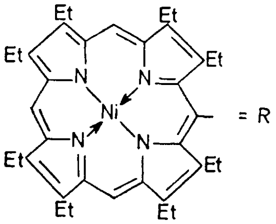
An Unusual Reaction of Nickel(II) *meso*-Hydroxymethyloctaethylporphyrin

By Dennis P. Arnold, Alan W. Johnson, and Manfred Winter
(*School of Molecular Sciences, University of Sussex, Falmer, Brighton* BN1 9QJ)

Summary The action of sulphuric acid on solutions of nickel(II)-*meso*-hydroxymethyloctaethylporphyrin causes reductive dimerisation to 1,2-bis[nickel(II) octaethyl-*meso*-porphyrinato]ethane.

In connection with another research topic, we heated a solution of the title compound (I) in *NN*-dimethylformamide with sulphuric acid (2—3 mol) under reflux conditions and obtained in *ca.* 50% yield a crystalline nickel-containing product which contained no oxygen. The ^{13}C n.m.r. spectrum suggested that the product was a *meso*-substituted alkyl derivative of nickel(II) octaethylporphyrin, with one quaternary *meso*-carbon at 112·75 p.p.m., two unsubstituted *meso*-carbons at 96·49 p.p.m., and one unsubstituted *meso*-carbon at 95·71 p.p.m. The ^{1}H n.m.r. and electronic spectra supported this conclusion, and the base peak in the mass spectrum appeared at *m/e* 604, the molecular weight of nickel(II) *meso*-methyloctaethylporphyrin. However, this compound was synthesised and shown to be different from the product from the acid reaction. Further examination of the mass spectrum of this product revealed the molecular ion at *m/e* 1206—1210, and this fact, together with the presence of a single methylene ^{13}C resonance at 36·94 p.p.m., has led us to formulate the product as 1,2-bis[nickel(II) octaethyl-*meso*-porphyrinato]ethane (III). The protons of the ethane bridge (integration ratio to *meso*-protons 2 : 3) appear as a singlet at 3·91 p.p.m. in the ^{1}H n.m.r. spectrum. A similar reaction of hydroxymethylferrocene has been reported,[1] where strong acids cause the formation of 1,2-bisferrocenylethane.

RCH_2OH	(I)
RMe	(II)
RCH_2CH_2R	(III)
RCH_2OEt	(IV)
RCH(OH)Me	(V)
$RCH{=}CH_2$	(VI)



The relative conformations of the porphyrin rings of (III) have not yet been determined but interactions between the rings are suggested by various spectral properties. In the n.m.r. spectrum ($CDCl_3$) of (III), the singlets for the two types of *meso*-hydrogens are abnormally separated ($\Delta\delta$ 0·18 p.p.m.), and there are also large upfield shifts ($\Delta\delta$ 1 p.p.m.) for the ethyl methylene groups adjacent to the ethane bridge. In the electronic spectrum the contributions from the two porphyrin rings were additive (*e.g.*, ϵ, 421 nm, 261,800).

Compound (III) was also obtained from the *meso*-ethoxymethyl derivative (IV) by a similar reaction and it has been shown that 1,2-dimethoxyethane or *NN*-dimethylacetamide can be substituted for *NN*-dimethylformamide as solvent. On the other hand, sulphuric acid treatment of (V) gave only the *meso*-vinyl derivative (VI). The presence of the metal was necessary for the formation of the dimeric product (III), as acid treatment of metal-free *meso*-hydroxymethyloctaethylporphyrin[2] gave a mixture of *meso*-formyl and *meso*-methyl-octaethylporphyrin as well as octaethylporphyrin itself.

The dimerisation reaction is viewed as involving an electron transfer from the metal to the primary carbonium ion giving the carbon radical which then dimerises. Reduction of the nickel(III) species may then be achieved either by the solvent or by a disproportionation reaction.

We thank S.R.C. for a Postdoctoral award (to D.P.A.).

(*Received*, 26*th July* 1976; *Com.* 842.)

---

[1] K. L. Rinehart, C. J. Michejda, and P. A. Kittle, *J. Amer. Chem. Soc.*, 1959, **81**, 3162.

[2] H. H. Inhoffen, J.-H. Fuhrhop, H. Voight, and H. Brockmann, Jr., *Annalen*, 1966, **695**, 133.