

Reaction of metallo-2-nitro-5,10,15,20-tetraphenylporphyrins with oxyanions. Temperature-dependent competition between nucleophilic addition and single-electron transfer processes

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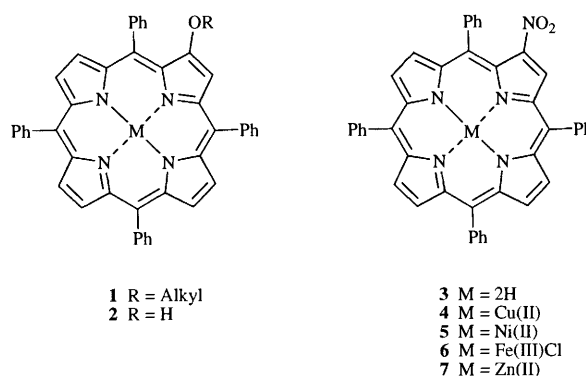
The outcome of the reaction of metallo-2-nitro-5,10,15,20-tetraphenylporphyrins with oxyanions is dependent both on the nature of the coordinated metal ion and on the reaction temperature. Metallo-2-nitro-5,10,15,20-tetraphenylporphyrins with relatively electronegative chelated metal ions (Cu^{II} , Ni^{II} and $\text{Fe}^{\text{III}}\text{Cl}$) react with methoxide ion in *N,N*-dimethylformamide to afford mainly the corresponding metallated 2-methoxy-3-nitroporphyrins and 2,2-dimethoxy-3-nitro-2,3-dihydroporphyrins. The zinc^{II} chelate **7** is unreactive towards methoxide under identical conditions. When the room temperature reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **5** with methoxide is quenched with water after 1 min, the *trans*-(2-methoxy-3-nitro-2,3-dihydroporphyrinato)nickel(II) **14** is obtained. Inclusion of nitrobenzene in the reaction of the copper(II) chelate **4** with methoxide is beneficial and results in the formation of the 2,2-dimethoxy-3-nitro-2,3-dihydroporphyrin **8** in 90% yield. Reaction of **4** with benzyl oxide ion gives analogous products but in lower yield, while the major product from reaction of **4** with hydroxide ion is the 2-hydroxy-3-nitroporphyrin **16**. At elevated temperatures the nature of the reaction of the copper(II) chelate **4** with methoxide changed to afford the corresponding copper(II) 2-alkoxyporphyrin **10** and the denitrated parent porphyrin **20**; the later compounds arise from radical reactions. A mechanistic rationale for the processes involved in these temperature-dependent reactions is presented. The ease with which these reactions occur is a consequence of the fact that all the reaction intermediates are able to retain macrocyclic aromaticity.

Incorporation of functionality at β -pyrrolic positions of the 5,10,15,20-tetraarylporphyrins offers the means by which the properties of the macrocycle can be modulated¹⁻¹¹ and also affords an entry into porphyrin-based molecular architecture by providing a site for further bond construction.¹²⁻²² The scope of these types of structural modification to produce more sophisticated porphyrin-based systems is dependent on the availability of methodology for the efficient introduction of functionality to the porphyrin periphery.

One potentially useful class of functionality is that comprising oxygen substituents. Such substituents provide the means of altering the electron density on the porphyrin ring⁶⁻⁹ and, for the case of an hydroxy group, a convenient point for covalently attaching ligands or potential substrate molecules for reaction at the chelated metal ion. The hydroxy group is also a convenient functionality for conversion into the α -dione unit²³ which allows the synthesis of laterally extended porphyrin systems.^{14,17,20,22}

The need for an efficient synthesis of 2-alkoxy- and 2-hydroxy-5,10,15,20-tetraphenylporphyrins, **1** and **2**, respectively, required the development of new methodology for functionalising the porphyrin β -pyrrolic position. Apart from total synthesis from oxygenated pyrrole precursors,^{4,24,25} at the outset of our studies, the only reported synthesis of such compounds was a low-yielding radical benzyloxylation of 5,10,15,20-tetraphenylporphyrin.²⁶

2-Nitro-5,10,15,20-tetraphenylporphyrin **3** undergoes nucleophilic substitution with benzenethiolate and ethanethiolate to afford porphyrin thioethers by displacement of the nitro group.²⁷ In view of the simplicity of this route to thioethers and as the required nitroporphyrin **3** and its metallated derivatives could be obtained in high yield,²⁸ an investigation of analogous nucleophilic methods for the introduction of β -pyrrolic oxygen functionality was undertaken. These studies involved the use of hard oxygen nucleophiles and reactions that take place at the β -pyrrolic carbon adjacent to that bearing the nitro group. We now report these studies in full.²⁹



Results and discussion

Reaction of 2-nitrotetraphenylporphyrins with sodium methoxide

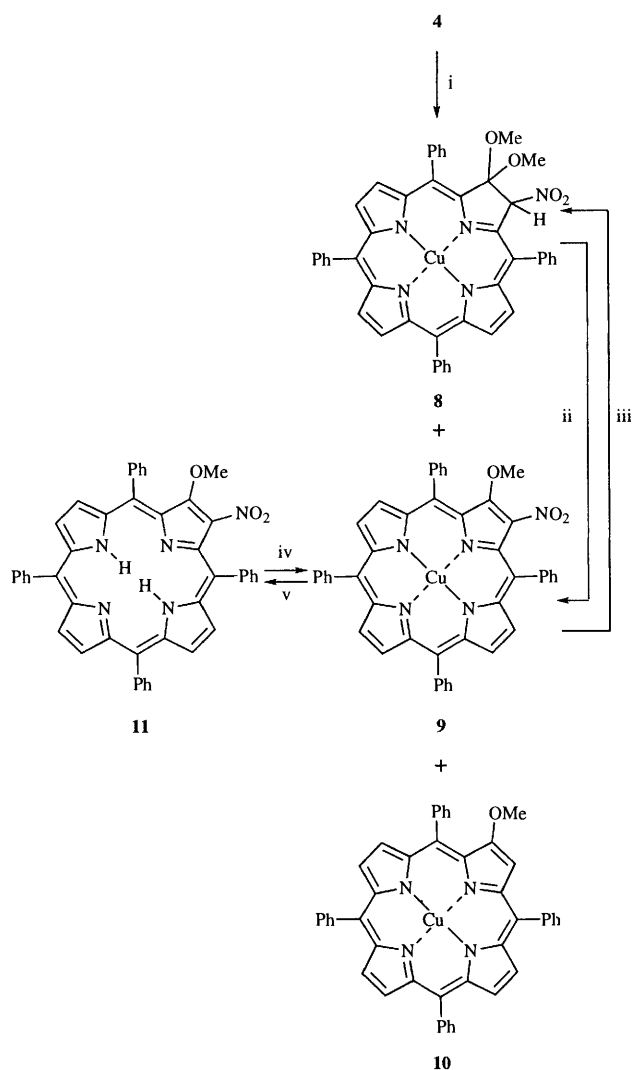
The reactions of a range of metallated 2-nitro-5,10,15,20-tetraphenylporphyrins were explored as a nucleophilic reaction on a metalloporphyrin was expected to depend on the net electron density on the porphyrin periphery and, therefore, on the electronegativity of the chelated metal ion. Thus, the reactions of oxygen nucleophiles with the copper(II) **4**, nickel(II) **5**, chloroiron(III) **6** and zinc(II) **7**, derivatives of 2-nitro-5,10,15,20-tetraphenylporphyrin **3**, as well as with the free base nitroporphyrin **3** itself, were investigated.

The reactions of these 2-nitrotetraphenylporphyrins were indeed found to be dependent on the nature of the central metal ion. In the absence of a coordinated metal the free base 2-nitro-5,10,15,20-tetraphenylporphyrin **3** was not a useful substrate for reaction with alkoxides. Treatment of a DMF solution of **3** with sodium methoxide resulted in an immediate colour change from brown to bright green which is characteristic of a porphyrin anion or dianion.³⁰ No further reaction occurred on prolonged standing and the starting porphyrin **3** was recovered in quantitative yield following aqueous work-up of the reaction

mixture. The methoxide was acting solely as a base in this case, causing deprotonation of the porphyrin inner NHs, to form the porphyrin anion or dianion, the resultant negative charge on the porphyrin thereby inhibiting nucleophilic attack on the outer periphery of the macrocycle.

The interior of the porphyrin can be protected from base by complexation with a metal ion. The copper(II), nickel(II) and chloroiron(III) 2-nitroporphyrins (**4**, **5** and **6**, respectively) all underwent reaction with sodium methoxide to afford methoxylated products.

Treatment of a solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** in dry, distilled DMF (approximately 7 mmol dm⁻³) with sodium methoxide (5–10 equivalents) afforded, after an 18 h reaction period, two major products which were isolated by chromatography over silica. (2,2-Dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** and (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** were obtained in a combined yield of 45–60% (based on recovered starting material) (Scheme 1).



Scheme 1 Reagents and conditions: i, nitrobenzene, DMF, NaOMe, N₂; ii, HCl (7 mol dm⁻³), CH₂Cl₂, 2 min; iii, NaOMe, DMF, N₂, 3 days; iv, excess Cu(OAc)₂·H₂O, CH₂Cl₂-MeOH, 30 min; v, conc. H₂SO₄, 15 min

Over a number of reactions it was found that the ratio of the chlorin **8** and porphyrin **9** products varied considerably with individual yields ranging from 23% and 32% to 51% and 0% respectively, presumably due to the facile interconversion of these products. Generally, however, the chlorin **8** was the major product. Small amounts of (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** (1–5%) were also obtained from

these reactions, together with unreacted starting material **4** (10–20%). Optimum conditions for the synthesis of **8** have been developed and are described below. The structures of the two major products **8** and **9** were established by a combination of spectral and chemical evidence.

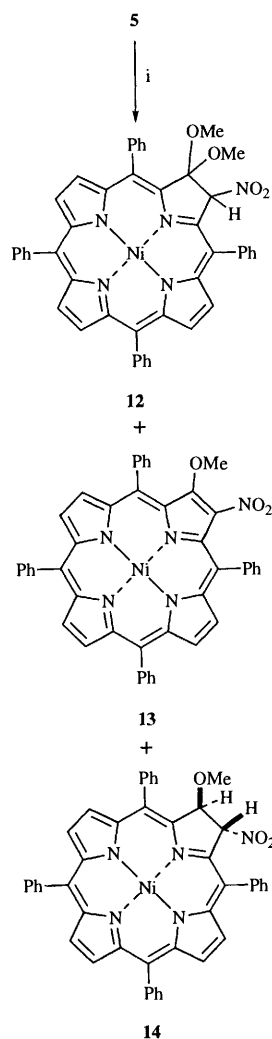
The structure of (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** was the more easily assigned of the two compounds. The IR spectrum of **9** showed a characteristic nitro group stretch (ν_{\max} 1520 cm⁻¹), and the compound has a visible spectrum with a three peak B and Q-band pattern that is characteristic of a metalloporphyrin electronic structure.³⁰ The mass spectrum gave a peak of highest mass corresponding to the parent ion. The structure of **9** was further established by demetallation of **9** with acid to afford 2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrin **11** in 91% yield. In addition to the other supporting spectral data, the ¹H NMR spectrum of this diamagnetic free base porphyrin **11** showed a characteristic three proton singlet at δ 3.83, corresponding to the methoxy group, and three β -pyrrolic AB quartets (δ 8.70–8.87) confirming the 2,3-disubstituted structure. Remetallation of this free base porphyrin **11** with copper(II) acetate³¹ afforded a quantitative yield of **9**, identical in all respects to that obtained from methoxide and copper(II) nitroporphyrin **4**, thereby confirming the assignment.

The nitrochlorin structure of (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** was indicated by the nitro stretch in the IR spectrum and a characteristic metallochlorin visible spectrum³⁰ but no parent ion was found in the mass spectrum (the peak of highest mass corresponded to a loss of 61 mass units from the proposed parent ion) and no useful NMR data could be obtained for this paramagnetic species. Consequently no definitive structural assignment could be made on the basis of spectra alone. The structure **8** was established by the chemical interconversion of **8** and **9**. Shaking of a dichloromethane solution of the chlorin **8** with 7 mol dm⁻³ hydrochloric acid (HCl) for 2 min effected quantitative formation of the copper(II) 2-methoxy-3-nitroporphyrin **9**. Conversely, treatment of a DMF solution of **9** with sodium methoxide achieved an 83% yield of **8**. This behaviour in association with the spectral data strongly supported the proposed structure for the copper(II) chlorin **8**, which is viewed as arising from the formal addition of methanol to the copper(II) 2-methoxy-3-nitroporphyrin **9**. This assignment was subsequently confirmed by analogy with the product from the reaction of methoxide ion with 2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **5**, see below, and by a single crystal X-ray structure.³²

(2-Nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **5** was found to react in a similar fashion to the copper(II) derivative **4**. Under the same reaction conditions treatment of **5** with sodium methoxide gave (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)nickel(II) **12** in 40% yield and (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **13** in 16% yield (Scheme 2). When the reaction was quenched after 1 min neither **12** nor **13** were observed but *trans*-(2-methoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)nickel(II) **14** was obtained in 29% yield, along with starting material **5** (47%). Quenching at intermediate times afforded mixtures of **12**, **13** and **14**.

The spectra and chemical behaviour of **12** and **13** were analogous to those of the corresponding copper(II) derivatives **8** and **9**. In addition, the diamagnetic nature of the nickel(II) ion in these complexes allowed ¹H NMR spectra to be acquired. The 2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrin structure **12** was evidenced by the appearance of two three-proton singlets, at δ 2.70 and 3.27, corresponding to the methoxy groups, and a one-proton singlet at δ 6.41 corresponding to the C(3) proton, α to the nitro group.

The structure of the compound assigned as *trans*-(2-methoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)-



Scheme 2 Reagents and conditions: i, NaOMe, DMF, N₂

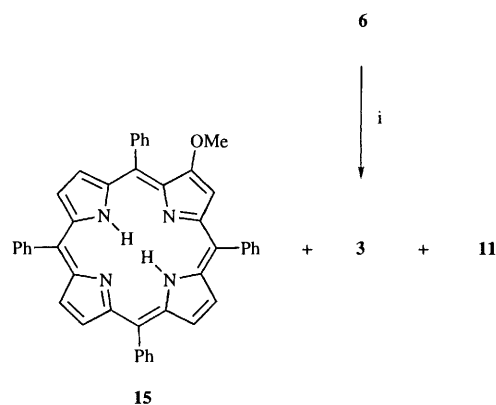
nickel(II) **14** (ν_{\max} 1550 cm⁻¹; metallochlorin visible spectrum) was confirmed by the occurrence of a single three-proton methoxy resonance at δ 3.13, and two one-proton singlets, at δ 5.62 and 6.55, corresponding to the C(2 and 3) protons. The absence of detectable coupling between these resonances at δ 5.62 and 6.55 established the *trans* relationship of the C(2 and 3) substituents. A comparison of the chemical shifts of these methine protons with that of the methine proton in the spectrum of (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)nickel(II) **12** confirmed the assignment of the methine proton in **14** as being α to the nitro group.

Dynamic broadening of the phenyl resonances in the 400 MHz ¹H NMR spectra of these two nickel(II) chlorins **12** and **14** was observed at room temperature. A discussion of this phenomenon will be presented elsewhere. The assignment of the structure of **12** has been confirmed by a single crystal X-ray structural analysis.³²

Similar treatment of chloro(2-nitro-5,10,15,20-tetraphenylporphyrinato)iron(III) **6** with methoxide gave a number of polar products. In this case demetallation of the crude product with concentrated sulfuric acid allowed isolation and identification of 2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrin **11** (16%), 2-methoxy-5,10,15,20-tetraphenylporphyrin **15** (5%) and demetallated starting nitroporphyrin **3** (12%) (Scheme 3), suggesting that the reaction of methoxide with **6** is following a similar course to those on the copper(II) and nickel(II) analogues **4** and **5**.

(2-Nitro-5,10,15,20-tetraphenylporphyrinato)zinc(II) **7** was found to be unreactive toward nucleophilic attack by sodium methoxide in DMF solution.

This pattern of reactivity of different metalloporphyrins



Scheme 3 Reagents and conditions: i, NaOMe, DMF, N₂, 17 h

reflects, in broad terms, the electronegativity of the central metal ions. It is expected that the greater the electron density on the porphyrin periphery, the less reactive the porphyrin will be toward nucleophilic attack, since greater coulombic repulsion of the negatively charged nucleophile should occur. Relatively electronegative metal ions such as copper(II), nickel(II) and iron(III) (Pauling electronegativities 1.90, 1.91 and 1.83, respectively) might therefore be expected to lower the electron density on the porphyrin ring and facilitate reaction with nucleophiles, with respect to more electropositive metal ions such as zinc(II) (Pauling electronegativity 1.65), as is the observed case. Consistent with this expectation, extended Hückel calculations applied to a range of metal(II) porphyrin complexes predict varying residual charges on the porphyrin ligand. The nett ring charge calculated for zinc(II) porphyrins was -0.40 compared with -0.28 for copper(II) porphyrins and -0.30 for nickel(II) porphyrins.³³ In these terms the zinc(II) porphyrin is again the most deactivated toward nucleophilic attack. Clearly a porphyrin anion or dianion is even further deactivated.

Attempts to displace halogen groups from analogous metallo-2-haloporphyrins by reaction with methoxide were not successful although substitution readily occurs by reaction with thiolate nucleophiles.¹⁶

Yield optimization

As the formation of products from the reaction of methoxide with 2-nitrotetraphenylporphyrins involves either loss of a hydride ion from, or oxidation of, an intermediate species, it was reasoned that the inclusion of a nitro-arene hydride ion acceptor or electron acceptor in the reaction mixture would facilitate the reaction.

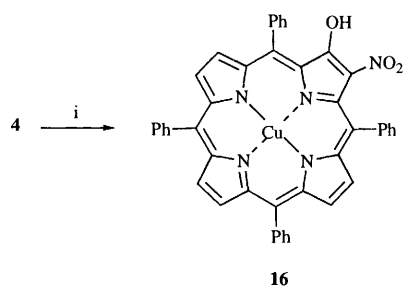
Treatment of a DMF solution of **4** with sodium methoxide in the presence of nitrobenzene (25 equivalents) at room temperature for 18 h afforded **8** and **9** in 89–97% combined yield. The chlorin **8** was again the major product, being obtained typically in 90% yield. Similarly, when the reaction was carried out in the presence of *m*-dinitrobenzene, the products **8** and **9** were obtained in yields of 70 and 10%, respectively. The inclusion of *m*-dinitrobenzene in the reaction mixture, however, was accompanied by the appearance of bright red colour in the solution, which was visible even in the presence of the strongly coloured porphyrins, presumably due to the formation of a Meisenheimer complex between methoxide ion and *m*-dinitrobenzene.³⁴

The reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) **4** with other oxygen nucleophiles

In order to gain access to 2-hydroxyporphyrin derivatives the reactions of **4** with hydroxide and benzyloxide ions were investigated.

The reaction between sodium (or potassium) hydroxide and **4** in DMF was found to be very slow at room temperature, requiring 2 to 4 days to proceed to near completion. The major

product obtained was (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16**, in yields which varied from 28 to 51% (Scheme 4). The product **16** was found to be unstable on



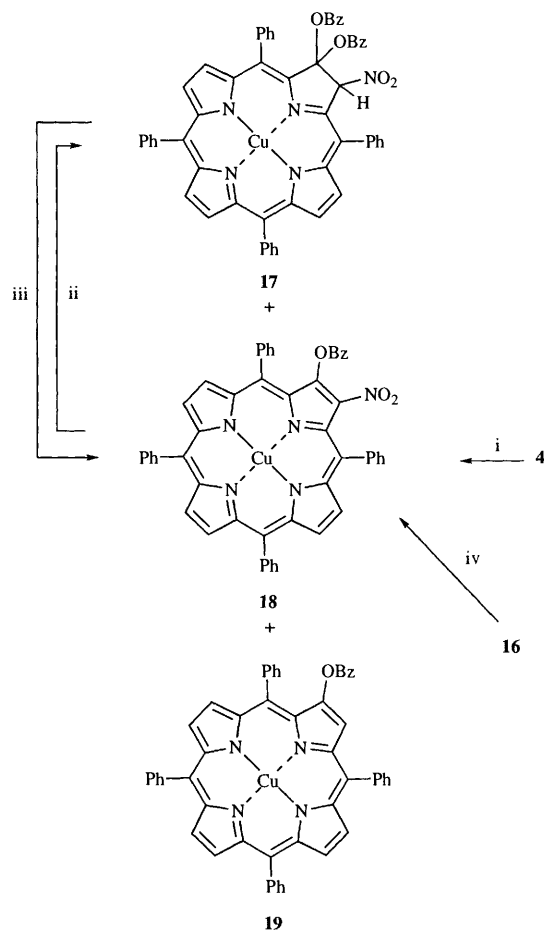
Scheme 4 Reagents and conditions: i, NaOH, DMF

exposure to light, particularly during chromatography, leading to reduced yields unless precautions were taken to exclude light during the reaction and subsequent work-up and purification steps. It was found that addition of nitrobenzene to the reaction mixture did not improve the yield of **16**.

The structure of **16** [ν_{\max} 3400 (OH) and 1565 cm^{-1} (NO_2)] could not be unequivocally assigned on the basis of spectral data alone. The base peak in the mass spectrum of **16** corresponded to a loss of 45 mass units from the parent ion. This fragment was observed in the mass spectra of all the 2-methoxy-3-nitroporphyrins and is explained by assuming that the 2,3-disubstituted nitroporphyrin undergoes hydrogenation across the 2,3-bond in the mass spectrometer inlet system followed by loss of nitrous acid. The occurrence of $M + 2$ peaks believed to be due to this type of hydrogenation has been reported for another porphyrin system.³⁵ The structure of **16** was confirmed, therefore, by the alkylation of the hydroxy group with methyl iodide to **9** in 82% yield, the structure of which had been unequivocally established (Scheme 4). The visible spectrum of **16** shows a substantial bathochromic shift compared with compounds **4**, **9** and (2-hydroxy-5,10,15,20-tetraphenylporphyrinato)copper(II).⁸ We attribute this shift to bond fixation in the substituted ring caused by a hydrogen bond between the hydroxy hydrogen and an oxygen of the adjacent nitro group; similar bathochromic shifts are seen in the spectra of related 2-amino-3-nitroporphyrins; we will discuss full details of our study of the phenomenon of bond fixation in such systems elsewhere.

Sodium benzyl oxide proved to be a poor choice of nucleophile for this reaction. Treatment of a DMF solution of **4** with sodium benzyl oxide afforded a large number of products, including (2,2-dibenzoyloxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **17** in 18–38% yield, (2-benzoyloxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18** in 0–7% yield, (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** in 21–30% yield and (2-benzoyloxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **19** in 3–17% yield (Scheme 5). The presence of nitrobenzene again failed to produce an improvement in yield.

The structures of the 2,2-dibenzoyloxy-3-nitrochlorin **17** (ν_{\max} 1540 cm^{-1} ; metallochlorin visible spectrum) and the 2-benzoyloxy-3-nitroporphyrin **18** [ν_{\max} 1560 cm^{-1} ; metalloporphyrin visible spectrum; m/z 781 ($M + 2H - \text{HNO}_2$)] were again confirmed by their chemical interconversion. Thus, treatment of a dichloromethane solution of the chlorin **17** with 7 mol dm^{-3} HCl afforded a quantitative yield of the 2-benzoyloxy-3-nitroporphyrin **18**, and treatment of a DMF solution of the 2-benzoyloxy-3-nitroporphyrin **18** with sodium benzyl oxide yielded the 2,2-dibenzoyloxy-3-nitro-2,3-dihydroporphyrin **17** (43%). The structure of **18** was further confirmed by the alkylation of (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** with benzyl bromide which gave **18** in 89% yield.



Scheme 5 Reagents and conditions: i, NaOBz, DMF, N_2 , 40 h; ii, NaOBz, DMF, N_2 , 24 h; iii, HCl (7 mol dm^{-3}), CH_2Cl_2 , 2 min; iv, BzBr, CH_2Cl_2 , acetone, K_2CO_3 (anhydrous), 3 days

Table 1 Effect of reaction temperature on product distribution for the reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** with sodium methoxide

Temperature $T/^\circ\text{C}$	Time t/h	Yield of product (%)			
		8	9	10	20
50	4	34	54	7	—
80	1	41	25	12	—
120	0.75	—	7	20	Trace
153	4	—	—	—	53

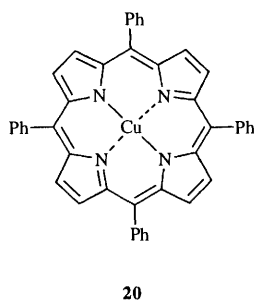
In other work we have developed efficient syntheses of 2-hydroxyporphyrins which use the soft nucleophile, the anion of aldoximes, in reactions of metallated 2-nitroporphyrins¹³ and of metallated 2-arylsulfinylporphyrins.²³

Effect of reaction temperature on the reaction of hydroxide and alkoxide ions with (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4**

The possibility of shortening reaction times by increasing the reaction temperature prompted an investigation of the reaction between **4** and the alkoxide and hydroxide nucleophiles discussed above. A systematic study of the reaction of sodium methoxide with **4** was undertaken. The reaction was carried out under standard conditions in the presence of nitrobenzene, at temperatures of 50 $^\circ\text{C}$, 80 $^\circ\text{C}$, 120 $^\circ\text{C}$ and refluxing DMF (153 $^\circ\text{C}$), and the results are collected in Table 1.

It is evident from the results that the nature of the reaction changes with increased reaction temperature. For the reaction carried out at 50 $^\circ\text{C}$, the combined yield of **8** and **9** was comparable to that obtained from the room temperature

reaction, with a reaction time shortened from 18 to 4 h suggesting that these are perhaps the optimum conditions for carrying out this reaction. With increasing reaction temperature above 50 °C the combined yield of **8** and **9** decreased while the yield of (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** increased to 20% for the reaction at 120 °C. Increasing the reaction temperature to that of refluxing DMF (153 °C) changed the product distribution again, affording the unsubstituted (5,10,15,20-tetraphenylporphyrinato)copper(II) **20** (53%) as the only isolated porphyrin product.



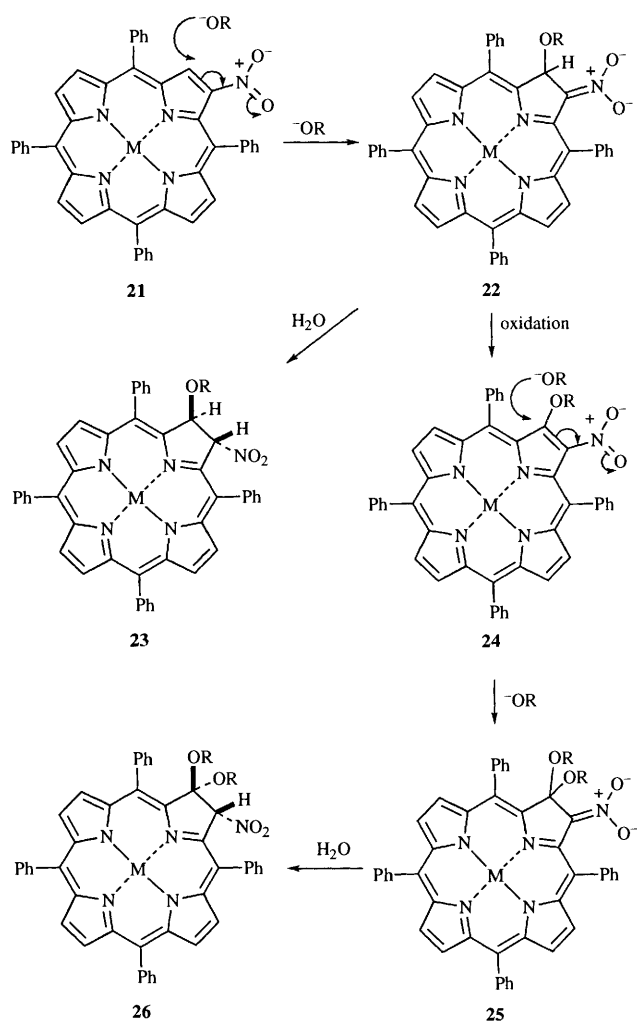
The reactions of sodium hydroxide and sodium benzyl oxide with **4** were also carried out at elevated temperature. The reaction of sodium hydroxide with **4** at 80 °C (in the presence of nitrobenzene) afforded (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** after 6 h in 68% yield with 80% conversion, representing a significant improvement over the room temperature reaction. In contrast, the reactions of sodium benzyl oxide with **4** at 50 and 80 °C afforded multiple products but no significant yield of (2,2-dibenzoyloxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **17** or (2-benzoyloxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18**.

Mechanism

Clearly a number of different mechanisms can operate in the reaction between alkoxide nucleophiles and metallo-2-nitrotetraphenylporphyrins, with a prevalence dependent on the reaction temperature.

In the reaction at room temperature (and up to 80 °C), in contrast to the apparent ipso substitution observed in the reaction of thiolates with 2-nitro-5,10,15,20-tetraphenylporphyrin **3**,²⁷ and reaction with the soft nucleophile, the anion of aldoximes,^{1,3} the major products of the reaction of alkoxide and hydroxide nucleophiles with metallo-2-nitroporphyrins arise from attack at the β -pyrrolic carbon α to that bearing the nitro group. Attack at this position has also been observed in the reactions of metallo-2-nitroporphyrins with the hydride and organoalkanes.^{18,19} A mechanism that would account for the products formed is shown in Scheme 6.

In this mechanism, an initial reversible Michael-like addition of alkoxide (or hydroxide) ion to the metallo-2-nitroporphyrin **21** gives the Meisenheimer-like nitronate **22**. Analogous anionic ' σ -complexes' are well known in the addition of the methoxy group to polynitroarenes.^{36,37} This nitronate **22** can then either be trapped by aqueous work-up to give the 2-monoalkoxy-3-nitro-2,3-dihydroporphyrin **23** or undergo oxidation to afford the 2-alkoxy-3-nitroporphyrin **24**. A Michael-like addition of alkoxide to **24** then affords the dialkoxylated nitronate **25** which on protic work-up gives the 2,2-dialkoxy-3-nitro-2,3-dihydroporphyrin **26**. The methoxy group of **24** is relatively sterically crowded. The stability of the *gem*-dimethoxy complex **25** may be due to the relief of strain which occurs in going from **24** to **25**. Similar steric factors³⁷ along with the formation of an ion pair where the cation is held by a cage effect of oxygen groups of *gem*-dioxy functionalities have been invoked to account for the stability of 1,1-dialkoxy-2,4,6-trinitrocyclohexadienyl anions.³⁸⁻⁴⁰ The value of an sp^3 hybridized centre in



getting the substituents into unencumbered space in the present case is readily seen in the X-ray crystal structures of **8** and **12**.³²

The intermediacy of **22** in this reaction is evidenced by the isolation of *trans*-(2-methoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)nickel(II) **14** from the reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **5** and methoxide after short reaction periods. Likewise the intermediacy of the 2-methoxy-3-nitroporphyrin **24** in the formation of the 2,2-dialkoxy-3-nitro-2,3-dihydroporphyrin **26** is evidenced by the ready conversion of the copper(II) 2-alkoxy-3-nitroporphyrins **9** and **18** to the corresponding 2,2-dialkoxy-3-nitro-2,3-dihydroporphyrins **8** and **17** on treatment with the appropriate alkoxide in DMF in yields of 83 and 55%, respectively.

The mechanism for the oxidation of the nitronate **22** to the metallo-2-alkoxy-3-nitroporphyrin **24** is not known but most likely involves a single electron transfer (SET) from the nitronate **22** to a molecule of starting nitroporphyrin **21** or nitrobenzene, followed by abstraction of a hydrogen atom from the resulting radical to afford the alkoxynitroporphyrin **24**. It has been shown that the reaction between bases and a number of nitroaromatics is accompanied by the formation of the radical anion of the nitro-aromatic (generally in low concentrations), presumably as a result of a SET from a Meisenheimer complex to the nitroaromatic.⁴¹

A SET mechanism for the oxidation of **20** to **22** is supported by the improvement in yield achieved by the addition of nitrobenzene or *m*-dinitrobenzene to reactions with methoxide ion. Both nitrobenzene and *m*-dinitrobenzene are electron acceptors for SET reactions.⁴² Furthermore, the large yield of (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)cop-

per(II) **16** from the reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** with benzyl oxide ion is also consistent with the occurrence of a SET process during the reaction since benzyl ethers are known to be cleaved under SET conditions.⁴³⁻⁴⁵ The hydroxy of compound **16**, under these reaction conditions and when generated by the reaction of nitroporphyrin **4** with hydroxide, should be readily deprotonated by base to give a porphyrin oxide which would be resistant to further nucleophilic addition.

The reaction of sodium methoxide with (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** at elevated temperatures indicated a change of reaction pathway with increased temperature. The predominance of the denitrated product, (5,10,15,20-tetraphenylporphyrinato)copper(II) **20** obtained from the reaction of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** with sodium methoxide in refluxing DMF is clearly due to a radical process and is consistent with both the postulated occurrence of single electron transfer processes at lower temperatures and the known ability of sodium methoxide to promote hydrogen atom abstraction in radical chain reactions.^{46,47} We have shown previously that metallo-2-nitroporphyrins can undergo radical denitration readily by reaction with 2-aminobenzenethiolate.⁴⁸ The increasing yields of (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10**, up to 120 °C, may reflect an increasing contribution from an ipso aromatic nucleophilic substitution (S_NAr) mechanism. At these higher temperatures more energy is available for the breaking of the porphyrin-nitro bond so that such an ipso substitution would be expected to be facilitated. A more likely source of **10**, however, is the radical denitration of the initial reaction product, 2-methoxy-3-nitroporphyrin **9**, in an analogous process to that giving **20**.

Conclusions

From the results presented above it is apparent that the incorporation into the porphyrin ring of relatively electronegative metal ions activates the porphyrin toward nucleophilic attack, a function akin in nature to the incorporation of electron withdrawing groups into a benzene ring. The central metal ions copper(II) and nickel(II) afforded the best results for the reaction between alkoxides and metallo-2-nitrotetraphenylporphyrins.

At room temperature, and temperatures up to 80 °C, the reaction between hydroxide or alkoxide nucleophiles and metallo-2-nitro-tetraphenylporphyrins proceeds with attack of the nucleophile at the β -pyrrolic position vicinal to the nitro group to afford the metallo-2,2-dialkoxy-3-nitrotetraphenylchlorin and/or metallo-2-(alkoxy or hydroxy)-3-nitrotetraphenylporphyrin as the major products. In the presence of nitrobenzene, and with methoxide as the nucleophile, high yields of (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** are obtained. The ease with which these reactions occur is a consequence of the fact that all the reaction intermediates are able to retain macrocyclic aromaticity.

While (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** may be obtained directly, though in low yield, by reaction of the corresponding 2-nitro-5,10,15,20-tetraphenylporphyrin **4** with sodium methoxide at 120 °C, in other work we have developed efficient methodology for conversion of 2-alkoxy-3-nitro-2,3-dihydroporphyrins into 2-alkoxy- and 2-hydroxy-porphyrins. We have also developed a direct efficient synthesis of 2-hydroxyporphyrins by reaction of metallated 2-nitroporphyrins and of metallated 2-halo- and 2-arylsulfinyl-porphyrins with the soft nucleophile, the anion of aldoximes.

This work is a further illustration that 2-nitroporphyrins are versatile starting materials for introduction of other functionalities to the porphyrin periphery.^{12-15,18-21,27,48}

Experimental

Melting points were recorded on a Kofler hot-stage microscope and are uncorrected. All reagents were purchased from commercial sources and used as received unless otherwise noted. All solvents were redistilled prior to use. *N,N*-Dimethylformamide (DMF) was dried over calcium hydride and distilled under reduced pressure. Elemental analyses were performed by the Australian Microanalytical Service, Melbourne, Australia. IR spectra were recorded on a Perkin-Elmer 221 spectrometer. Visible spectra were recorded in chloroform on a Hitachi 150-20 spectrophotometer. ¹H NMR spectra were recorded at 400 MHz on a Bruker WM400 spectrometer with tetramethylsilane as the internal standard; *J* values are given in Hz. Mass spectra were recorded on an AEI MS 902 spectrometer at 70 eV. Column chromatography was performed on Merck (Type 9385) silica gel. The chromatotron is a preparative, thin-layer, centrifugally accelerated chromatograph supplied by Harrison Research. Chromatotron separations were carried out on 4 mm thick plates prepared with Merck silica gel PF₂₅₄. Preparative thin-layer chromatography (TLC) plates were prepared with Merck silica gel 60 PF₂₅₄₊₃₆₆.

Reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) **4** and sodium methoxide at room temperature

(a) **In the presence of nitrobenzene.** A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II)^{28,49} **4** (100 mg, 0.139 mmol) and nitrobenzene (0.5 cm³, 5 mmol) in DMF (20 cm³) was treated with a solution of sodium methoxide in methanol (3.1 mol dm⁻³, 0.6 cm³) and the mixture was stirred under nitrogen overnight. The mixture was then diluted with dichloromethane (100 cm³), washed with water (6 × 200 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was triturated with light petroleum (3 × 50 cm³) and the soluble fractions were filtered under vacuum through a silica column (4 cm diameter, 20 g). This process was repeated with dichloromethane–light petroleum (1:1) (3 × 50 cm³), the column was eluted with dichloromethane–light petroleum (1:1) and the coloured fractions were collected, combined and evaporated to dryness. The crude product was chromatographed on a chromatotron eluted with dichloromethane–light petroleum (1:1) to yield four fractions. The front running red band afforded on evaporation (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** (1 mg, 1%). This product was identical with authentic material by TLC and visible spectrum comparison. The second, major, blue–green band yielded on evaporation (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** (76 mg, 70%, 91% based on consumed starting porphyrin). Recrystallization from dichloromethane–hexane afforded **8** as small purple needles, mp > 350 °C (decomposed > 250 °C) (Found: C, 70.5; H, 4.8; N, 9.1. C₄₆H₃₃CuN₅O₄ requires C, 70.5; H, 4.3; N, 8.9%); ν_{\max} (Nujol)/cm⁻¹ 1560 (NO₂); λ_{\max} (CHCl₃)/nm 421 (log ϵ 5.13), 517 (3.65), 589 (3.93) and 620 (4.36); *m/z* (relative intensity) 723 (17%), 722 (17), 721 (30), 708 (27), 707 (52), 706 (49), 705 (100), 678 (20), 677 (34), 676 (39) and 675 (47).

The third, red–green band afforded starting nitroporphyrin **4** (23 mg, 23%) and the fourth, red band yielded (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (5 mg, 5%, 6% based on consumed starting porphyrin). Recrystallization from dichloromethane–hexane afforded **9** as dark red microcrystals, mp 333–338 °C (Found: C, 72.2; H, 3.9; N, 8.9. C₄₅H₂₉CuN₅O₃ requires C, 71.9; H, 3.9; N, 9.3%); ν_{\max} (Nujol)/cm⁻¹ 1520 (NO₂); λ_{\max} (CHCl₃)/nm 414 (log ϵ 5.38), 543 (4.20) and 580 (3.65); *m/z* (relative intensity) 753 (29%), 752 (60), 751 (57), 750 (M⁺, 100), 723 (10), 722 (20), 721 (20), 720 (34), 708 (11), 707 (21), 706 (23), 705 (40), 704 (23), 703 (20), 702 (19), 693 (14), 692 (21), 690 (18), 689 (14), 688 (11) and 673 (14).

(b) In the absence of nitrobenzene. To a solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (83 mg, 0.115 mmol) in DMF (20 cm³) was added solid sodium methoxide (31 mg, 0.57 mmol) and the mixture was stirred under nitrogen for 16 h. The mixture was then diluted with dichloromethane (100 cm³), washed with water (6 × 200 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on preparative TLC plates to afford four major bands. The front running red band afforded (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** (2.5 mg, 3%). The second, blue-green band afforded (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** (43 mg, 48%, 55% based on consumed starting material). The third band afforded starting nitroporphyrin **3** (11 mg, 13%) and the fourth band afforded a red-brown band of (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (3 mg, 3%, 4% based on consumed starting material). All products were identical with authentic materials.

Demetallation of porphyrin **9** to give 2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrin **11**

(2-Methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (60 mg, 0.080 mmol) was dissolved in concentrated sulfuric acid (15 cm³) over 15 min and the resulting mixture was then extracted with dichloromethane (5 × 30 cm³). The combined organic layers were then washed with water (100 cm³, 50 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness to yield a brown residue. Recrystallization from dichloromethane-light petroleum yielded purple-brown needles of 2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrin **11** (50 mg, 91%). This product was identical in all respects with the authentic sample.

Metallation of porphyrin **11** to give (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9**

A solution of 2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrin **11** (2 mg) in a mixture of dichloromethane-methanol (9:1) was treated with an excess of copper(II) acetate monohydrate and stirred at room temperature for 30 min to give a quantitative yield of (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** after work up and column chromatography. This product was identical in all respects with the authentic material.

Conversion of chlorin **8** into (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9**

A solution of (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** (50 mg, 0.064 mmol) in dichloromethane (50 cm³) was shaken with hydrochloric acid (7 mol dm⁻³, 50 cm³) for 2 min. The organic layer was separated, washed with water (100 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness to yield a red residue of (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (48 mg, 100%). Recrystallization from dichloromethane-light petroleum afforded dark red microcrystals. This product was identical in all respects with the authentic sample.

Conversion of porphyrin **9** into (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8**

To a solution of (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (29 mg, 0.039 mmol) in dry, distilled DMF (20 cm³) was added solid sodium methoxide (90 mg, 1.7 mmol) and the mixture was stirred under nitrogen for 3 days. The solution was then diluted with dichloromethane (50 cm³), washed with water (6 × 70 cm³), dried over anhydrous sodium sulfate and evaporated to dryness. The residue was purified by preparative TLC developed with dichloromethane-light petroleum (1:1), to yield a major blue-green band of (2,2-

dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** (25 mg, 83%). This product was identical in all respects with the authentic sample.

O-Methylation of porphyrin **16** to give (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9**

A solution of (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** (50 mg, 0.068 mmol) in a mixture of acetone (20 cm³) and dichloromethane (20 cm³) was stirred with methyl iodide (1 cm³, 16 mmol) and potassium carbonate (200 mg, 0.811 mmol) for 1 day. The mixture was filtered and the solvent was removed by rotary evaporation. The residue was chromatographed on a silica column (4 cm diameter, 200 g) eluted with dichloromethane-light petroleum (1:1) to yield (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (42 mg, 82%). This product was identical in all respects with the authentic sample.

Reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)-nickel(II) **5** and sodium methoxide at room temperature

(a) Extended reaction time. Treatment of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **5** (99 mg, 0.138 mmol) with sodium methoxide under identical conditions to those described above for (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (Method 2) afforded on chromatography a front running blue-green band of (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)nickel(II) **12** (43 mg, 40%) which was recrystallized from dichloromethane-hexane to afford small purple needles, mp 232–236 °C (Found: C, 71.4; H, 4.3; N, 8.6. C₄₆H₃₃N₅NiO₄ requires C, 71.0; H, 4.3; N, 9.0%; ν_{\max} (Nujol)/cm⁻¹ 1550 (NO₂); λ_{\max} (CHCl₃)/nm 419 (log ϵ 5.19), 506 (3.63), 576 sh (3.98) and 613 (4.36); δ_{H} (400 MHz; CD₂Cl₂) 2.70 (3 H, s, OMe), 3.27 (3 H, s, OMe), 6.41 (1 H, s, 3-H), 6.75–8.35 (10 H, br m, 5-, 10-, 15- and 20-H_{o,m,p}), 7.47 (1 H, m, 5-, 10-, 15- or 20-H_m or *p*), 7.58–7.71 (9 H, m, 5-, 10-, 15- and 20-H_{m,p}), 7.73 and 8.28 (2 H, ABq, *J*_{AB} 5, β -pyrrolic H), 8.08 and 8.35 (2 H, ABq, *J*_{AB} 5, β -pyrrolic H), 8.17 and 8.22 (2 H, ABq, *J*_{AB} 5, β -pyrrolic H); *m/z* (relative intensity) 731 (12%), 730 (14), 718 (14), 717 (14), 716 (22), 705 (16), 704 (19), 703 (33), 702 (68), 701 (63) and 700 (100).

A second, red band afforded (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **13** (16 mg, 16%) which was recrystallized from dichloromethane-hexane to afford fine red microcrystals, mp 301–303 °C. The characterization of this compound has been reported elsewhere.¹⁸

(b) Short reaction time. To a solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) **5** (59 mg, 0.083 mmol) in DMF (40 cm³) was added a solution of sodium methoxide in methanol (3.1 mol dm⁻³, 0.5 cm³) and the mixture was stirred for 1 min. The mixture was then diluted with dichloromethane (50 cm³), washed with water (6 × 100 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (4 cm diameter, 200 g) eluted with dichloromethane-light petroleum (2:3) to yield a front running blue-green band of trans-(2-methoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)nickel(II) **14** (18 mg, 29%, 56% based on consumed starting porphyrin) which was recrystallized from dichloromethane-hexane to afford small purple needles, mp > 350 °C (Found: C, 72.6; H, 4.5; N, 9.1. C₄₅H₃₁N₅NiO₃ requires C, 72.2; H, 4.2; N, 9.4%; ν_{\max} (Nujol)/cm⁻¹ 1550 (NO₂); λ_{\max} (CHCl₃)/nm 418 sh (log ϵ 4.99), 505 (3.50), 573 sh (3.78) and 609 (4.13); δ_{H} (400 MHz; CD₂Cl₂) 3.13 (3 H, s, OMe), 5.62 (1 H, s, 2-H), 6.55 (1 H, s, 3-H), 6.95–8.35 (10 H, v br m, 5-, 10-, 15- and 20-H_{o,m,p}), 7.56–7.70 (10 H, m, 5-, 10-, 15- and 20-H_{m,p}), 8.05 (1 H, d, *J* 5, β -pyrrolic H), 8.08 (1 H, d, *J* 5, β -pyrrolic H), 8.08 (1 H, d, *J* 5, β -pyrrolic H), 8.27 (2 H, ABq, *J*_{AB} 6, β -pyrrolic H), 8.39 (1 H, d, *J* 5, β -pyrrolic H) and 8.41 (1 H, d, *J* 5, β -pyrrolic H); *m/z* (relative intensity) 731 (16%), 707 (12), 706 (13), 705 (25), 704 (14), 703 (31), 702 (47), 701 (53) and 700

(100). A second band afforded starting nitroporphyrin **5** (28 mg, 47%).

Reaction between chloro(2-nitro-5,10,15,20-tetraphenylporphyrinato)iron(III) **6** and sodium methoxide

A solution of chloro(2-nitro-5,10,15,20-tetraphenylporphyrinato)iron(III) **6** (75 mg, 0.10 mmol) in DMF (8 cm³) was stirred under nitrogen with sodium methoxide (52 mg, 0.96 mmol) for 17 h. The mixture was diluted with dichloromethane (40 cm³), washed with water (7 × 40 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was taken up in dichloromethane (30 cm³) and poured into concentrated sulfuric acid (15 cm³). The mixture was stirred rapidly for 5 min then poured onto ice (150 g). The organic layer was separated, the aqueous phase was extracted with dichloromethane (3 × 50 cm³) and the combined organic phases were washed with water (2 × 100 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a preparative TLC plate developed in dichloromethane–light petroleum (7:3) to yield three major bands. The front running red–brown band afforded 2-methoxy-5,10,15,20-tetraphenylporphyrin **15** (3.4 mg, 5%), mp > 350 °C (Found: C, 83.9; H, 5.0. C₄₅H₃₂N₄O requires C, 83.8; H, 5.0%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1215, 1000 and 965; $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 418 (log ϵ 5.40), 514 (4.24), 547 (3.69), 588 (3.68) and 642 (3.22); $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ –2.83 (2 H, br s, NH), 3.98 (3 H, s, OMe), 7.63–7.80 (13 H, m, 5-, 10-, 15-, 20-H_{m,p} and 3-H), 8.00–8.05 (2 H, m, 20-H_o), 8.15–8.23 (6 H, m, 5-, 10- and 15-H_o), 8.69 and 8.81 (2 H, ABq, J_{AB} 5, β -pyrrolic H), 8.75 (2 H, s, 12- and 13-H), 8.76 and 8.85 (2 H, ABq, J_{AB} 5, β -pyrrolic H); m/z (relative intensity) 705 (M + ⁶³Cu, 14%), † 646 (26), 645 (60) and 644 (M⁺, 100).

The second brown band afforded demetallated starting porphyrin **3** (8 mg, 12%) and the third, brown band afforded 2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrin **11** (11 mg, 16%) which was crystallized from dichloromethane–hexane to afford purple–brown needles, mp 316–318 °C (Found: C, 78.4; H, 4.5; N, 10.4. C₄₅H₃₁N₅O₃ requires C, 78.4; H, 4.5; N, 10.2%); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 1520 (NO₂); $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 425 (log ϵ 5.37), 523 (4.20), 557sh (3.66), 596 (3.66) and 658 (3.68); $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ –2.83 (2 H, br s, NH), 3.83 (3 H, s, OMe), 7.65–7.80 (12 H, m, 5-, 10-, 15- and 20-H_{m,p}), 8.08–8.12 (2 H, m, 20-H_o), 8.16–8.24 (6 H, m, 5-, 10- and 15-H_o), 8.70 (2 H, s, β -pyrrolic H), 8.78 and 8.85 (2 H, ABq, J_{AB} 5, β -pyrrolic H) and 8.87 (2 H, s, β -pyrrolic H); m/z (relative intensity) 705 (M + ⁶³Cu – NO – CH₃ or M + ⁶³Cu + 2H – HNO₂, 13%), † 702 (13), 691 (25), 690 (60), 689 (M⁺, 100), 660 (15), 659 (25), 645 (27), 644 (53), 643 (23), 642 (13), 631 (12), 630 (25) and 629 (12).

(2-Hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) **16**

(a) **Reaction at room temperature.** A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (100 mg, 0.139 mmol) in DMF (2.5 cm³) was stirred with powdered sodium hydroxide (230 mg, 5.8 mmol) for 18 h. The mixture was then diluted with dichloromethane (50 cm³) and washed with water (6 × 50 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The crude product was then purified by preparative TLC, developed in dichloromethane, to afford a major broad green band (R_f 0.5) of (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** (52 mg, 51%) which was crystallized from dichloromethane–hexane to afford fine purple microcrystals, mp 336–338 °C (Found: C, 72.0; H, 3.7; N, 9.2. C₄₄H₂₇CuN₅O₃ requires C, 71.7; H, 3.7; N, 9.5%); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 3400 br (OH), 1598, 1565 (NO₂) and 1345

(NO₂); $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 436 (log ϵ 4.85), 563 (3.85) and 660 (3.80); m/z (relative intensity) 709 (21%), 708 (21), 707 (38), 695 (16), 694 (34), 693 (71), 692 (54), 691 (100), 690 (13) and 689 (13).

(b) **Reaction at 80 °C.** A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** and nitrobenzene (0.25 cm³, 1.7 mmol) in DMF (10 cm³) was stirred with sodium hydroxide (60 mg, 1.5 mmol) under nitrogen at 80 °C for 6 h. On cooling, the mixture was diluted with dichloromethane (50 cm³), washed with water (6 × 100 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (4 cm diameter, 50 g) eluted with dichloromethane–light petroleum (1:1) to yield a front running band of starting material **4** (11 mg, 22%), thence with dichloromethane–ethyl acetate (19:1) to yield a major band of (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** (28 mg, 54%, 68% based on consumed starting porphyrin). This product was identical in all respects to the sample prepared by Method A.

Reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) **4** and sodium benzyl oxide

A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (99 mg, 0.14 mmol) in DMF (30 cm³) was stirred with sodium benzyl oxide (202 mg, 1.55 mmol) under nitrogen for 40 h. The mixture was diluted with dichloromethane (100 cm³), washed with water (6 × 200 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a preparative TLC plate developed with dichloromethane–light petroleum (1:1) to yield five major bands.

The least polar red band afforded (2-benzyl-5,10,15,20-tetraphenylporphyrinato)copper(II) **19** (3 mg, 3%), mp 289–290 °C (Found: C, 78.5; H, 4.5; N, 7.3. C₅₁H₃₄CuN₄O requires C, 78.3; H, 4.4; N, 7.2%); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 1580 br, 1170, 1070 and 995; $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 420 (log ϵ 5.44), 506 sh (3.65), 545 (4.31) and 578 (3.76); m/z (relative intensity) 784 (40%), 783 (68), 782 (70) and 781 (M⁺, 100).

The next, blue–green band afforded (2,2-dibenzyl-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **17** (23 mg, 18%), which was recrystallized from dichloromethane–hexane to give small purple needles, mp 183–185 °C (Found: C, 74.6; H, 4.8. C₅₈H₄₀CuN₅O₂ requires C, 74.5; H, 4.4%; $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 1585, 1540 (NO₂) and 1340 (NO₂); $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 418 (log ϵ 5.31), 515 (3.60), 585 (3.97) and 618 (4.36); m/z (relative intensity) 783 (16%), 782 (15), 781 (23), 709 (16), 708 (14), 707 (27), 696 (19), 695 (44), 694 (53), 693 (100), 692 (44), 691 (66) and 690 (28).

The third, green band afforded starting nitroporphyrin **4** (6 mg, 6%), the fourth band contained (2-benzyl-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18** (8 mg, 7%) which was recrystallized from dichloromethane–light petroleum to give small purple needles, mp 290–291 °C (Found: C, 74.3; H, 4.1; N, 8.2. C₅₁H₃₃CuN₅O₃ requires C, 74.0; H, 4.0; N, 8.5%); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 1560 (NO₂), 1490 and 1335 (NO₂); $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 420 (log ϵ 5.39), 546 (4.22) and 583 (3.76); m/z (relative intensity) 783 (14%), 782 (18), 781 (18), 780 (14), 779 (25), 778 (25), 777 (36), 720 (11), 708 (13), 707 (24), 706 (13), 705 (19), 695 (18), 694 (34), 693 (68), 692 (57) and 691 (100).

The most polar, green band afforded (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** (21 mg, 21%), identical with authentic material by TLC and visible spectrum comparison.

Conversion of chlorin **17** into (2-benzyl-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18**

A solution of (2,2-dibenzyl-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **17** (42 mg, 0.045 mmol) in dichloromethane (50 cm³) was shaken with hydrochloric acid (7

† Mass spectra of these free base porphyrins contain peaks due to sequestering of copper(II) ions from the copper tubes of the spectrometer.

mol dm⁻³, 50 cm³) for 2 min. The organic layer was separated, washed with water (100 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness to yield (2-benzyloxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18** in quantitative yield. Recrystallization from dichloromethane–light petroleum afforded small purple needles. This product was identical in all respects with the authentic sample.

Conversion of porphyrin **18** into (2,2-dibenzyloxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **17**

A solution of (2-benzyloxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18** (53 mg, 0.064 mmol) in dry, distilled DMF (10 cm³) was stirred with sodium benzyl oxide (80 mg, 0.74 mmol) under nitrogen for 24 h. The mixture was diluted with dichloromethane (80 cm³), washed with water (6 × 200 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on preparative TLC plates developed with dichloromethane–light petroleum (1:1) to yield three bands. The least polar band afforded (2,2-dibenzyloxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **17** (26 mg, 43%). The second band contained the starting (2-benzyloxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18** (11 mg, 21%) and the third, polar, green band afforded (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** (14 mg, 30%). These products were identical in all respects with the authentic samples.

Benzylation of porphyrin **16** to give (2-benzyloxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18**

A solution of (2-hydroxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **16** (30 mg, 0.04 mmol) in a mixture of dichloromethane (10 cm³) and acetone (10 cm³) was stirred with benzyl bromide (1 cm³) and anhydrous potassium carbonate (150 mg) for 3 days. The mixture was then filtered and the solvent was removed by rotary evaporation. The residue was chromatographed on a silica column (1 cm diameter, 30 g) eluted with light petroleum (50 cm³) then dichloromethane–light petroleum (1:1) until the major red band was eluted to yield (2-benzyloxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **18** (30 mg, 89%). This product was identical in all respects with the authentic sample.

Reaction between (2-nitro-5,10,15,20-tetraphenylporphyrinato)-copper(II) **4** and sodium methoxide at elevated temperatures

(a) **Reaction at 50 °C.** A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (50 mg, 0.069 mmol) and nitrobenzene (0.25 cm³, 1.7 mmol) in DMF (10 cm³) was treated with a solution of sodium methoxide in methanol (3.1 mol dm⁻³, 0.3 cm³) and the mixture was stirred at 50 °C for 4 h. On cooling the mixture was diluted with chloroform (100 cm³), washed with water (5 × 200 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (4 cm diameter, 200 g) eluted with chloroform–light petroleum to yield four fractions. The first fraction afforded (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** (3 mg, 6%). The second fraction contained (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** (15 mg, 28%, 34% based on consumed starting porphyrin). The third fraction afforded starting nitroporphyrin **4** (9 mg, 18%) and the fourth fraction afforded (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (23 mg, 44%, 54% based on consumed starting porphyrin).

(b) **Reaction at 80 °C.** (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (50 mg, 0.069 mmol) was treated with sodium methoxide according to the procedure described above with the exception that the reaction was carried out at 80 °C for 1 h. The reaction yielded three major products after

chromatography. The first fraction contained (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** (6 mg, 21%), the second fraction afforded (2,2-dimethoxy-3-nitro-5,10,15,20-tetraphenyl-2,3-dihydroporphyrinato)copper(II) **8** (22 mg, 41%) and the third fraction contained (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (13 mg, 25%).

(c) **Reaction at 120 °C.** (2-Nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (50 mg, 0.069 mmol) was treated with sodium methoxide according to the procedure described above, with the exception that the reaction was carried out at 120 °C for 30 min. After chromatography three porphyrinic products were obtained from a multitude of minor products. The first fraction afforded (5,10,15,20-tetraphenylporphyrinato)copper(II) **20** (2 mg, 4%), mp > 350 °C, ν_{\max} (Nujol)/cm⁻¹ 1590, 1335, 1060 and 990; λ_{\max} (CHCl₃)/nm 416 (log ϵ 5.70), 541 (4.30) and 576 (3.43); m/z 679 (10%), 678 (33), 677 (69), 676 (69) and 675 (M⁺, 100). This is in agreement with the visible spectrum data of Dorough, Miller and Huennekens.⁵⁰

The second fraction afforded (2-methoxy-5,10,15,20-tetraphenylporphyrinato)copper(II) **10** (10 mg, 20%) and the third fraction afforded (2-methoxy-3-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **9** (7 mg, 13%).

(d) **Reaction at 153 °C.** A solution of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (100 mg, 0.139 mmol) in DMF (50 cm³) was refluxed with sodium methoxide (100 mg, 1.85 mmol) for 4 h. On cooling, the reaction mixture was diluted with dichloromethane (150 cm³), washed with water (6 × 100 cm³), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was chromatographed on a silica column (4 cm diameter, 250 g) eluted with chloroform–light petroleum (2:1). The front running red band afforded (5,10,15,20-tetraphenylporphyrinato)copper(II) **20** (46 mg, 49%, 53% based on consumed starting material). A second band afforded starting (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper(II) **4** (7 mg, 7%). All products obtained were identical with authentic samples.

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