

NOVEL MERCURY(II) PORPHYRINS - III:<sup>1</sup> METAL TRANSFER DURING  
DEMETALLATION OF meso-TETRAPHENYLPORPHYRINATOMERCURY(II)

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meso-Tetraphenylporphyrinatomercury(II) (HgTPP) can be prepared by treatment of meso-tetraphenylporphyrin (TPPH<sub>2</sub>) with mercury(II) acetate in pyridine, followed by removal of the pyridine ligand from the resulting py.HgTPP.<sup>2</sup> We have found that HgTPP can be prepared directly by reaction of TPPH<sub>2</sub> with one equivalent<sup>3</sup> of mercury(II) acetate in tetrahydrofuran - methylene chloride; the product,  $\lambda_{\text{max.}}$  (CHCl<sub>3</sub>), 426 (ε 415,000), 487 (6250)sh, 519 (7400)inf, 549 (9500), 590 (4500)sh, and 647 nm (2600), was identical with authentic material<sup>2</sup>, gave a satisfactory elemental analysis and mass spectrum, and showed no evidence of acetate ligands in its NMR or infrared spectra.<sup>3</sup>

In acid free methylene chloride, HgTPP is stable. However, in methylene chloride containing traces of dry hydrogen chloride (or better, in methylene chloride which has been allowed to stand in clear glass bottles in daylight), a series of transformations occur which can be readily observed by repeated-scan spectrophotometry. The overall process involves demetallation of HgTPP to give free base TPPH<sub>2</sub>.

Figure 1 shows the Soret region of the visible absorption spectrum of HgTPP in methylene chloride containing a trace of hydrogen chloride. Band A (HgTPP) rapidly disappears, giving rise to approximately equal amounts (cf. Figure 2)<sup>4</sup> of two new species B and C. With time (Figure 2), band B increases at the expense of band C. We have positively identified band B as TPPH<sub>2</sub>, and on the basis of our characterisation of  $\mu$ -meso-tetraphenylporphyrinato-bis[aquomercury(II) acetate], (AcO-Hg-TPP-Hg-OAc), we assign band C to the corresponding dichloride (Cl-Hg-TPP-Hg-Cl). The di-acetate underwent transformations similar to those in Figure 2 when dissolved in methylene chloride containing small amounts of hydrogen chloride (Figure 3)(compare isosbestic points).

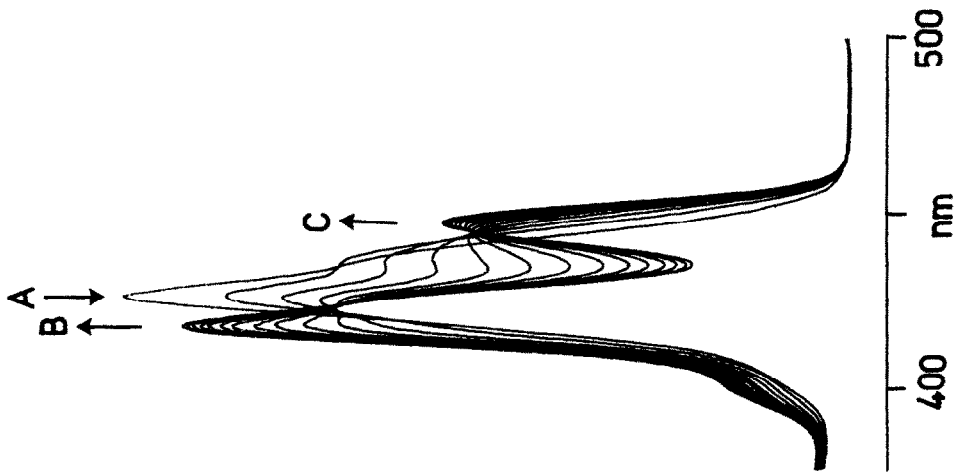


Figure 1

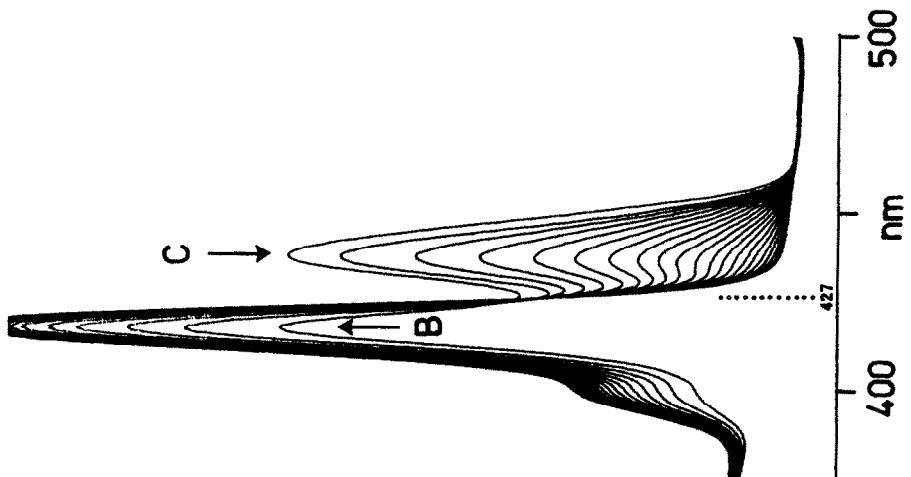


Figure 2

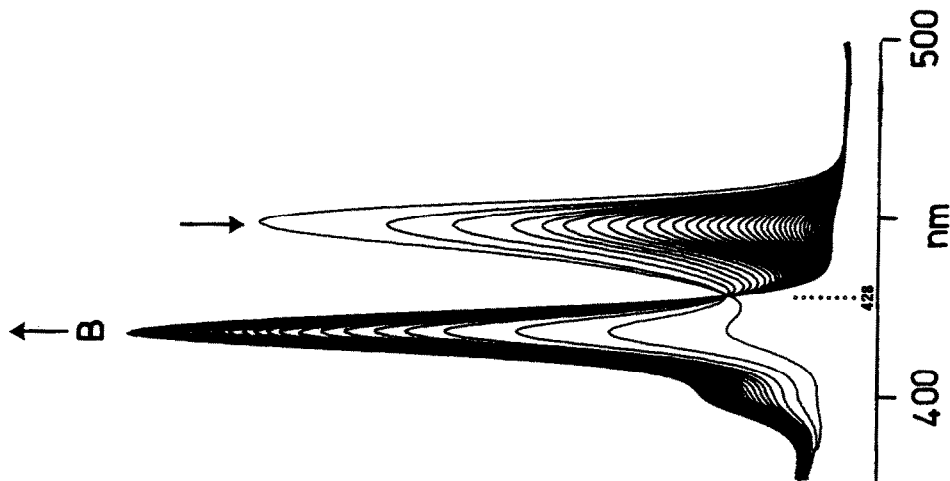
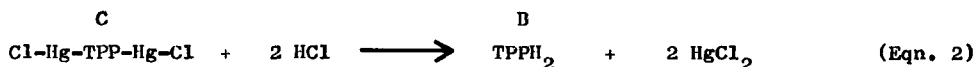
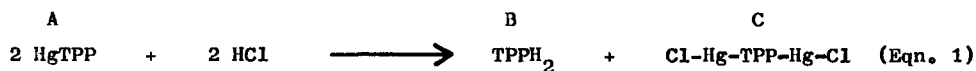


Figure 3

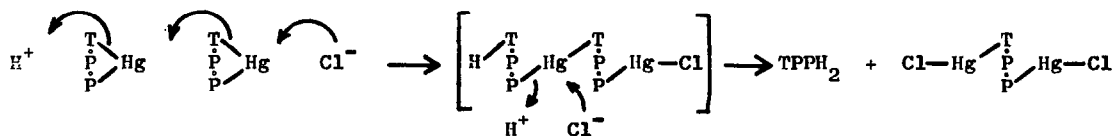
AcO·Hg·TPPHg·OAc → TPPH<sub>2</sub>

In solutions containing larger amounts of acid, HgTPP was transformed directly into  $\text{TPPH}_4^{2+}$  without detection of any intermediates. Isosbestic points were not obtained in Figure 1 because of the presence of three overlapping and altering absorptions; however, Figure 2 shows clean transformation of C into B.

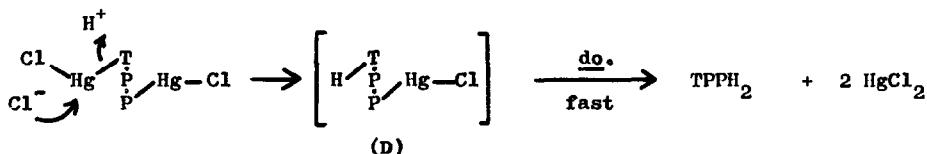
The transformations occurring in Figures 1 and 2 can be interpreted in terms of metal transfer during demetallation:



Tentative suggestions for the mechanisms occurring within Eqns. 1 and 2 can be made. Since demetallation of zinc(II) porphyrins is thought<sup>5</sup> to proceed by protonation of the chelate, followed by loss of the metal ion from the other face of the molecule, Eqn. 1 can be broken down as follows:



Similarly with Eqn. 2:



Alternative identities for band C in Figures 1 and 2 are the mononuclear species (D), obtained by protonation of HgTPP, or the dication,  $\text{TPPH}_4^{2+}$ . The former possibility is excluded by the spectroscopically determined stoichiometry of the reaction whereby one mole of  $\text{TPPH}_2$  and one mole of C are produced (cf. Eqn. 1) from HgTPP; the second possibility was ruled out by monitoring the reactions in the visible region 500-700 nm, no evidence of the characteristic spectrum of  $\text{TPPH}_4^{2+}$  being observed. In any case, deprotonation of  $\text{TPPH}_4^{2+}$  in acid solution to give  $\text{TPPH}_2$  (Figure 2) is unlikely.

It is significant that the mononuclear dimetallic species (C) which is identified herein as an intermediate in the acid catalysed demetallation of HgTPP is similar to those which have been proposed<sup>6,7</sup> as models for the intermediate of metal insertion into the porphyrin macrocycle. In addition, analogues of the monohydrogen species (D) have actually been isolated by Tsutsui and his co-workers.<sup>7</sup> Reversibility of the arrows in Eqns. 1 and 2 would broadly account for both the metallation and demetallation phenomena in certain cases, particularly when the metal ion has a large ionic radius.

#### REFERENCES

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- 4 Figure 2 was derived from a separate experiment (from Figure 1) involving use of methylene chloride containing slightly more acid; in this way the decomposition of material in band A was hastened to give an approximately 1:1 mixture of bands B and C. In Figure 1, decomposition of band A to give B and C is being complicated by the concurrent transformation of band C into band B.
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