic for the C_4-strapped case, (1a) where the affinity has dropped by a factor of 40, relative to the unstrapped complex.

A number of factors have been invoked to account for the variation of the affinity of model complexes for dioxygen. Among these are (*i*) the effect of solvent polarity; (*ii*) cavity size (with the approach of dioxygen to the binding site being hindered by smaller cavities, or the bound dioxygen interacting unfavourably with the protecting group); (*iii*) electronic effects, due to changes in the substituents on the porphyrin ligand; (*iv*) changes in contribution to the strain energy, associated with 'doming' of the porphyrin; * this strain energy must be overcome in the binding of the dioxygen to the metal ion; (*v*) an unfavourable steric interaction between the axial ligand of the metal ion and the porphyrin ring, hindering the motion of the iron(II) toward the plane of the porphyrin. The high-spin iron centre, as it binds dioxygen, changes to low spin, and moves into the porphyrin plane, so any hindrance to this motion will serve to lower dioxygen affinity.

Studies with iron(II) C_2-capped unstrapped porphyrins in a variety of solvents have shown that changes in solvent polarity have much less effect on dioxygen affinity than for other model complexes.[17] This presumably arises because the solvent is less able to enter the cavity of the capped complexes and so the $Fe{-}O_2$ unit has a very similar environment, regardless of the nature of the solvent. It seems highly unlikely that any change in solvation which results from introduction of the strapping unit will affect the dioxygen affinity.

For all these complexes, whose affinities for O_2 are listed in the Table, the cap has the same size, so this cannot be a factor in the observed differences in affinity.

The introduction of substituents on the pyridine may result in a small electronic effect, but in these cases this should serve to enhance the dioxygen affinity. The alkyl side chains in the 3- and 5-positions should inductively supply electron density to the pyridine ring, enhancing its ability as a base. This should favour the binding of O_2.

The drop in affinity of the iron(II) C_2-capped strapped complexes can be accounted for by a combination of the remaining two effects. The unstrapped iron(II) C_2-capped complex has a low O_2 affinity relative to the natural systems, haemoglobin and myoglobin, and to other models such as the 'picket fence porphyrin' complex.[3] This low affinity has been ascribed to the 'locking' of the unoxygenated complex in a domed con-

* Doming is the term given to the configuration of the five-co-ordinate metal porphyrin complex, in which the pyrrole groups are tilted toward the metal atom. Thus the mean porphyrin plane is different from the plane of the four co-ordinating nitrogen atoms.[19]

figuration, brought about by the capping group. This hinders the movement of the iron(II) toward the porphyrin plane and consequently lowers the affinity. Since the pyridine in the strapping group binds to the iron, this can serve to lock the complex even more rigidly in the domed configuration, since undoming will now involve movement of the whole strapping group and consequently will require more energy. With the shorter strapping group, the conformation will be more rigidly locked, due to the tighter fit of the strap across the face of the porphyrin, and hence shorter straps will reduce the affinity of the complex still more. Alternatively, the lowered affinity could result from an unfavourable steric interaction between the side arms of the appended pyridine group and the rest of the porphyrinate ligand. The 3- and 5-positions of the pyridine were deliberately chosen as sites of attachment of the side arms to minimise any possible steric interaction with the porphyrin plane. It is well established that such an interaction can dramatically reduce the affinity of an iron(II) complex for dioxygen; for example, for the unstrapped Fe^{II} C_2-capped complex, in toluene solution at 0 °C, the affinity drops from $P_{\frac{1}{2}} = 4.5$ Torr when 1-methylimidazole is the axial ligand, to 930 Torr when 1,2-dimethylimidazole is used. The methyl group in the 2-position interacts strongly with the porphyrin ring, hindering the motion of the iron(II).

In the strapped complexes, another possible steric interaction must be considered. The sites of attachment of the strap to the *meso*-aromatic rings of the parent porphyrin are pointing down and away from the position where the pyridine must lie in order to bind to the metal ion (Figure 1). Thus the side arms must fold back on themselves to bring the pyridine to the desired position. The consequence of this folding may be to induce a steric interaction between the side arms of the pyridine group and the *meso*-aromatic rings of the porphyrin. This would in turn result in inhibition of motion for the iron centre toward the porphyrin plane. Again, this effect would be enhanced by the shorter, tighter strap, resulting in a yet lower dioxygen affinity.

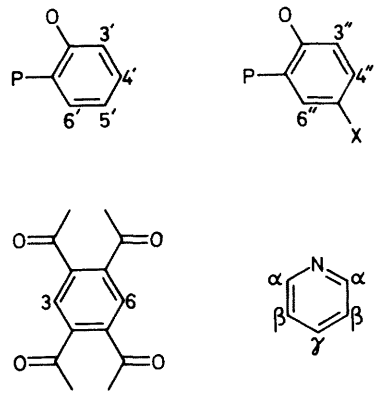
We ascribe the lowered affinity of the strapped complexes for dioxygen to a combination of the two effects described above, which both serve to inhibit the motion of iron(II): a prerequisite for dioxygen binding.

Of interest, in the light of the above discussion, are recent results from the literature, for a doubly strapped complex where one of the straps contains a 3,5-disubstituted pyridine.[9] The strapped base is attached to the parent porphyrin at sites which point toward the position which a co-ordinated pyridine will occupy, and so there is no unfavourable interaction of the side chain with the *meso*-aromatic rings of the porphyrin, as described above. Also the doming effect will be less since the other face of the porphyrin is protected by a strap and not a group similar to a 'cap', with its four sites of attachment.

For the doubly strapped complex, at 20 °C in toluene solution, $P_{\frac{1}{2}}$ was found to be *ca.* 19 Torr, which is a very much higher affinity than either of our two strapped complexes, and indeed is higher than our unstrapped complex, with externally added pyridine. Thus low affinities are not an intrinsic property of strapped base complexes but depend upon the structural features of the molecule.

Experimental

Microanalyses were performed by Dr. F. B. Strauss of the Dyson Perrins Laboratory. Melting points are uncorrected. Electronic spectra were measured on a Perkin-Elmer 555 u.v.-visible spectrophotometer. Oxygen affinity determinations were carried out using a Pye-Unicam PU8800 spectrophotometer. I.r. spectra were recorded on Perkin-Elmer 521, 297, or 257 spectrometers. ^{1}H N.m.r. spectra were recorded using a Bruker WH300 (300 MHz) spectrometer. Spectra were referenced with respect to $SiMe_4$, and were assigned according to the scheme shown below, for the *meso*-aromatic groups, the capping moiety, and the pyridine rings.



Mass spectra were determined using a VG-ZAB-IF or VG-16F instrument. Solvents were purified by conventional means and, where necessary, stored over activated 3A molecular sieves.

Dioxygen affinities of the iron(II) complexes were measured according to the method of Basolo and co-workers [17] and the results were calculated by the method of Collman *et al.*[18] Pressures of oxygen were measured using an MKS Baratron, Type 222B. The temperature was controlled by means of an Oxford Instruments DN704 variable-temperature liquid nitrogen cryostat linked to a DTC 2 thermal controller unit. The cell containing the reaction solution was manually agitated to ensure equilibration between the solution and the measured pressure of O_2. Absorbance *vs.* pressure data were collected at four wavelengths across the spectrum. Affinity results were reproducible to within 10%, under a given set of conditions.

Sodium 5-Nitro-2-oxidobenzaldehyde, (7).—This was prepared by standard procedures. Yield 236.1 g, 34.3%. ^{1}H N.m.r. ([$^2H_6$]dmso), δ 6.30 (d, 1 H, J = 9, H^3), 7.90 (dd, 1 H, J = 9 and 3, H^4), 8.32 (d, 1 H, J = 3 Hz, H^6), and 10.20 p.p.m. (s, 1 H, CHO).

2-(2-Hydroxyethoxy)-5-nitrobenzaldehyde, (8).—The sodium salt of 5-nitrosalicylaldehyde (75.6 g, 0.4 mol) and KI (5.2 g, 0.03 mol) were dissolved in boiling water (400 cm^3) and 2-chloroethanol (33.6 g, 0.42 mol) added over 10 min. The mixture was heated at reflux for 48 h. Concentration and cooling gave a brown solid which was redissolved in CH_2Cl_2, dried over Na_2SO_4, and chromatographed on a silica-gel column, eluting first with CH_2Cl_2, then with CH_2Cl_2–diethyl ether (7 : 3). The product crystallised from CH_2Cl_2–light petroleum (b.p. 40—60 °C) as pale yellow needles (yield 29 g, 34%), m.p. 79 °C. ^{1}H N.m.r. ($CDCl_3$), δ 2.70 (s, br, 1 H, OH), 4.00—4.50 (m, 4 H, CH_2), 7.15 (d, 1 H, J = 8, H^3) 8.35 (dd, 1 H, J = 8 and 2, H^4), 8.59 (d, 1 H, J = 2 Hz, H^6), 10.42 p.p.m. (s, 1 H, CHO). ^{13}C N.m.r. broad band decoupled ([$^2H_6$]dmso), δ 59.49 ($C^{2'}$), 72.12 ($C^{1'}$), 115.11 (C^3), 123.31 (C^1), 124.33 (C^6), 131.00 (C^4), 141.00 (C^5), 165.54 (C^2), and 188.68 p.p.m. (C–*C*HO).

Formation of the Diacid Diester, (5).—Compound (4) (89.95 g, 0.4 mol) and 2-(2-hydroxyethoxy)benzaldehyde, (3) (132.8 g, 0.41 mol) were mixed in pyridine (300 cm^3) and heated at reflux for 6 h. The pyridine was removed *in vacuo*

and the resulting brown oil dissolved in acetone (1 dm^3). Diethyl ether (300 cm^3) was added and the mixture was cooled in a refrigerator overnight. The resulting slurry was filtered and washed well with Et_2O. The solid was boiled in $CHCl_3$, cooled, the solvent removed and the resulting solid dried under vacuum at 50 °C. ^1H N.m.r. of the solid showed it to be *ca.* 70% of the desired isomer. Recrystallisation from glacial acetic acid gave the 1,4-diacid 2,5-diester (5) as a colourless solid (yield 32 g, 15%), m.p. 189—192 °C (Found: C, 61.1; H, 4.05. $C_{28}H_{22}O_{12}$ requires C, 60.85; H, 4.05%). *m/z* (chemical ionization), 551 $(M + 1)^+$. ^{1} HN.m.r. ([$^2H_6$]dmso), δ 4.57—4.67 (m, 8 H, $^-CH_2^-$), 6.93—7.77 (m, 8 H, aromatic H), 7.98 (s, 2 H, H^3 and H^6), 10.40 (s, 2 H, ^-CHO). I.r., $\nu_{max.}$ at 3 250, 2 300, 1 740, 1 725, and 1 648 cm^{-1}.

Formation of the Dinitrotetra-aldehyde, (9).—The diacid diester (5) (11 g, 0.02 mol), compound (8) (10 g, 0.047 mol), and 4-*NN*-dimethylaminopyridine (0.75 g, 0.061 mol) were mixed together and dry *NN*-dimethylformamide (dmf) (20 cm^3) added with vigorous stirring. A dmf solution (5 cm^3) of dicyclohexylcarbodi-imide (dcci) (9.2 g, 0.044 mol) was added over a period of 30 min. The slurry was stirred for a further 16.5 h. The mixture was filtered and the solid residue washed with dmf (10 cm^3) and CH_2Cl_2 (50 cm^3). The filtrate was diluted to 80 cm^3 with CH_2Cl_2 and washed with 5% aqueous HCl solution (2 × 150 cm^3), water (150 cm^3), 3% aqueous $NaHCO_3$ (2 × 150 cm^3), and finally water (3 × 150 cm^3). The organic layer was dried over $MgSO_4$, filtered and reduced in volume to *ca.* 20 cm^3. The product crystallised as a white solid (yield 5.59 g, 30%). Two recrystallisations from glacial acetic acid gave a white product, m.p. 164.5—167 °C (Found: C, 57.85; H, 4.35; N, 2.80. $C_{46}H_{36}N_2O_{20}$·$MeCO_2H$ requires C, 57.85; H, 4.05; N, 2.80%). ^1H N.m.r. ([$^2H_6$]dmso), δ 4.34—4.88 (m, 16 H, $^-CH_2^-$), 7.01 (d, J = 7.5, 2 H, $H^{3'}$), 7.19 (d, J = 8.9, 2 H, $H^{5'}$), 7.44 (d, J = 9.3, 2 H, $H^{3''}$), 7.56—7.62 (m, 4 H, $H^{4'}$ and $H^{6'}$), 8.09 (s, 2 H, H^3 and H^6), 8.31 (d, J = 3, 2 H, $H^{6''}$), 8.43 (dd, J = 9.3 and 3.0 Hz, 2 H, $H^{4''}$), 10.28 (s, 4 H, CHO). I.r., $\nu_{max.}$ at 1 730, 1 680, 1 610, 1 600, 1 530, 1 490, 1 460, 1 380, and 1 350 cm^{-1}.

Preparation of the Dinitro C_2*-Capped Porphyrin*, (11).—This compound was prepared by similar procedures to those of other capped porphyrins,[5] using the dinitrotetra-aldehyde (9) (2.1 g). Yield 0.17 g, 6.73% (Found: C, 66.3; H, 3.70; N, 7.10. $C_{62}H_{42}N_6O_{16}$ requires C, 66.05; H, 3.75; N, 7.45%). ^1H N.m.r. ($CDCl_3$), δ −3.40 (s, br, 2 H, NH), 3.80—4.02 (m, 4 H, CH_2), 4.25—4.63 (m, 12 H, CH_2), 5.44 (s, 2 H, H^3 and H^6), 7.39 (td, 2 H, J = 7 and 1, $H^{5'}$), 7.47 (d, 2 H, J = 9, $H^{3''}$), 7.58 (dd, 2 H, J = 9 and 1, $H^{3'}$), 7.76—7.81 (m, 4 H, $H^{4'}$ and $H^{6'}$), 8.57 (d, 2 H, J = 5, pyrrolic H), 8.66 (d, 2 H, J = 5, pyrrolic H), 8.70 (dd, 2 H, J = 9 and 3, $H^{4''}$), 8.75 (d, 2 H, J = 5, pyrrolic H), 8.80 (d, 2 H, J = 5, pyrrolic H), 8.84 (d, 2 H, J = 3 Hz, $H^{6''}$). Electronic spectrum ($CHCl_3$ solution), $\lambda_{max.}$ ($\log_{10}\varepsilon$) 406 (4.95), 422 (5.52), 485 (sh) (3.51), 516 (4.26), 545 (3.65), 589 (3.77), and 643 nm (3.26).

Preparation of the Diamino C_2*-Capped Porphyrin*, (12).—The dinitro C_2-capped porphyrin (11) (25 mg, 0.023 mmol) and 10% Pd on carbon (25 mg) were placed in a flask under Ar and dry CH_2Cl_2 and propan-2-ol added. $NaBH_4$ (25 mg, 0.68 mmol) was added and the mixture stirred. After *ca.* 1 h, more $NaBH_4$ (10 mg, 0.27 mmol) was added. After a further 30 min, the mixture was filtered through Celite and the solvent removed *in vacuo*. The resulting solid was triturated with CH_2Cl_2 and refiltered. The dark red solution was taken to dryness. Purification of the resulting solid by chromatography on silica and then on Sephadex LH-20-100 gave the diamine (yield 17.2 mg, 74%) as a purple, irridescent solid, which was recrystallised from benzene–methanol. ^1H N.m.r. ($CDCl_3$), δ −3.4 (s, br, 2 H, NH), 3.6 (s, br, 4 H, $^-NH_2$), 3.80—4.55 (m, 16 H, CH_2), 5.42 (s, 2 H, H^3 and H^6), 6.95 (d, J = 2.5, 2 H, $H^{6''}$), 7.00 (dd, J = 7.5 and 2.9, 2 H, $H^{4''}$), 7.3—7.38 (m, 4 H, $H^{3''}$ and $H^{5'}$), 7.49 (d, J = 8.1, 2 H, $H^{3'}$), 7.7 (m, 4 H, $H^{4'}$ and $H^{6'}$), 8.68, 8.76, 8.81, 8.85 (4 × d, J = 4.8 Hz, 8 H, pyrrolic H). *m/z* (field desorption): found, 1066.3184; calc. for $C_{62}H_{46}N_6O_{12}$, 1066.3173. Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ ($\log_{10}\varepsilon$), 404 (4.90), 421 (5.51), 483 (3.48), 515 (4.24), 548 (368), 591 (374), and 646 nm (3.38). I.r., $\nu_{max.}$ at 1 732 , 1 500, and 1 280 cm^{-1}.

Bis(benzylamino) C_2*-Capped Porphyrin*, (13).—Diamino C_2-capped porphyrin (12) (150 mg, (0.14 mmol) and activated 3A molecular sieves were placed under Ar. Dry tetrahydrofuran (thf) (15 cm^3), distilled benzaldehyde (34 μl, 0.33 mmol) and a trace of toluene-*p*-sulphonic acid monohydrate (tsa) were added, and the mixture stirred for 2 h. Some $Na(NCBH_3)$ (66 mg, 1.05 mmol), NH_4O_2CMe (360 mg, 4.68 mmol), distilled MeOH (1.5 cm^3), and glacial acetic acid (0.5 cm^3) were added and the mixture stirred overnight. The mixture was filtered and the solvent removed *in vacuo*. The purple solid was partitioned between 3% aqueous $NaHCO_3$ and CH_2Cl_2. The organic layer was collected and the product purified by chromatography on silica, to yield 135 mg (76%) of bis(benzylamino) C_2-capped porphyrin which could be crystallised from benzene–methanol. *m/z* (field desorption): found, 1246.4119; calc. for $C_{76}H_{58}N_6O_{12}$, 1246.4112. ^1H N.m.r. ($CDCl_3$), δ −3.32 (s, br, 2 H, NH), 3.8—4.6 (m, 22 H, CH_2 and aromatic CH_2NH), 5.40 (s, 2 H, H^3 and H^6), 6.97 (d, J = 3, 2 H, $H^{6''}$), 7.05 (dd, J = 8.8 and 3, 2 H, $H^{4''}$), 7.25—7.39 (d, 10 H, Ph*H*), 7.42 (t, J = 7.4, 2 H, $H^{5'}$), 7.46 (d, J = 8.5, 2 H, $H^{3''}$), 7.54 (d, J = 8.4, 2 H, $H^{3'}$), 7.77—7.82 (m, 4 H, $H^{4'}$ and $H^{6'}$), 8.66, 8.74, 8.79, 8.85 (4 × d, J = 4.7 Hz, 8 H, pyrrolic H). Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ ($\log_{10}\varepsilon$), 421 (5.41), 480 (sh) (3.55), 516 (4.25), 548 (3.72), 591 (3.75), and 648 nm (4.47). I.r., $\nu_{max.}$ at 1 735 cm^{-1} (ester carbonyl).

Pyridine-3,5-dicarbaldehyde, (14).—This was prepared by the method of Beeby and Sondheimer [14] in 49.6% yield.

(3-Carboxypropyl)triphenylphosphonium Bromide.—This was prepared by the literature procedure [20] in 68% yield, m.p. 232—238 °C (lit.,[20] 234—240 °C). ^1H N.m.r. (CD_3OD), δ 1.88 (sextet, J = 5.5, 2 H, $^-CH_2^-CH_2^-CH_2$), 2.58 (dd, J = 5.5 and 1 Hz, 2 H, $^-CH_2^-CO^-$), 3.45 (m, 2 H, $CH_2^-P^+$), 7.8 (m, 15 H, aromatic *H*). The product was recrystallised from acetonitrile–chloroform (1 : 1)–diethyl ether (excess). Recrystallisation from ethanol–diethyl ether [20] resulted in formation of the ethyl ester of (3-carboxypropyl)triphenylphosphonium bromide.

Pyridine-3,5-dipentanoic acid, (16a).—Pyridine-3,5-dicarbaldehyde, (14) (0.2 g, 1.5 mmol) and (3-carboxypropyl)-triphenylphosphonium bromide (1.2 g, 3.12 mmol), as a slurry in dmf (20 cm^3) and dimethyl sulphoxide (11 cm^3), were added to sodium hydride (0.345 g, 50% dispersion in oil; 7.2 mmol), *via* cannula, under argon. After 15 min the mixture was heated to 50 °C, for 28 h. The reaction mixture changed from yellow to dark brown in colour. Water was added and then the solvent removed *in vacuo*. The light yellow residue was triturated with water and the insoluble $Ph_3P{=}O$ (0.85 g, 98%) collected. The filtrate, at pH 13, was washed with CH_2Cl_2, the pH adjusted to <1 with dilute HCl, and the solution extracted with ethyl acetate. Finally the pH was adjusted to 4.0—4.8 whereupon a white precipitate appeared which was extracted with ethyl acetate. Evaporation of the organic layer gave the product as a yellow oily solid (0.278 g).

This solid was added to a mixture of 10% Pd on carbon in ethanol (30 cm^3) and H_2 admitted to the flask. After reaction

was complete the mixture was filtered and the solvent removed *in vacuo* to yield an oil which solidified in the freezer. This solid was recrystallised from ethyl acetate–methanol (2 : 1)–light petroleum (excess) (b.p. 40—60 °C) to yield the final product as off white hygroscopic needles (0.166 g, 40%), m.p. 128—131 °C (Found: C, 64.4; H, 7.50; N, 5.00. $C_{15}H_{21}NO_4$ requires C, 64.5; H, 7.60; N, 5.00%). ^{1}H N.m.r. (CD_3OD), δ 1.67 [m, 8 H, $CH_2(CH_2)_2CH_2$], 2.33 (t, 4 H, $-CH_2-CO$), 2.67 (t, 4 H, $-CH_2-C_5H_3N$), 7.59 (m, 1 H, H^γ ring), 8.22 (m, 2 H, H^α ring). I.r., $\nu_{max.}$ at 3 100 (br), 1 727, 1 670, 1 595, 1 460, 1 405, 1 377, 1 227, and 1 173 cm^{-1}. *m/z* (electron impact), 279 (M^+).

Pyridine-3,5-dihexanoic acid.—This material was prepared by the same route as for (16a), in 31% yield, and crystallised from ethyl acetate, m.p. 90—94 °C (Found: C, 66.05; H, 8.35; N, 4.95. $C_{17}H_{25}NO_4$ requires C, 66.4; H, 8.20; N, 4.55%). ^{1}H N.m.r. (CD_3OD), δ 1.39 [m, 4 H, $-CH_2(CH_2)_2CO_2H$], 1.65 [m, 8 H, $-CH_2CH_2CO_2H$ and $-CH_2(CH_2)_3CO_2H$], 2.29 (m, 4 H, CH_2-CO), 2.66 (m, 4 H, $CH_2-C_5H_3N$), 7.57 (m, 1 H, H^γ ring), 8.20 (m, 2 H, H^α ring). *m/z* (electron impact), 307 (M^+).

Preparation of the C_2-Capped C_4-Strapped Porphyrin, (2a).—Three solutions, (*i*) bis(benzylamino) C_2-capped porphyrin (13) (0.124 g, 0.1 mmol) and tri-n-butylamine (125 μl, 0.53 mmol) in CH_2Cl_2 (40 cm^3), (*ii*) compound (16a) (28 mg, 0.010 mmol) in dmf (2 cm^3) and CH_2Cl_2 (38 cm^3), and (*iii*) 2-chloro-*N*-methylpyridinium iodide in dmf (6 cm^3), were added together, under argon, over a period of 5 h, using syringe pumps. The mixture was heated at reflux overnight, allowed to cool and the solvent removed *in vacuo*. The solid was partitioned between CH_2Cl_2 and 3% aqueous $NaHCO_3$. The organic layer was washed with water, dried and the solvent removed. Chromatography on silica gave the desired product in 13.6% yield. ^{1}H N.m.r. ($CDCl_3$), δ −3.47 (s, br, 2 H, NH), 0.48 (m, 4 H, $-CH_2CH_2C_5H_3N$), 0.92 (m, 4 H, $-CH_2C_5H_3N$), 1.25 (q, 4 H, CH_2CH_2CO), 2.25 (t, 4 H, CH_2CO), 3.70—4.75 (m, 17 H, $O-CH_2-CH_2-O$ and H^γ of pyridine ring), 5.12 (AB, 4 H, CH_2Ph), 5.31 (s, 2 H, H^3 and H^6), 6.87 (d, J = 2 Hz, 2 H, $H^{6''}$), 7.23—7.35 (m, 12 H, $H^{3'}$, Ph*H*), 7.39 (td, J = 8 and 1, 2 H, $H^{5'}$), 7.50 (dd, J = 8 and 1, 2 H, $H^{6'}$), 7.65 (d, J = 8.8, 2 H, $H^{3''}$), 7.79 (td, J = 8 and 1, 2 H, $H^{4'}$), 8.45, 8.49, 8.61, 8.66 (4 × d, J = 4.5 Hz, 8 H, β-pyrrolic H). Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ ($\log_{10}\varepsilon$), 353 (sh) (4.23), 370 (4.30), 421 (5.58), 483 (sh) (4.09), 515 (4.24), 548 (3.68), 591 (3.73), and 647 nm (3.31). I.r., $\nu_{max.}$ ($CHCl_3$) at 1 732, 1 645, and 1 495 cm^{-1}. *m/z* (field desorption): found, 1490.5460 (M + H)$^+$; calc. for $C_{91}H_{76}N_7O_{14}$, 1490.5450.

Preparation of the C_2-Capped C_5-Strapped Porphyrin, (2b).—This compound was prepared by the same procedure as for (2a), in 25% yield. *m/z* (in beam electron impact), 1 517 (M^+). ^{1}H N.m.r. ($CDCl_3$), δ −3.40 (s, br, 2 H, NH), 0.6 (br, 4 H, strap CH_2), 0.89 (br, 4 H, strap CH_2), 1.37 (br, 4 H, strap CH_2), 1.68 (br, 4 H, strap CH_2), 2.33 (br, 4 H, strap CH_2CO), 3.80—4.68 (m, 17 H, $-O-CH_2-CH_2-O-$ and H^γ of pyridine ring), 5.00 (br, 4 H, $-CH_2-Ph$), 5.38 (s, 2 H, H^3 and H^6), 6.89 (d, J = 2.5 Hz, 2 H, $H^{6''}$), 7.10—7.57 (m, 18 H, $H^{3''}$, $H^{4''}$, $H^{3'}$, $H^{5'}$, and phenyl H), 7.63 (d, J = 8.5, 2 H, $H^{6'}$), 7.76 (t, br, 2 H, $H^{4'}$), 7.89 (d, J = 2, 2 H, H^α of pyridine ring), 8.39, 8.49, 8.64, 8.72 (4 × d, J = 4.5 Hz, 8 H, β-pyrrolic H). Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ ($\log_{10}\varepsilon$), 370 (4.32), 419 (5.56), 483 (3.48), 514 (4.24), 546 (3.68), 590 (3.73), and 646 nm (3.36). I.r., $\nu_{max.}$ ($CHCl_3$) at 1 735, 1 645, and 1 495 cm^{-1}.

Monochloroiron(III) *Complex of the C_2-Capped C_4-Strapped Porphyrin.*—This complex was prepared by standard procedures.[2] Electronic spectrum ($CHCl_3$): $\lambda_{max.}$, 382 (sh), 421, 507, 580, and 640 (sh) nm. Treatment of the solution with HCl gas resulted in formation of the pyridinium hydrochloride derivative of the complex, in 73% yield. Electronic spectrum ($CHCl_3$): $\lambda_{max.}$ ($\log_{10}\varepsilon$), 349 (sh) (4.43), 378 (4.58), 417 (4.83), 512 (3.97), 586 (3.37), 668 (3.35), and 686 nm (3.34).

Monochloroiron(III) *Complex of the C_2-Capped C_5-Strapped Porphyrin.*—This complex was prepared by standard procedures, in 74% yield. It was isolated as the pyridinium hydrochloride derivative. Electronic spectrum ($CHCl_3$) : $\lambda_{max.}$ ($\log_{10}\varepsilon$), 380 (3.72), 424 (4.00), 512 (3.10), 585 (2.54), 648 (2.47), and 656 nm (2.48).

Carbon Monoxide Complex of the Iron(II) C_2-*Capped* C_5-*Strapped Porphyrin.*—Some of the iron(II) porphyrin complex (1b) was dissolved in [$^2H_8$]toluene, under carbon monoxide, to give a deep red solution. ^{1}H N.m.r. ([$^2H_8$]toluene), δ 0—2 (m, 16 H, strap CH_2), 1.50 (d, J = 1.8, 2 H, H^α of pyridine ring), 2.50 (m, 4 H, CH_2CO), 3.5—4.0 (m, 16 H, $O-CH_2-CH_2-O$), 4.83 (t, br, 1 H, H^γ of pyridine ring) 5.25 (AB, 4 H, CH_2Ph), 6.53 (s, 2 H, H^3 and H^6), 6.78—7.20 (m, 8 H, aromatic H), 7.24 (m, 6 H, aromatic H), 7.40 (m, 6 H, aromatic H), 7.68 (dd, J = 7.5 and 2.5, 2 H, aromatic H), 7.83 (d, J = 2.5, 2 H, $H^{6''}$), 8.50, 8.52, 8.61, 8.64 (4 × d, J = 4.5 Hz, 8 H, β-pyrrolic H). Electronic spectrum (toluene): $\lambda_{max.}$, 422, 540, 580 (sh), and 650 nm. I.r., $\nu_{max.}$(CO) at 2 005 cm^{-1}.

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