

NOVEL MERCURY(II) PORPHYRINS - II:¹ MERCURY(II) CHELATES
OF meso-TETRAPHENYLPORPHYRIN AND N-METHYLPORPHYRINS

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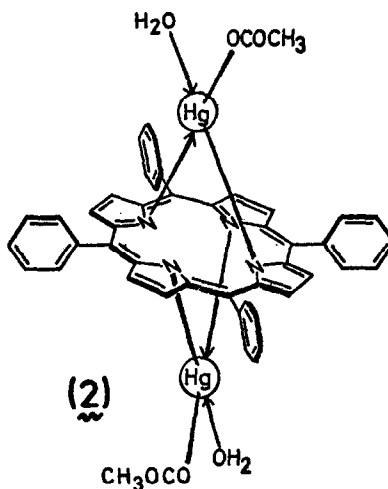
Several examples of metalloporphyrins in which two metal atoms are bound to one porphyrin molecule have been described.² Since the best explanation³ of the mechanism for metal insertion into the porphyrin ligand is that which postulates deformation of the macrocycle with a metal ion (or a proton) while the inserting metal ion approaches in an SN_2 manner from the other face of the molecule, these mononuclear dimetallic species have, in some instances, been likened to intermediates in the metal insertion process.

Recently, we published¹ details of novel mercury(II) porphyrins for which, in the absence of suitable crystals for X-ray analysis, we postulated a generic dinuclear trimetallic "double sandwich" structure, $AcO-Hg-Por-Hg-Por-Hg-OAc$ (1), (Por = aetio- or coproporphyrin). We considered also that these compounds were candidates as intermediates in the metallation reaction.

On account of protracted difficulties in obtaining suitable crystals for absolute structural analysis we began chemical studies to substantiate our "double sandwich" structure and we now report two further examples of novel mercury(II) porphyrins. It was anticipated that because of the tendency of the phenyl rings in meso-tetraphenylporphyrin (TPPH₂) to be almost at right angles to the plane of the macrocycle (below ca. 60°C), the "double sandwich" complex derived from TPPH₂ would be unstable owing to steric repulsions between the phenyl groups of the layered porphyrins. Indeed, under our experimental conditions, such a compound cannot be obtained in the TPP series; treatment of TPPH₂ with an excess of mercury(II) acetate in tetrahydrofuran - methylene chloride gave a chelate to which the structure (2) was

assigned on the evidence of its elemental analysis and spectroscopic data. The NMR spectrum was similar to that of TPPH_2 itself, without non-equivalence of the *o*-phenyl protons and implying a symmetrical arrangement of the two metal atoms; a sharp acetate resonance (integrated intensity 6 protons per porphyrin ligand) appeared at τ 9.44. The infrared spectrum (KBr disc) featured a strong band at 1565 cm^{-1} , readily assigned quantitatively to two metal bound acetates in the molecule. Visible absorption spectrum: (CHCl_3), 447 nm (ϵ 427,500), 525 (3100)sh, 558 (8300), 581 (11,600), 603 (10,500)sh, and 641 (4800).

Further evidence for structure (2) was obtained from its treatment with pyridine in the presence of 1 equivalent of TPPH_2 to give pyridine monomercury TPP (py.HgTPP); approximately one half of the added TPPH_2 was consumed when the same experiment was carried out in presence of 2 added equivalents of TPPH_2 . Treatment of (2) with tetrahydrofuran - methylene chloride caused collapse to HgTPP .



N-Methylporphyrins should also be incapable of furnishing "double sandwich" complexes since one of the nitrogen atoms is blocked. Though a dinuclear monometallic complex is possible, treatment of *N*-methyloctaethylporphyrin (or *N*-methylaetioporphyrin-I) with various quantities of mercury(II) acetate in tetrahydrofuran - methylene chloride gave only the mononuclear chelates (3). These compounds gave satisfactory elemental analyses and their NMR spectra (Figure) featured sharp 3-proton singlets around τ 9.9 due to the acetate ligands. In addition, the infrared spectra (KBr disc) showed strong bands at 1580 and 685 cm^{-1} . These NMR and infrared measurements are similar to those of other metalloporphyrins possessing metal-bound acetate ligands.⁴ The *N*-methyl group in compounds (3) resonated at ca. τ 15.0 ($J_{\text{H-}^{199}\text{Hg}} \sim 10\text{ Hz}$) (cf. *N*-Me group at $14.61\tau^5$ in zinc^{II} *N*-methyloctaethylporphyrin chloride).

We consider that the identification of the porphyrins (2) and (3) adds weight to our proposal of the "double sandwich" structure for aetio-, copro-, and other porphyrins, since TPPH_2 and *N*-methylporphyrins have constraints within them which might reasonably be

expected to prevent formation of the dinuclear trimetallic chelates (1). Even more evidence for this structure has been obtained⁶ from INDOR ^1H [^{199}Hg] experiments; the chelate (1) prepared from aetioporphyrin-I showed two mercury signals at 17.8866 and 17.8854 MHz (intensities ca. 1:2), whereas compound (3a) showed only one signal at 17.8898 MHz.

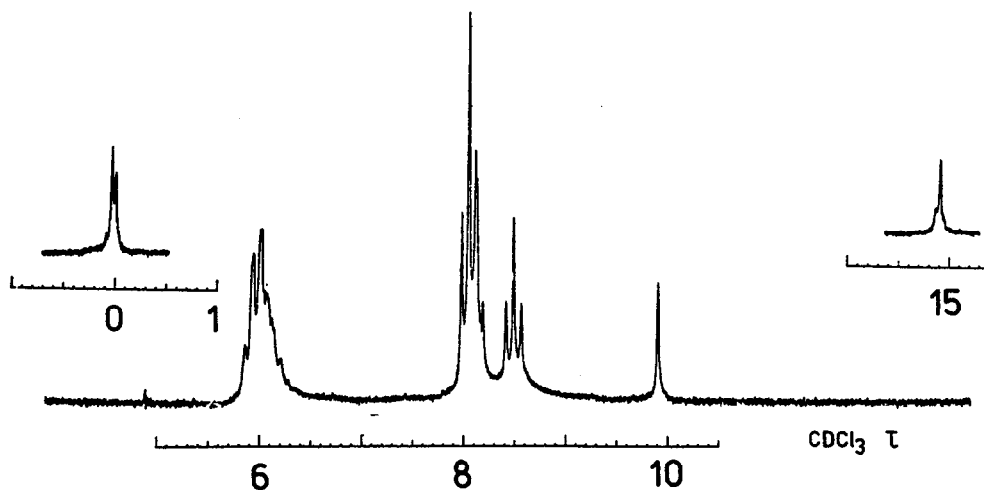
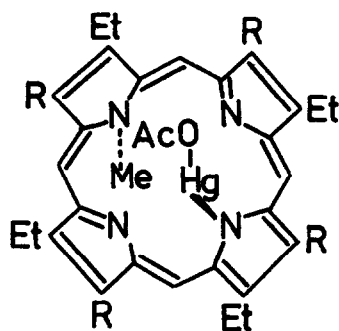


Figure: NMR Spectrum of (3a)



(3)

a; R = Et

b; R = Me

Whether or not molecules such as (1) and (2) are reasonable models for the intermediates of metal insertion into the macrocycle is currently under debate. If one seriously considers the mononuclear dimetallic chelates² in these terms then the "double sandwich" complexes (1) must also be considered, since we were only able to prepare the species (2) under conditions which would not enable (1) to be obtained. In our opinion, metal insertion in concentrated solution (which are the normal conditions for metallation) is a highly co-operative phenomenon between layers of porphyrin molecules and metal ions.⁷ The isolation of compounds with the structures (1) and (2) was possible as a result of peculiar stability factors associated with geometries of mercury and ligand orbitals somewhere along or near the reaction co-ordinate for metal insertion. The ease of decomposition of (1) and (2) to mononuclear monometallic chelates also supports this argument, as does the work described in the accompanying paper.

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