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A Novel Oxygen Atom Transfer Reaction. Isomerization of Nickel(II) Octaethylporphyrin *N*-Oxide to Nickel(II) Octaethyloxochlorin

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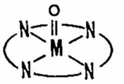
The heme group in heme proteins is subject to destruction by a variety of pathways. The transfer of functional groups from the metal to the porphyrin (particularly the transfer of an aryl group to form an *N*-aryl porphyrin) has proven to be one mode of porphyrin modification [1–7]. We have previously suggested that the transfer of an oxo group between the isomeric structures **1** and **2** may initiate the heme destruction produced by heme oxygenase [7].



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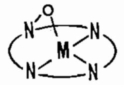

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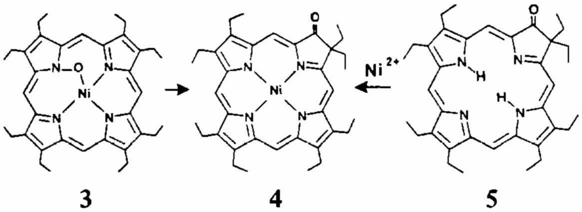
Consequently we have been exploring the chemical reactivity of a variety of metal complexes of porphyrin *N*-oxides [9] which embody structure **2** [8, 9].



3 **4** **5**

Here we report our observation of the thermal isomerization of nickel(II) octaethylporphyrin *N*-oxide, **3**, [8, 9] to nickel(II) octaethyloxochlorin, **4**. A xylene solution of **3** was heated under reflux in an argon atmosphere for 30 h. The solvent was removed by vacuum evaporation and the residue was subject to chromatography on silica gel. Elution with 1:1 hexane/benzene gave three bands containing material in a 5:2:3 ratio. The first, pink band contained nickel(II) octaethylporphyrin, the second, green band contained **4**, while the identity of the material(s) in the third, green band remains to be determined. Compound **4** has been identified on the basis of spectroscopic data and independent synthesis. The ^{1}H NMR spectrum of a chloroform-d_1 solution of **4** is shown in Fig. 1. The four meso resonances at 9.43, 9.36, 9.29 and 8.56 ppm are characteristic of the lower symmetry of the altered porphyrin. Likewise the observation of unique methyl and methylene resonances, which are shifted upfield of their more normal counterparts, are consistent with the presence of a markedly altered pyrrole ring. The electron impact mass spectrum of **4** shows a base (and parent) peak at *m/e* 606 (for ^{58}Ni) which confirms the molecular composition. The infrared spectrum shows a strong absorption at 1720 cm^{-1} due to the carbonyl group. This feature is not present in the infrared spectra of **3** or of nickel(II) octaethylporphyrin. The electronic spectrum of **4** is shown in Fig. 2. Absorption maxima occur at 373, 410, 506, 544, 572 and 618 nm. The intense absorption at 618 nm is characteristic of a chlorin structure.

Substance **4** has also been prepared by the insertion of nickel into the preformed octaethyloxochlorin **5**. The latter compound has previously been prepared by Fisher [10] and identified by Bonnett and coworkers [11]. Metal insertion was accomplished by treatment of **5** with nickel acetate in a boiling

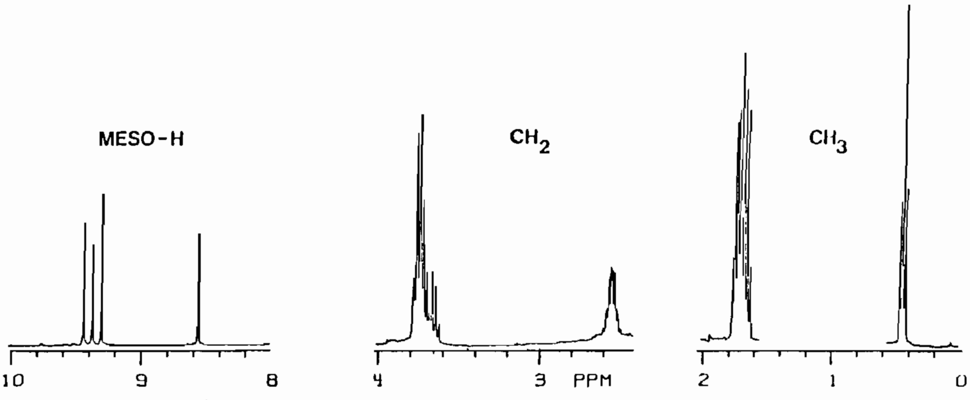


Fig. 1. The 360 MHz ^{1}H NMR spectrum of 4 in chloroform-d_1 at 25 °C.

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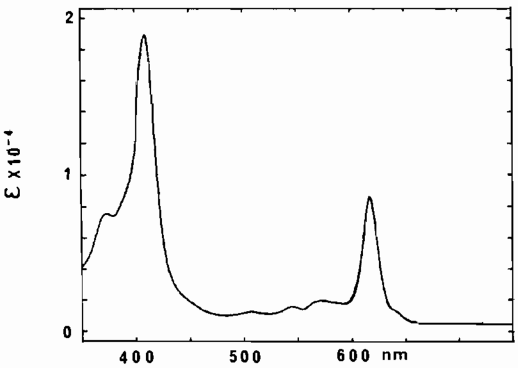

Fig. 2. The electronic spectrum of a dichloromethane solution of 4.

mixture of methanol/chloroform (1:7 *v*:*v*). The reaction was monitored by optical spectroscopy: the absorption at 642 nm due to **5** diminished as the absorption of **4** at 618 nm grew. The product was purified by chromatography on silica gel. The physical properties of the material obtained by nickel(II) insertion into **5** were identical in all respects to those of the material obtained by heating of **3**.

The mechanism of this novel isomerization of **1** to **2** is under study. If it proves to be an intramolecular process, then it will add to our suggestion that oxidative heme destruction can originate with the formation of a metal oxo species followed by migration of an oxygen atom across the porphyrin plane.

Acknowledgements

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