Novel Mercury(II) Porphyrins: Identification of Porphyrin Primary 'Type-isomers'

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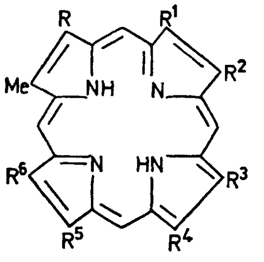
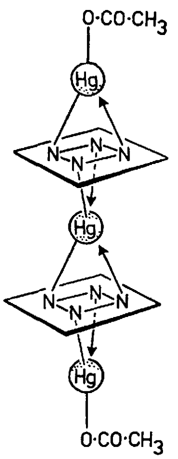
Summary N.m.r. spectroscopy of some novel mercury(II) porphyrins is used to differentiate between the individual aetio- and copro-porphyrin 'type-isomers;' the unusual 'double-sandwich' structure (**1**) is proposed for these chelates.

NORMAL one-to-one chelates are obtained[1] when porphyrins are treated with mercury(II) acetate (in pyridine). We now report details of novel mercury(II) porphyrins for which, on the basis of spectroscopic and analytical evidence, we propose the generic 'double-sandwich' structure (**1**); in addition, some features of the ^{1}H n.m.r. spectra of these chelates allow the unambiguous identification of the four primary type-isomers of porphyrins.



(**2**) R = Et (**3**) R = $CH_2{\cdot}CH_2{\cdot}CO_2Me$
a; $R^1 = R^3 = R^5 = Me$; $R^2 = R^4 = R^6 = R$
b; $R^1 = R^4 = R^5 = R$; $R^2 = R^3 = R^6 = Me$
c; $R^1 = R^3 = R^6 = Me$; $R^2 = R^4 = R^5 = R$
d; $R^1 = R^3 = R^6 = R$; $R^2 = R^4 = R^5 = Me$

Treatment of aetioporphyrin-I (**2a**)[2] with mercury(II) acetate in tetrahydrofuran and methylene chloride rapidly gave a complex with a visible absorption spectrum [λ_{max} 406 nm (ϵ 158,000), 545inf (9000), 570 (11,000), and 607sh (4500)] at variance with the spectrum expected for a mercury(II) porphyrin. The i.r. spectrum of the crystalline product featured a strong broad band at 1580 cm^{-1} (KBr), characteristic[3] of a metal-bound acetate group, and indicating that only one of the acetate functions had been displaced from the metal by the porphyrin ligand. This was confirmed by the ^{1}H n.m.r. spectrum, which showed a sharp singlet[†] at τ 10·24; this chemical shift was as expected[3] for a metalloporphyrin with an axial acetate ligand. Additionally, the *meso*-proton resonances (Table) were considerably upfield from the normal position (*e.g.*, ref. 3). The most surprising feature of the n.m.r. spectrum of the aetioporphyrin-I chelate was the 1:1 doublet for the methyl groups; a singlet would be expected for the methyl groups of a regularly substituted porphyrin such as aetioporphyrin-I. Elemental analysis suggested a molecular composition corresponding to two porphyrin groups, three mercury atoms, and two acetate functions.[‡] An independent mercury analysis gave values compatible with this composition.[§]



(**1**)

FIGURE. *Schematic representation of mercury chelates.*

On the basis of the above evidence, we propose the generic 'double-sandwich' structure (**1**) for this chelate. The high-field *meso*-proton resonances can be rationalised by taking into account the anisotropic effect of one porphyrin ring above another,[4] and the doublet methyl resonances are presumably observed because of the existence of diastereoisomers in the aetioporphyrin-I case.

TABLE. *Proton chemical shifts* (τ) *of diagnostic peaks in mercury chelates* (**1**).

Mercury(II) complex of	*meso*-H[a]	Ring methyl groups
(**2a**)	1·03	6·52, 6·55
(**2b**)	0·96, 1·00	6·49
(**2c**)	0·82, 0·93, 1·12, 1·18	6·40, 6·49, 6·52, 6·58[b]
(**2d**)	0·84(1), 1·13(2), 1·42(1)	6·54, 6·71
(**3a**)	0·93	6·33, 6·35
(**3b**)	0·97, 0·99	6·51
(**3c**)	0·90, 0·95, 1·08, 1·13	6·4—6·8 (m)
(**3d**)	0·76(1), 0·99(2), 1·13(1)	6·40, 6·53

[a] Satellite peaks were observed, due to ^1H—^{199}Hg couplings (*J ca.* 10 Hz). Figures in parentheses refer to relative peak intensities. [b] Additional fine structure observed.

The Table shows some of the chemical shifts for the chelates (**1**) derived from the aetioporphyrins (**2**) and coproporphyrin tetramethyl esters (**3**). All the spectra are compatible with the structure (**1**) and it is interesting to note the way in which the normal differences in the n.m.r.

[†] Integrated intensity, three protons per porphyrin ligand.

[‡] Depending upon the crystalline form and solvents used in crystallisation, these chelates can be obtained either anhydrous or bearing two molecules of water (combustion analysis). It is not certain that these water molecules, when present, are co-ordinated to the metal atoms. The determination of the precise geometrical arrangements and bond orders in these chelates await single crystal *X*-ray studies. All eight mercury(II) chelates (**1**) described herein gave satisfactory combustion analyses.

[§] Found: Hg, 35·3 ± 1%. $C_{68}H_{78}Hg_3N_8O_4$ requires: Hg, 36·0%.

spectra of porphyrin type-isomers are often exaggerated in the new mercury complexes. This allows, for the first time, the unambiguous differentiation of the aetioporphyrin type-isomers, and the detection of mixtures of isomers. One consequence of this is the fact that the aetioporphyrin-II, prepared by Fischer's method[5] from 3,3′-diethyl-4,4′-dimethylpyrromethane-5,5′-dicarboxylic acid in hot formic acid, is a mixture of type-isomers.¶ Indeed, we have also shown that similarly prepared[7] coproporphyrin-II tetramethyl ester is an isomeric mixture; we believe that other porphyrins prepared by this general method (*e.g.* ref. 8) are also mixtures of the four possible type-isomers.

Molecular weights of the chelates (**1**) were not accessible from their mass spectra. The highest-mass fragments observed were of the constitution porphyrin–mercury–acetate; a significant feature of these mass spectra was, however, loss of the metal atom to give the free porphyrin ligand, usually as the base peak.[9]

Treatment of the chelates (**1**) with pyridine resulted in collapse to the 'normal' chelates (λ_{max} 421, 555, and 586 nm). When this was carried out in the presence of 1 equiv. of metal-free porphyrin, spectrophotometry revealed no evidence of free porphyrin; in the presence of 2 equiv. of metal-free porphyrin, a pyridine solution of (**1**) consumed approximately one half of the added porphyrin. This confirmed the excess of one mercury atom over porphyrin ligands in the chelates (**1**).

Both a mono-rhenium and a di-rhenium porphyrin (the latter with the metal atoms either side of the porphyrin plane) have been proposed[10] as good models for the intermediates of metal insertion into the porphyrin ligand. We believe that the chelate (**1**) is another such model, particularly in view of the ease with which it may be decomposed into the normal chelate.

We see no reason why the generic structure (**1**) should be unique to mercury(II) porphyrins and investigations of other metals are in hand.

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¶ The n.m.r. spectrum of the metal-free porphyrin was apparently compatible with an isomerically pure product; however, the spectrum of the mercury chelate (**1**) (prepared from the same sample) was not that of isomerically pure material[6] (Table) but rather was identical to that of the chelate prepared from the random mixture of type-isomers obtained by polymerisation of the appropriate monopyrrole.

[1] *Cf.* J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964; J. R. Miller and G. D. Dorough, *J. Amer. Chem. Soc.*, 1952, **74**, 3977.

[2] K. M. Smith, *J.C.S. Perkin I*, 1972, 1471.

[3] *Cf.* J. W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H. H. Schneehage, and D. Weck, *Annalen*, 1971, **745**, 133; R. J. Abraham, G. H. Barnett, and K. M. Smith, *J.C.S. Perkin I*, in the press.

[4] However, only a small downfield shift of the resonances was observed upon dilution: *cf.* R. J. Abraham, G. H. Barnett, E. S. Bretschneider, and K. M. Smith, *Tetrahedron*, 1973, **29**, 553 and refs. therein.

[5] H. Fischer and H. Orth, 'Die Chemie des Pyrrols,' Akademische Verlag., Leipzig, Vol. IIi, 1937, p. 197.

[6] M. F. Hudson and K. M. Smith, unpublished results.

[7] Ref. 5, p. 488.

[8] A. Treibs and L. Schulze, *Annalen*, 1971, **751**, 127.

[9] *Cf.* K. M. Smith, *Org. Mass Spectrometry*, 1972, **6**, 1401.

[10] R. Khosropour and P. Hambright, *J.C.S. Chem. Comm.*, 1972, 13; D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Coordination Chem.*, 1972, **2**, 101.