Novel products from bromination reactions of 5,10,15,20-tetraisopropylporphyrins

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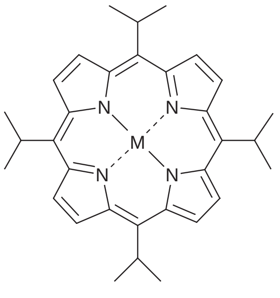
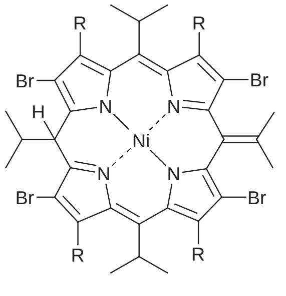
Bromination reactions of nickel(II) or copper(II) complexes of 5,10,15,20-tetraisopropylporphyrin afford the unusual porphodimethenes 2–5; crystallographic data for some of these compounds are presented and possible mechanisms for their formation are discussed.

2,3,7,8,12,13,17,18-Octahalo-5,10,15,20-tetraarylporphyrins have recently received considerable attention due to their usefulness as catalysts for the oxidation of organic substrates.[1] Although the syntheses and properties of these porphyrins have been extensively investigated, comparatively little is known about the bromination reactions of other porphyrins such as those with alkyl substituents. Bonnett *et al.*[2] have reported that halogenation of deuteroporphyrins preferentially yields peripherally as opposed to *meso* halogenated products, and that attempts to brominate 2,3,7,8,12,13,17,18-octaethylporphyrin (H_2OEP) resulted in bromodealkylation and benzylic-type subsitution reactions. Vicente and Smith[3] have also shown that treatment of H_2OEP with NBS in the presence of AIBN affords *trans*-(2-bromovinyl)heptaethylporphyrin, as well as (1-alkoxyethyl)heptaethylporphyrins when alcohols are present. We have recently described the novel chemical and spectroscopic properties of some 5,10,15,20-tetraalkylporphyrins with isopropyl or *tert*-butyl substituents.[4,5] We now show that one of these porphyrins also yields unexpected and unusual products upon bromination with NBS or Br_2.

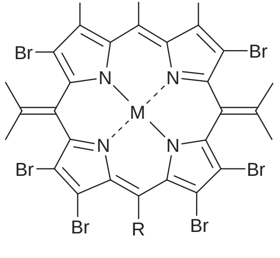
When the nickel(II) complex of 5,10,15,20-tetraisopropylporphyrin **1a** was treated with 8 equiv. of NBS, or excess Br_2 in $CHCl_3$ in the dark at room temperature, a dark green solid **2** was isolated as the major product in 7.2 and 46% yield, respectively. The structure of **2**, as determined by X-ray crystallography,‡ is shown in Fig. 1. The structure reveals a cyclic tetrapyrrole in which all of the pyrrole 3,4-positions have been brominated. Remarkably, the macrocycle is no longer a porphyrin but has a porphodimethene-like structure with two exocyclic double bonds on opposite *meso* positions. The molecule also adopts an extremely nonplanar ruffled conformation, with a maximum deviation of the 24 core atoms from the mean plane of 1.44 Å (for a *meso* carbon atom) and an average deviation from the mean plane of 0.57 Å. As is expected for such a nonplanar macrocycle, the average Ni–N distance is very short (1.88 Å). The absorption spectrum, which shows two broad bands at 482 nm (ε 48 100) and 594 (30 700), resembles that of 5,15-dimethyl-2,3,7,8,12,13,17,18-octaethyl-5H,15H-porphinato)nickel(II).[6] The ^1H NMR spectrum, which features two sets of methyl protons [δ 1.74 (d, 12H), 2.11 (s, 12H)] and one set of isopropyl methine protons [δ 4.42 (septet, 2H)], is consistent with the observed symmetrical structure.



1a M = Ni
b M = Cu



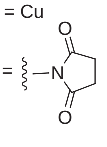
3 R = Br
4 R = H



2 M = Ni
R = CH(CH$_3$)$_2$

5 M = Cu

R =



When compound **1a** was treated with 8 equiv. or less of Br_2, two other compounds were also isolated. These materials did not yield crystals suitable for X-ray structure determination but the structures **3** (10% yield) and **4** (75%) were established from NMR experiments and mass spectral data. Both compounds share a common porphodimethene-type structure with one exocyclic double bond and one sp^3 *meso* carbon atom. Interestingly, in compound **4** the β-pyrrolic carbons have been brominated in a regiospecific fashion.

Only a few porphyrins bearing exocyclic double bonds have been described in the literature; these include a cyclic tetrapyrrole bearing four *meso* exocyclic carbonyl groups (octaethylxanthoporphyrinogen),[7] the exocyclic alkene analogue octaethyl-*meso*-tetrakis(methylene)porphyrinogen,[8] and certain oxidation products of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyirn described by Milgrom.[9] The formation of compounds with exocyclic double bonds from the bromination of **1a** suggests that the reaction may involve the addition of HBr or Br_2 across the opposite *meso* carbons of a partially brominated species, followed by elimination of one or two molecules of HBr, respectively, to yield compounds **3** and **4** or compound **2**. Addition of molecules to the porphyrin periphery in this fashion has previously been observed in

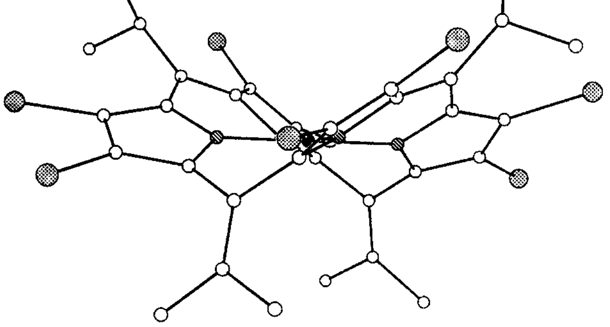


Fig. 1 Molecular structure of **2**. Hydrogen atoms are omitted for clarity.

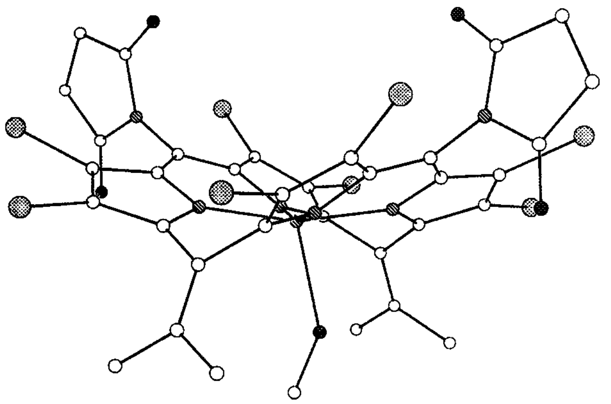


Fig. 2 Molecular structure of **5**. Hydrogen atoms are omitted for clarity.

5,10,15,20-tetra-*tert*-butylporphyrin and some of its metal complexes.[4] We believe that similar addition reactions may occur for compound **1a** because they result in a release of steric congestion between the *meso* isopropyl and the adjacent pyrrole bromo groups. In theory, bromination could also occur at the isopropyl benzylic positions *via* a radical mechanism when NBS is used as the brominating agent. If followed by elimination of the benzylic bromine atom and loss of a methine proton from the opposite isopropyl group, this would also furnish the two opposite exocyclic double bonds seen in compound **2**.

In order to investigate the effects of different metals on the bromination reaction, the copper(II) complex (**1b**) of 5,10,15,20-tetraisopropylporphyrin was treated with 8 equiv. of NBS in $CHCl_3$ in the dark at room temperature. One of three major products (**5**) isolated from this reaction gave high quality crystals enabling its definitive characterization by X-ray crystallography§ (Fig. 2). Compound **5** is similar to compound **2** in that all of the pyrrole positions have been brominated, and the macrocycle has a very ruffled porphodimethene-like structure; the maximum and average deviations of the 24 core atoms from the macrocycle mean plane in **5** of 1.27 and 0.51 Å, respectively, are slightly smaller than those seen for **2**. An unusual feature of the structure is that it no longer has any isopropyl groups attached to the porphyrin periphery! Instead, it bears two exocyclic alkene groups and two succinimido moieties. In addition, the copper atom is penta-coordinated, with a MeOH molecule serving as the fifth ligand (Cu–O 2.29 Å, Cu–$N_{average}$ 1.98 Å). This unusual axial ligation is presumably a consequence of the very electron-deficient nature of the macrocycle. It has previously been shown that 5-succinimido-OEP can be obtained when zinc(II)-OEP is treated with NBS in the presence of AIBN.[3] When *N*-chlorosuccinimide was used in place of NBS under the same conditions, however, only the mono- and di-*meso*-chloroporphyrins were obtained. This, and our current data, suggest that bromodeprotonation and bromodealkylation of the *meso* proton and isopropyl groups, respectively, could be intermediate steps in the formation of these unusual *meso*-succinimido products.

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Notes and References

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‡ *Crystal data* for **2** ($C_{32}H_{26}N_4Br_8Ni\cdot CH_2Cl_2$): crystals were grown by the slow diffusion of MeOH into a solution of **2** in CH_2Cl_2. The selected crystal was cut to dimensions of 0.22 × 0.14 × 0.06 mm for cell determination and data collection. The unit cell was triclinic, space group $P1$ with cell dimensions a = 11.6952(13), b = 13.214(3), c = 14.909(3) Å, α = 98.04(2), β = 106.547(14), γ = 115.526(14)°, V = 1899.0(6) $Å^3$, and Z = 2 (FW = 1249.5). Diffraction data were collected on a Siemens P4 diffractometer with a rotating anode [λ(Cu-Kα) = 1.54178 Å] at 130(2) K in $\theta/2\theta$ scan mode to $2\theta_{max}$ = 112.8°. Of 5310 reflections measured (+h, ±k, ±l), 5007 were independent (R_{int} = 0.081), and 4315 had $I > 2\sigma$ (T_{min} = 0.25, T_{max} = 0.55 °C, ρ_{calc} = 2.182 g cm^{-3}, μ = 12.14 mm^{-1}). The structure was solved by direct methods and refined (based on F^2 using all independent data) by full-matrix least-squares methods with 253 parameters (Siemens SHELXTL ver. 5.03). All bromines and the central nickel ion were refined with anisotropic thermal parameters; all other atoms were refined with isotropic thermal parameters. Hydrogen atom positions were generated by their idealized geometry and refined using a riding model. An empirical absorption correction was applied (XABS2) (ref. 10). The final difference map had a largest peak of 1.37 e $Å^{-3}$ and a largest hole of −1.19 e $Å^{-3}$. Final R factors were $R1$ = 0.054 (observed data) and w$R2$ = 0.147 (all data).

§ *Crystal data* for **5** ($C_{35}H_{23}N_6O_5Br_8Cu$): crystals were grown by the slow diffusion of MeOH into a solution of **5** in CH_2Cl_2. The single crystal was selected with dimensions of 0.46 × 0.22 × 0.10 mm. The unit cell was monoclinic, space group $C2/c$ with cell dimensions a = 26.977(4), b = 6.7493(14), c = 25.623(4) Å, β = 121.561(9)°, V = 3975.2(11) $Å^3$, and Z = 2 (FW = 1310.41). Diffraction data were collected on a Siemens P4 diffractometer with a rotating anode [λ(Cu-Kα) = 1.54178 Å] at 130(2) K in $\theta/2\theta$ scan mode to $2\theta_{max}$ = 113°. Of 3655 reflections measured (+h, +k, ±l), 2573 were independent (R_{int} = 0.077), and 2309 had $I > 2\sigma$ (T_{min} = 0.13, T_{max} = 0.41 °C, ρ_{calc} = 2.19 g cm^{-3}, μ = 10.65 mm^{-1}). The final difference map had a largest peak of 1.834 e $Å^{-3}$ and a largest hole of −1.287 e $Å^{-3}$. Final R factors were $R1$ = 0.0729 (observed data) and w$R2$ = 0.218 (all data). The structure was solved by direct methods and refined (based on F^2 using all independent data) by full-matrix least-squares methods with 136 parameters (Siemens SHELXTL V. 5.03). The bromines and the central nickel ion were refined with anisotropic thermal parameters. Hydrogen atom positions were generated by their idealized geometry and refined using a riding model. An empirical absorption correction was applied (XABS2) (ref. 10). CCDC 182/920.

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