

NOVEL MERCURY(II) COMPLEXES OF MESO-TETRAPHENYLPORPHYRIN AND N-METHYLPORPHYRINS¹

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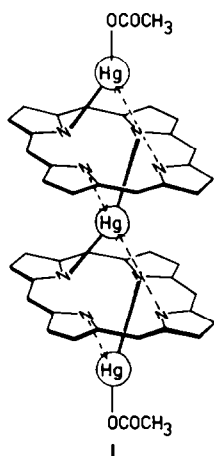
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Abstract—Treatment of *meso*-tetraphenylporphyrin, H₂TPP, with just over one equivalent of mercury(II) acetate in methylene chloride-THF gives mercury(II) *meso*-tetraphenylporphyrin, HgTPP. With excess of mercury(II) acetate, H₂TPP and HgTPP afford a novel dimetallic mononuclear porphyrin, AcO-Hg-TPP-Hg-OAc. In contrast, HgTPP reacts with mercury(II) chloride to give the chloro-analogue, Cl-Hg-TPP-Hg-Cl, but there is no reaction between H₂TPP and mercury(II) chloride. Demetallation of HgTPP in methylene chloride containing small amounts of hydrogen chloride proceeds via the dimetallic compound, Cl-Hg-TPP-Hg-Cl, to give free base HTPP. The reaction rate is dependent upon acid concentration suggesting that the rate determining step is protonation, but dilution causes no decrease in the rate; a mechanism which invokes the intermediacy of monohydrogen-*meso*-tetraphenylporphyrinatomercury(II) chloride, H(TPP)HgCl, in the formation of Cl-Hg-TPP-Hg-Cl and in its subsequent decomposition into H₂TPP, is proposed.

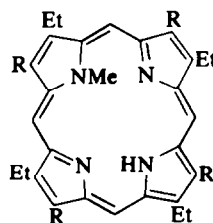
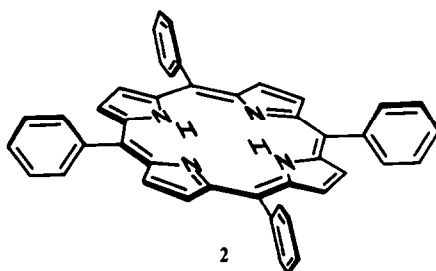
N-Methylporphyrins react with mercury(II) acetate in methylene chloride-tetrahydrofuran to give the corresponding N-methylporphyrinatomercury(II) acetates, Me(P)HgOAc.

An earlier paper² described the isolation of novel mercury(II) complexes of octa-alkylporphyrins which, on the evidence of physical and spectroscopic data, were assigned the unique "double-sandwich" generic structure (1). On account of difficulties in obtaining a crystal



suitable for absolute structural assignment by X-ray methods, we were prompted to investigate other chemical methods in order to add further confirmation to our structural proposal (1). In this paper we describe the formation of and propose structures for novel mercury(II) complexes of *meso*-tetraphenylporphyrin (2) (H₂TPP) and N-methylporphyrins (3). Though a negative approach, we reasoned that if our proposal concerning (1) was correct then neither H₂TPP nor N-methylporphyrins should form this type of complex when treated with mercuric acetate under those conditions which are successful in the octa-alkylporphyrin series;² because of the tendency, both in solution at room temperature³ and in the crystal,⁴ for the phenyl ring planes in H₂TPP (2) to be nearly at right angles to the porphyrin ring plane, and because N-methylporphyrins are "blocked" with respect

to complexation on the N-Me substituted side we considered that formation of complexes with mercuric acetate which showed any spectroscopic or physical similarities with those from octa-alkylporphyrins² would be evidence against structure (1). In the event, H₂TPP and the N-methylporphyrins (3) from the octaethyl- and aetioporphyryn-I series formed quite different complexes, and one of these in the H₂TPP case may be significant in some mechanisms for metal insertion into the porphyrin ligand.⁵



a: R = Et
b: R = Me

Steric hindrance to layering in the H₂TPP series has been noted previously. H₂TPP and its zinc(II) complex in methylcyclohexane solution do not dimerise at low temperatures⁶ (220–140°K), whereas aetioporphyryn, octaethylporphyrin, and their zinc(II) complexes do. More recently, the ruthenium porphyrin dimer has been shown⁷ not to form in the H₂TPP case.

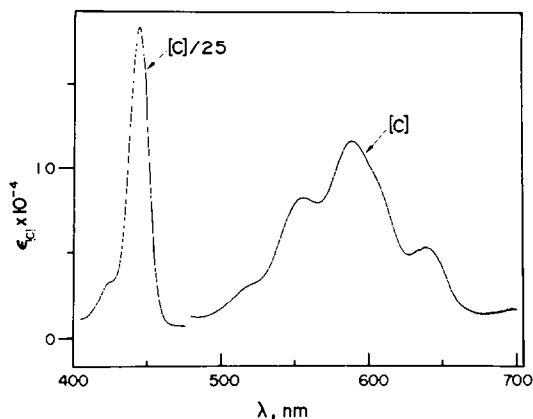
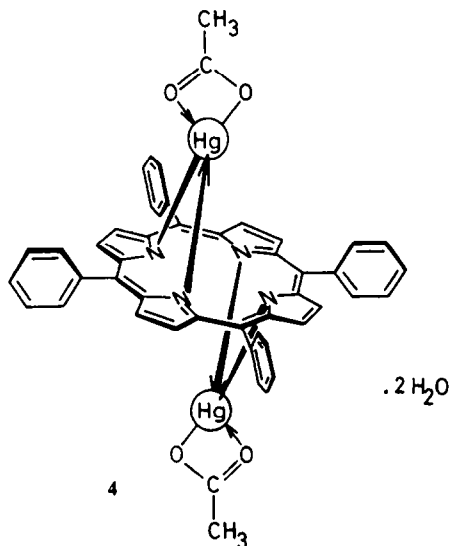


Fig. 1. Visible absorption spectrum, in $\text{CH}_2\text{Cl}_2/\text{THF}$ of AcO-Hg-TPP-Hg-OAc (4).

Treatment of H_2TPP with a five molar excess of mercury(II) acetate in methylene chloride-THF afforded a metal complex, the visible spectrum (Fig. 1) of which resembled neither the "double-sandwich" species (taking into account the normal spectroscopic differences between octaethylporphyrin and *meso*-tetraphenylporphyrin) nor that for monometallic HgTPP .⁸ The combustion analysis indicated that the product was μ -*meso*-tetraphenylporphyrinato-bis [mercury(II) acetate] (4). The NMR spectrum of this compound (4) was similar to that of H_2TPP itself, the *ortho*-phenyl protons being

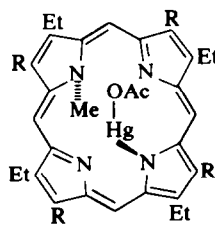


equivalent and suggesting a symmetrical arrangement of the two metal atoms. The two acetate ligands were evidenced by a six proton singlet at τ 9.44, and by a very intense absorption band in the IR spectrum at 1565 cm^{-1} (KBr) typical of a metal-bound bidentate acetate.²

A grass green solution similar to that reported⁹ for $\text{py} \rightarrow \text{HgTPP}$ was obtained when a solution of 4 was treated with pyridine. When an equimolar mixture of H_2TPP and $(\text{AcO-Hg})_2\text{TPP}$ (4) was treated with pyridine the absorption spectrum of the solution showed no sign of

free porphyrin; if the same experiment was carried out using 2 moles of H_2TPP and only one of $(\text{AcO-Hg})_2\text{TPP}$ there was evidence of uncomplexed free H_2TPP , indicating that compound 4 contains approximately one Hg atom in excess of the expectation for a monometallic complex.

With N-methylporphyrins (3), HMe(P) , a monometallic dinuclear complex, Me(P)Hg(P)Me , is feasible, but a "double-sandwich" structure (1) is clearly impossible. However, treatment of N-methyloctaethylporphyrin (3a), HMeOEP , with various quantities of mercury(II) acetate in methylene chloride-THF afforded a compound with a visible absorption spectrum resembling that of a porphyrin monocation, and probably more significantly, similar to that reported¹⁰ for the zinc(II) complex of N-methyloctaethylporphyrin. Combustion analysis of the mercury complex confirmed it as N-methyloctaethylporphyrinato-mercury(II) acetate (5a). The NMR spectrum showed a sharp three proton singlet assigned to the acetate Me at τ 9.9, and the IR spectrum (KBr) possessed strong bands at 1580 and 685 cm^{-1} .



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a: R = Et
b: R = Me

The N-Me group resonated at τ 14.95, the signal showing satellite peaks due to coupling with ^{199}Hg ($J = 10\text{ Hz}$). The 6s orbitals of the Hg atom are so large that coupling can occur due to interaction through space with the nitrogen orbitals. INDOR $^{199}\text{Hg}\{^1\text{H}\}$ experiments^{1a} revealed only one kind of Hg atom which gave rise to a signal at 17.8898 MHz and this molecule served as a reference standard for the "double-sandwich" species which showed² two types of Hg atom in an approx. 2:1 ratio. The mass spectrum showed an ion at m/e 747 corresponding to the molecular ion less the acetate ligand; this ion lost mercury to give rise to N-methylporphyrin (m/e 548) as the base peak.

N-Methylaetioporphyrin-I (3b) gave a mercury complex (5b) with spectroscopic and physical properties similar to those for 5a.

Mercury(II) *meso*-tetraphenylporphyrin and its demetalation in acid

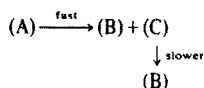
Treatment of H_2TPP (2) with slightly more than one equivalent of mercury(II) acetate in methylene chloride-THF afforded the "normal" monometallic complex, HgTPP . This material was identical with the complex obtained by refluxing H_2TPP with mercury(II) acetate in pyridine.⁸ Significantly (*cf* compound 4) this material showed no band in the IR spectrum (KBr) which could be attributed to a residual metal-bound acetate ligand. The NMR spectrum of HgTPP in CDCl_3 , containing a little pyrrolidine† was similar to that of H_2TPP itself except that the signals were shifted to higher field, possibly due to the added pyrrolidine since similar effects have been noted¹² with H_2TPP and CdTPP . On treatment of a suspension of HgTPP and mercury(II) acetate in

†We have found that pyrrolidine aids solubilisation of some metalloporphyrins, probably by coordination with the metal atom.¹¹

methylene chloride-THF, the metalloporphyrin dissolved due to formation of the more soluble dimercury(II) complex (4).

In pure methylene chloride, HgTPP is stable. However, a dilute solution of HgTPP in methylene chloride which has been standing in a clear glass bottle for several days or which has been treated with a little dry hydrogen chloride, undergoes a series of changes which can be conveniently monitored by repeated-scan spectrophotometry. The overall process involves the acid-promoted demetallation of HgTPP to give *free base* H₂TPP.

Figure 2(a) shows the Soret region of the visible absorption spectrum of HgTPP in methylene chloride containing a trace of hydrogen chloride. The Soret band of HgTPP (A) gradually collapses, giving rise to two new absorptions (B and C); with time, band C begins to diminish with further increase in band B. If methylene chloride with more dry hydrogen chloride in it was used then it was not possible to observe band A at all, equal amounts of bands B and C being formed but once more (Fig. 2(b)) band C was slowly transformed into band B; a clear isobestic point was observed in Fig. 2(b) at 427 nm because unlike Fig. 2(a), only two species are observed spectrophotometrically. The inference from Fig. 2(b) is that the transformation of HgTPP (A) into (B) and (C) is faster than the subsequent conversion of (C) into (B):



Scheme 1.

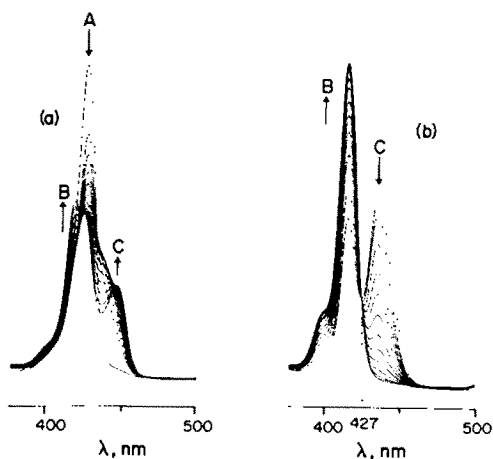


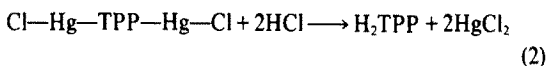
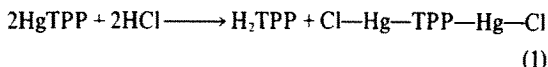
Fig. 2. Soret region of the visible absorption spectra of HgTPP, (a) in methylene chloride with a trace of hydrogen chloride; (b) in methylene chloride with approx. 10 times more hydrogen chloride. Band A = HgTPP; Band B = H₂TPP; Band C = Cl-Hg-TPP-Hg-Cl.

†Alternative identities for band C are the monohydrogen mononuclear species, H(TPP)HgCl, or the diprotonated porphyrin, H₂(TPP)²⁺ (note that slow protonation, on the NMR time scale, has been reported¹³ for H₂TPP to form the dication). The H(TPP)HgCl possibility is ruled out by the stoichiometry of the reaction whereby one mole of H₂TPP and one mole of material in Band C are produced from two moles of HgTPP. The second alternative was excluded by monitoring the reaction in the 500–700 nm region, no evidence of H₂(TPP)²⁺ being observed; in any event, deprotonation of the porphyrin dication in acidic solution to give the free base is unlikely.

Band B was readily assigned to H₂TPP by direct comparison; on the basis of our characterisation above of (AcO-Hg)₂TPP (4), and by comparison, we assign band C to the chloro-analogue, (Cl-Hg)₂TPP (6). Also, on the basis of the extinction coefficients of the Soret bands in H₂TPP and (AcO-Hg)₂TPP it is possible to say from Fig. 2(b) that HgTPP decomposes in presence of hydrogen chloride to give initially, half a mole of H₂TPP and half a mole of (Cl-Hg)₂TPP.

More confirmation of the identity of band C as (Cl-Hg)₂TPP[†] is presented in Fig. 3 which shows the acid promoted decomposition of (a) (AcO-Hg)₂TPP and (b) (Cl-Hg)₂TPP in methylene chloride. The material used in Fig. 3(b) was prepared by treatment of HgTPP with mercuric chloride in a reaction analogous to the formation of 4 (*vide supra*) from HgTPP using mercuric acetate. It is significant that 6 cannot be prepared from H₂TPP using mercuric chloride, only starting material being recovered. Both Figs. 3(a) and 3(b) show isobestic points at about 427 nm (cf. Fig. 2(b)).

It therefore appears that the dimercury complex (6) is an intermediate in the acid promoted demetallation of HgTPP, following the general reactions outlined in eqns (1) and (2).



At spectroscopic dilution (*ca.* 10⁻⁶M) the rate of decomposition of HgTPP was found to be proportional to the acid concentration, suggesting that protonation is the rate determining step. In the absence of kinetic data, our preliminary communication^{1b} suggested direct transfer of the metal from HgTPP to a second molecule of HgTPP (after protonation). This mechanism should give rise to bimolecular reaction kinetics but we have observed that there is no decrease in the rate of transfer of the metal when the dilution is increased; direct metal transfer in formation of Cl-Hg-TPP-Hg-Cl (6) is therefore not taking place.

The demetallation of zinc(II) porphyrins is believed to proceed via protonation of the metalloporphyrin, followed by loss of the metal ion from the other face of the

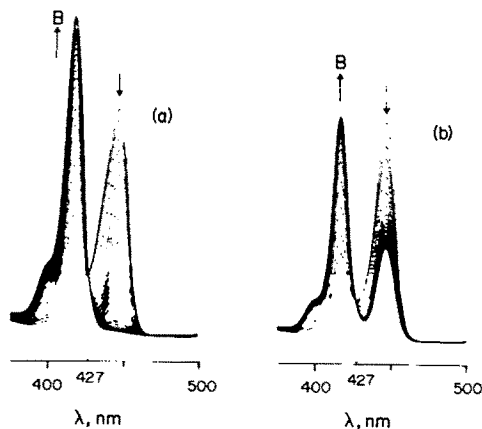
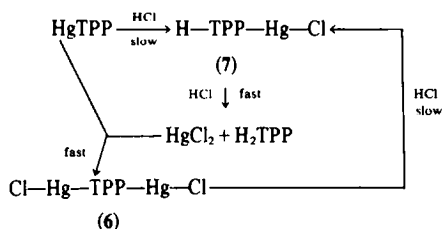


Fig. 3. Soret region of the visible absorption spectra in methylene chloride containing a small amount of hydrogen chloride, showing the formation of H₂TPP from: (a) AcO-Hg-TPP-Hg-OAc (4); (b) Cl-Hg-TPP-Hg-Cl (6).

molecule.¹⁴ We propose that the initial step in the demetallation of HgTPP is protonation to form the species H(TPP)HgCl (7), this being the rate determining step. A second protonation (Scheme 2) then causes formation of H₂TPP and HgCl₂. Since mercuric chloride does not react with H₂TPP, but does form Cl-Hg-TPP-



Scheme 2.

Hg-Cl when treated with HgTPP (*vide supra*) it is likely that the mercuric chloride produced reacts with HgTPP to give 6.

The mechanistics in eqn (2) presumably involve protonation, as suggested in our preliminary publication,^{1b} to give the monohydrogen species H-TPP-Hg-Cl (7), which therefore appears twice as an intermediate in the overall demetallation. Fast reaction with hydrogen chloride then affords H₂TPP and mercuric chloride.

In more strongly acidic media the porphyrin dication, H₂TPP²⁺ is obtained almost instantaneously.

It is of interest that a basically similar disproportionation has been previously reported by Tsutsui *et al.* Heating of a monohydrogen technetium porphyrin, H(P)Tc(CO)₃, afforded^{15,16} a mixture of porphyrin free base, H₂P, and a dimetallic complex, [(CO)₂Tc]₂(P). Also, monohydrogen rhenium complexes, H(P)Re(CO)₃, have been prepared¹⁶ and likened to the "sitting-atop" intermediate in metalloporphyrin formation. We consider that our own work, bearing in mind the reversibility of many of the reactions discussed, adds further weight to the argument that monohydrogen metalloporphyrins are intermediates in metalloporphyrin formation. Tsutsui *et al.* have also reported¹⁶ dimetallic mononuclear complexes in the rhenium and technetium series, as well as a rhenium-technetium hybrid, all of which are structurally similar to the dimeric porphyrins described herein. In this context, we are attempting to obtain crystals of (AcO-Hg)₂TPP suitable for X-ray study¹⁷ and direct comparison with the compounds prepared by Tsutsui.

Isolation of compounds such as 1, 4 and 6 depends upon favourable interactions between metal orbitals and porphyrin orbitals on or near the reaction coordinate for metal insertion, and only in certain favourable cases can one isolate "intermediates". Whether or not the compounds isolated are actual intermediates in the metal insertion or just novel metalloporphyrins is still an open question. Metal insertion in concentrated solution is a highly cooperative phenomenon between layers of porphyrins and metal ions. If one seriously considers the dimetallic

compounds 4 and 6 to be intermediates in the formation of HgTPP then the "double-sandwich" compounds I must also be considered since it was only possible to prepare the dimetallic mononuclear species when steric constraints were devised such that "double-sandwich" complex formation was impossible.

EXPERIMENTAL

General conditions were as described in our earlier paper. *meso*-Tetraphenylporphyrin¹⁸ and *N*-methylporphyrins¹⁹ were prepared according to literature procedures.

meso-Tetraphenylporphyrinatomercury(II), HgTPP. Chlorin-free H₂TPP (100 mg) was stirred in acid-free CH₂Cl₂ (50 ml) and THF (10 ml); Hg(OAc)₂ (52 mg; 1 equiv) was added and after stirring for a further 15 min, spectrophotometry indicated incomplete metallation. More Hg(OAc)₂ (10 mg) was added and after 15 min the visible spectrum indicated complete metal insertion. The mixture was concentrated *in vacuo* to about 20 ml and an equal volume of *n*-hexane was added. The purple microcrystalline powder so precipitated was filtered off and dried under high vacuum at 100°, giving 111 mg (84%) of product, m.p. > 300°. (Found: C, 64.98; "H + Hg", 5.98; N, 6.86. If H = 3.47 then Hg = 22.62%; if H = 3.17 then Hg = 25.30%. Calc. for C₄₄H₂₈HgN₄: C, 64.97; H, 3.47; N, 6.89; Hg, 25.30%; λ_{max}(CHCl₃), 426 (ε 415,000), 487 sh (6300), 519 inf (7400), 550 (9500), 590 sh (4500), and 647 nm (2600).

μ-*meso*-Tetraphenylporphyrinato-bis[mercury(II) acetate], (4). Chlorin-free H₂TPP (200 mg) was stirred with Hg(OAc)₂ (470 mg; 4.5 equiv) in CH₂Cl₂ (120 ml) and THF (40 ml) during 1 hr with occasional warming. Silicagel (Kieselgel G) (7 g) was added and stirring was continued for a further 15 min before filtration through a bed of silicagel; the filtrate was evaporated to dryness and the residue was crystallised from CH₂Cl₂-*n*-hexane to give the *di*-mercury(II) complex (317 mg; 83%) as purple microcrystals, m.p. > 300°. (Found: C, 49.57; "H + Hg", 6.86; N, 4.49. If H = 3.28 then Hg = 32.02%; if H = 2.98 then Hg = 34.69. C₄₄H₂₈Hg₂N₄O₄·2H₂O requires: C, 49.35; H, 3.28; N, 4.80; Hg, 34.35%; λ_{max}(0.5% THF in CH₂Cl₂), 447 (ε 427,500), 525 sh (3100), 558 (8300), 581 (11,600), 603 sh (10,500), and 641 nm (4800). τ, (CDCl₃), 1.06 (8 H, s; β-H), 1.75 (8 H, m; *ortho*-phenyl-H), 2.24 (12 H, m; *meta*, *para*-phenyl-H), and 9.44 (6 H, s; CH₃CO-O), ν_{max}(KBr) C=O, 1565 cm⁻¹, m/e (%), 812 [²⁰⁰Hg] (4), 614 (100), 537 (8), 342 (9), and 307 (27).

N-Methyloctaethylporphyrinatomercury(II) acetate, (5a). To a stirred soln of *N*-methyloctaethylporphyrin^{10,19} (60 mg) in CH₂Cl₂ (40 ml) and THF (12 ml) was added Hg(OAc)₂ (53 mg; 1.5 equiv) and stirring was continued for a further 15 min. After a silicagel work-up as described, the *mercury* complex was obtained as a red gum. Slow crystallisation from THF-*n*-heptane gave large purple needles (80 mg; 90%), m.p. 198–200°. For microanalysis, a sample was recrystallised from CH₂Cl₂-*n*-hexane, (Found: C, 57.86; "H + Hg", 8.79; N, 6.92. If H = 6.24 then Hg = 22.80%; if H = 5.94 then Hg = 25.46. C₄₀H₄₀HgN₄O₂ requires: C, 58.01; H, 6.24; N, 6.94; Hg, 24.85%; λ_{max}(CHCl₃), 434 (ε 172,800), 511 sh (4600), 541 (13,500), 586 (10,800), and 628 nm (4000). τ, (CDCl₃), -0.20, -0.16 (each 2 H, s; *meso*-H), 6.0 (16 H, m; CH₂CH₃), 8.0 (18 H, m), 8.46 (6 H, t) CH₂CH₃, 9.88 (3 H, s; CH₃CO-O), and 14.95 (3 H, s with satellites, J = 10 Hz; N-Me), ν_{max}(KBr) C=O, 1580 and 685 cm⁻¹, m/e (%), 747 [²⁰⁰Hg] (1), 548 (100), 547 (14), 534 (15), and 274 (8).

1,3,5,7 - Tetraethyl - 2,4,6,8, N - pentamethylporphyrinatomercury(II) acetate, (5b) was similarly prepared from *N*-methylaetioporphyrin-I¹⁹ (67 mg) and gave 85 mg (83%) of the *mercury* complex, m.p. 208–210° from THF-*n*-heptane. (Found: C, 55.55; "H + Hg", 8.19; N, 7.39. If H = 5.63 then Hg = 22.65%; if H = 5.33 then Hg = 25.52%. C₃₅H₄₂HgN₄O₂ requires: C, 55.95; H, 5.63; N, 7.46; Hg, 26.70%; λ_{max}(CHCl₃), 432 (ε 101,400), 510 sh (3000), 540 (8000), 586 (10,400), and 631 nm (2200). τ, (CDCl₃), -0.08 (2 H), -0.05 (1 H), -0.02 (1 H) *meso*-H, 6.09 (8 H, m; CH₂CH₃), 6.47 (6 H), 6.50 (3 H), 6.68 (3 H) 2,4,6,8-Me, 8.17 (9 H, m), 8.60 (3 H, t) CH₂CH₃, 10.00 (3 H, s; CH₃CO-O), and 15.01 (3 H, s with satellites, J = 10 Hz; N-Me), ν_{max}(KBr) C=O, 1570 cm⁻¹, m/e (%), 691 [²⁰⁰Hg] (1), 492 (100), 491 (24), 478 (22), 246 (8), and 239 (3).

[†]As described previously,² conventional combustion analysis of mercury compounds is complicated by distillation of mercury into the water collection tube. This gives a high H% figure which we report as "H + Hg". However, if one assumes the H% (or Hg%) figure, it is possible to carry out a back-calculation to obtain the Hg% (or H%) content. The results of these back-calculations are given with the observed figures.

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