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NOVEL MERCURY(II) COMPLEXES OF PORPHYRINS[1]

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Abstract—Treatment of octa-alkylporphyrins (e.g. **1**–**3**) with mercury(II) acetate in methylene chloride and tetrahydrofuran affords novel complexes (**4**) containing two porphyrin rings layered between three Hg atoms. A new type of stereoisomerism in regularly substituted porphyrins (e.g. **1a**, **2a**) is identified; it is observed by NMR spectroscopy and occurs because two forms of the complex (**4**) are possible, depending upon which faces of the porphyrin molecule are turned in towards the central Hg atom. The NMR spectra also indicate that in concentrated solution the double sandwich complexes (**4**) are stable towards disproportionation and recombination. On the basis of the inherent geometrical arrangements in the complexes (**4**), an efficient NMR method for unambiguous identification of the four primary type isomers of the aetio- and copro-porphyrin series is described.

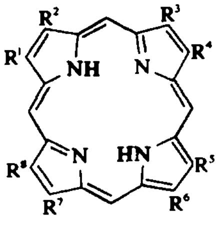
In very dilute solution, or in mixtures containing nucleophilic solvents such as pyridine, methanol, dioxan, or tetrahydrofuran (in the absence of excess mercury(II) acetate), the double sandwich complexes (**4**) are destroyed to afford normal 1:1 metalloporphyrins.

Metalloporphyrins have been the subject of intense research during the last decade,[2] and the reason for this interest is associated with the vital biological roles of some metalloporphyrins in Nature. One of the more recent developments in metalloporphyrin chemistry has been the synthesis of some porphyrin complexes which deviate from the usual 1:1 stoichiometry of metal to porphyrin. A number of complexes containing two metal ions complexed with the same porphyrin molecule are known,[3-10] and some of these have been implicated as models for the intermediates of metalloporphyrin formation.[10,11] Recently, a complex having a different metal ion on either side of the porphyrin molecule has been described.[9]

Treatment of porphyrins with mercury(II) acetate in refluxing pyridine results in the formation of the normal 1:1 chelate,[3,4,12] occasionally isolated as the pyridine adduct. However, treatment of aetioporphyrin-I (**1a**) in methylene chloride and tetrahydrofuran with mercury(II) acetate rapidly yielded a complex with a visible absorption spectrum (Fig. 1) quite unlike that expected for a normal mercury(II) chelate. When the product was shaken with water or chromatographed on alumina (in order to remove excess mercury(II) acetate), only metal-free aetioporphyrin-I was isolated. The excess acetate could, however, be removed by passage of the reaction mixture through a bed of Kieselgel G silica, and from this solution the required chelate was obtained crystalline.

The combustion analytical data were also at variance with calculated figures on the basis of a 1:1 complex. By normal semi-micro C, H, and N analysis, the C and N figures were surprisingly low, whereas the H percentage found was very high. The high H figure could be explained by the tendency of mercury from such complexes to condense in the water condensation tube normally employed in this type of combustion analysis.

Infrared spectroscopy of the novel mercury complex from aetioporphyrin-I showed a broad, strong absorption band at 1580 cm^{-1}, characteristic (Table 1) of a metal-bound acetate group in the apical position of a metalloporphyrin. This fact suggested that only one of the acetate groups in the reagent had been replaced by the porphyrin ring. Taking into account the C and N combustion values, this allowed the molecular composition [Aetioporphyrin-I]$_2$ Hg$_3$[OAc]$_2$ to be derived, and since it was known that metal bound apical acetate ligands were present from the IR spectrum, the novel "double sandwich"[1] or "triple decker"[13] structure **4** was formulated. Assuming the correct H figure in the combustion analysis, it was possible to back-calculate for the mercury figure "found"; in many, but not all cases (*vide infra*) these manipulated combustion figures gave close agree-



1: R = Et
2: R = CH$_2$CH$_2$CO$_2$Me
a: R^1 = R^3 = R^5 = R^7 = Me
R^2 = R^4 = R^6 = R^8 = R
b: R^1 = R^4 = R^5 = R^8 = Me
R^2 = R^3 = R^6 = R^7 = R
c: R^1 = R^3 = R^5 = R^8 = Me
R^2 = R^4 = R^6 = R^7 = R
d: R^1 = R^4 = R^6 = R^7 = Me
R^2 = R^3 = R^5 = R^8 = R
3: R$^{1-8}$ = Et

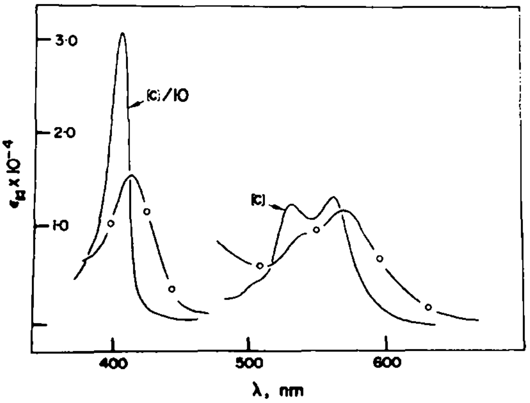


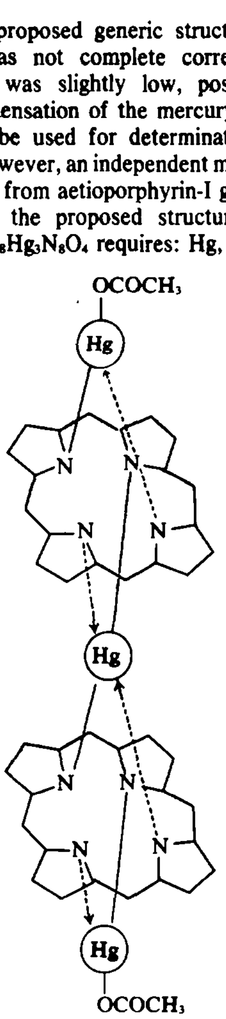
Fig. 1. Visible absorption spectra in CHCl$_3$ of: ○, novel complex (**4**) from aetioporphyrin-I; —, normal 1:1 mercury-porphyrin complex (**7**).

Table 1. Comparison of physical properties of axial acetate ligands in metalloporphyrins

	Data on axial acetate ligand		
Porphyrin complex with	NMR (τ)	IR (cm.$^{-1}$)	Ref.
Hg(II)	10.24	1580	This work
Sc(III)	9.80	1570	a
Tl(III)	9.95	1565	b
Zr(IV)	-	1560	a
Hf(IV)	-	1560	c

[a] J. W. Buchler, G. Eikelmann, J. Ruppe, K. Rohbock, H. H. Schneehage and D. Weck, *Ann. Chem.* 745, 135 (1971); [b] R. J. Abraham, G. H. Barnett and K. M. Smith, *J. Chem. Soc.*, Perkin Trans. I, 2142 (1973); [c] J. W. Buchler and K. Rohbock, *Inorg. Nucl. Chem. Lett.* 8, 1073 (1971).

ment with the proposed generic structure 4. In cases where there was not complete correspondence, the mercury figure was slightly low, possibly owing to incomplete condensation of the mercury into the water condensation tube used for determination of the H% composition. However, an independent mercury analysis† on the chelate 4 from aetioporphyrin-I gave data well in agreement with the proposed structure (Found: Hg, 35·3 ± 1%. $C_{68}H_{78}Hg_3N_8O_4$ requires: Hg, 36·0%).



4

The NMR spectrum of the aetioporphyrin-I complex (4) showed a number of interesting features, all of which added confirmation to the proposed structure. A resonance at 10·24τ which integrated for 3 protons per porphyrin ligand was observed (HA 100, $CHCl_3$ lock), and this is assigned to the methyls of the acetate ligands, being at high field owing to the effect of the ring current in the porphyrin ring; this shift is similar to those observed (Table 1) in thallium(III) and scandium(III) porphyrin acetates. The NMR spectrum (Fig. 2) also featured a *meso*-proton resonance at surprisingly high field; on the basis of structure 4, this shift was readily interpreted in terms of the anisotropic effect of one porphyrin ring lying above another in the layer compound, and such upfield shifts in concentrated solutions of porphyrins and metalloporphyrins have been extensively examined.[14] However, as might be expected from the "fixed" layering occurring in (4), only a small downfield shift of the resonances was observed upon dilution (contrast with Ref. 14). The *meso*-proton resonance (Fig. 2) showed satellite peaks due to coupling of the *meso*-protons with ^{199}Hg ($J = 5$ Hz).‡ The observation of this coupling enabled an INDOR ^{199}Hg[^{1}H] experiment to be carried out; this revealed two Hg signals at 17·8866 and 17·8854 MHz with approximate relative intensities of 2 : 1. This indicated the presence in the molecule of two different types of Hg atom, and this conclusion was checked by performing a similar experiment with N-methyloctaethylporphyrinatomercury(II) acetate[15] which possesses a clearly observed ^{199}Hg coupling to the N-Me group, has only one type of Hg atom, and showed only one ^{199}Hg[^{1}H] INDOR resonance at 17·8898 MHz.

Another interesting feature of the ^{1}H NMR spectrum of the complex (4) from aetioporphyrin-I was the two singlets for the nuclear Me groups and the two sets of triplets for the terminal Me's of the Et groups (Fig. 2). This is somewhat surprising in that aetioporphyrin-I is a regularly substituted porphyrin, but the observation is explained by the fact that two different stereoisomers are possible (Fig. 3) depending upon which faces of the aetioporphyrin-I molecule turn inwards towards the central Hg atom. Each stereoisomer has an approximately equal probability of being formed and this explains the equal intensities of the two nuclear Me singlets and the two Me triplets from the Et groups. The fact that these NMR signals do not equilibrate in solution indicates that no disproportionation and recombination of the complex is occurring. Our preliminary publication[1] represented the first observation of this type of stereoisomerism in porphyrins, and we chose to formulate the complex 4 in the eclipsed (Fig. 4A) rather than staggered form (Fig. 4B) since it appeared to cause least geometrical complications in the bonding of the porphyrin N atoms to the central Hg atom. However, none of the NMR experiments can

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† By flame ionisation; we are grateful to Prof. J. P. Riley, Department of Oceanography (Liverpool), for these analyses.

‡ The INDOR experiment revealed that the ^{199}Hg-^{1}H coupling actually gives rise to a doublet of doublets rather than the single doublet assumed in our preliminary communication;[1] thus the J value is 5 Hz and not 10 Hz as originally quoted.

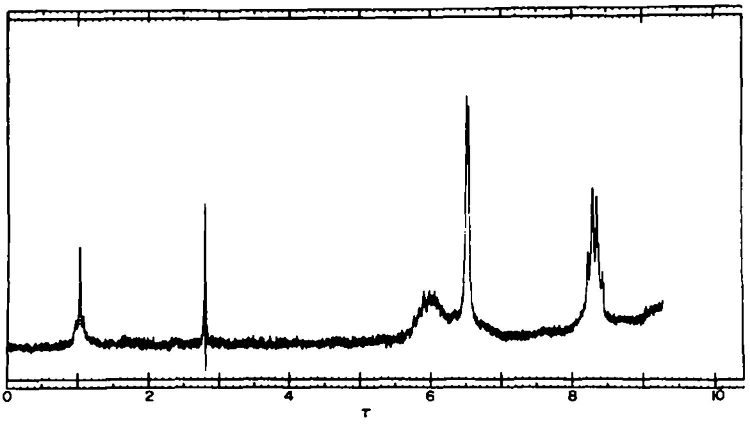


Fig. 2. NMR spectrum (in CDCl$_3$, Varian HA 100 instrument) of complex (4) obtained from aetioporphyrin-I (1a).

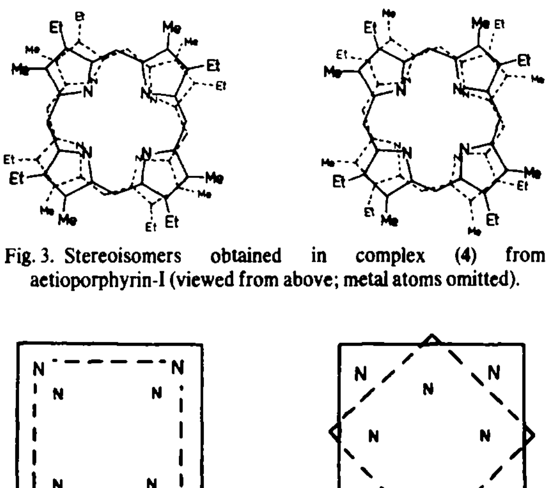


Fig. 3. Stereoisomers obtained in complex (4) from aetioporphyrin-I (viewed from above; metal atoms omitted).

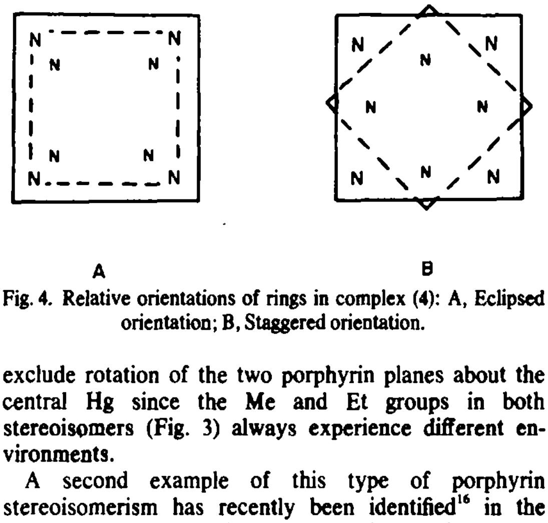


Fig. 4. Relative orientations of rings in complex (4): A, Eclipsed orientation; B, Staggered orientation.

exclude rotation of the two porphyrin planes about the central Hg since the Me and Et groups in both stereoisomers (Fig. 3) always experience different environments.

A second example of this type of porphyrin stereoisomerism has recently been identified[16] in the complex (aetioporphyrin-I)$_2$Ru$_2$, which exhibits an extremely strong ruthenium-ruthenium bond; significantly, orbital models indicated that the eclipsed type of structure (Fig. 4A) should be preferred in this dimer.

The final point in the NMR spectrum of 4 from aetioporphyrin-I (Fig. 2) concerns the complex pattern for the methylene protons of the Et groups. Rather than attempt to interpret this, we prepared the more symmetrical compound 4 from octaethylporphyrin (3) since there could be no complication due to stereoisomerism of the type in Fig. 3. The NMR spectrum of the octaethylporphyrin complex is shown in Fig. 5, and possessed all of the features expected for the "double sandwich" complex 4. The Me portions of the Et groups showed no evidence of stereoisomerism, serving to reinforce the conclusions regarding the two sets of triplets in Fig. 2. Significantly, the methylene protons occurred as a complex pattern; irradiation of the Me triplet signal caused this pattern to collapse to an AB quartet (Fig. 5) indicating that the methylene protons of the Et groups are diastereotopic. Non-equivalence of the methylene protons in thallium(III) octaethylporphyrin chelates has been observed before;[17,18] our initial preference for non-equivalence of the methylene protons due to hindered rotation[17] was modified[18] in favour of diastereotopicity due to the metal atom being out of the plane of the porphyrin ring, in the light of observations of the spectra of thallium complexes of the aetioporphyrins and of *meso*-tetraphenylporphyrin (which showed[18] non-equivalence of the *ortho*-protons in the *meso*-phenyl rings). An X-ray investigation of octaethylporphyrinatothallium(III) chloride, which showed[19] the thallium atom to be well out of the porphyrin plane was also instrumental in this change of opinion. The diastereotopic methylene protons in the complex 4 from octaethylporphyrin are another dramatic demonstration of this effect.

The mass spectra of the complexes 4 do not give a mass ion corresponding to the double sandwich structure; the highest mass ion of any significance is due to the ion with composition porphyrin-Hg-OAc. This ion loses the acetate and then Hg to give the metal-free porphyrin ion as the base peak (*cf* Ref. 20). The mercury complex 4 is therefore much more unstable with respect to dissociation than is the ruthenium dimer.[16]

On treatment with pyridine, the complex 4 affords a deep red solution with a visible absorption spectrum (λ_{max} 421, 555, and 586 nm) resembling that of a normal metalloporphyrin. Formation of the normal 1:1 metal complex in this reaction must occur with liberation of one mole of Hg(II). When equimolar amounts of the complex 4 from aetioporphyrin-I and free aetioporphyrin-I were mixed together in pyridine, spectrophotometry revealed that all of the added free aetioporphyrin had been consumed in forming the 1:1 Hg(II) complex pyridinate. However, when a mixture of two moles of aetioporphyrin-I was added to one of the double sandwich complex 4 in pyridine, spectrophotometry indicated the presence of uncomplexed porphyrin. Thus, further proof that the novel complex possessed one atom of Hg in excess of porphyrin nuclei was obtained.

Hg(II) bis(trifluoroacetate) reacted with aetioporphyrin-I to give a double sandwich complex 4 containing trifluoroacetate ligands (ν_{max} KBr, 1675 cm^{-1}); however, the complex was very sensitive towards hydrolysis and could not be fully characterised.

One of the greatest difficulties in porphyrin chemistry is

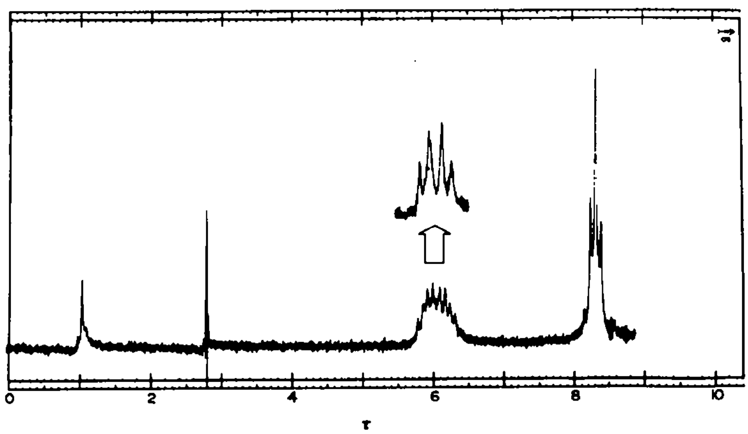
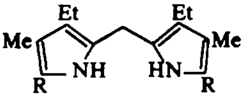


Fig. 5. NMR spectrum (in $CDCl_3$, Varian HA 100 instrument) of complex (4) obtained from octaethylporphyrin (3). The insert shows collapse of the complex methylene proton pattern upon irradiation of the methyl triplet.

associated with the methods available for "type-isomer" identification, and with detection of small amounts of one type isomer in another. There are four primary type isomers[2] for porphyrins possessing only two kinds of substituent with one of each on the four pyrrole-type subunits. Table 2 shows the NMR data of the primary type isomers of the aetioporphyrins (**1a–d**), and illustrates the problem. Apart from aetioporphyrin-IV (**1d**), the type isomers cannot be assigned on the basis of NMR spectroscopy alone. Likewise, mps and visible and mass spectra[2] cannot be used for isomer identification, and no method is available for separation of the aetioporphyrin type-isomers. Thus, excepting absolute structure determination by X-ray methods, there exists no procedure which can be used to confirm that a total synthesis, for example, of a discrete aetioporphyrin isomer, has afforded an isomerically pure product, or even the desired isomer at all.

Type-I isomers of porphyrins (e.g. **1a**, **2a**) usually give very simple NMR spectra because all four sets of substituents on the rings are in identical environments. Thus, the unexpected multiplicity of the substituent resonances in the NMR spectrum from the complex **4** from aetioporphyrin-I (Fig. 1) indicated that it might be possible to differentiate the aetioporphyrin type isomers using this method.

Aetioporphyrin-II (**1b**) was prepared‡ by condensation of the 5,5'-diformylpyrromethane (**5**) with the pyrromethane 5,5'-dicarboxylic acid **6** in the presence of toluene *p*-sulphonic acid.[21,22] The chelate **4** was easily prepared as described above, and the NMR spectrum showed (Table 3), as predicted on the basis of the double sandwich structure, two peaks for the *meso*-protons, but a sharp singlet for the nuclear Me's and a single triplet for the Me groups in the Et side-chains; the spectrum clearly distinguished aetioporphyrins-I and -II. The simplification of the resonances from the side-chains was expected because the Me and Et groups all experience similar environments, and because the asymmetry about the C_2 axis observed in the aetioporphyrin-I complex is no longer present.



5: R = CHO
6: R = CO_2H

Significantly, "aetioporphyrin-II" prepared by the well-established Fischer method[23] involving heating of the symmetrically substituted pyrromethane-5,5'-

Table 2. Chemical shifts (τ, measured on HA 100) of aetioporphyrin type isomers measured in $CDCl_3$ and TFA

	In $CDCl_3$				In TFA*		
Type isomer (Structure)	*meso*-H	CH_2(q)	CH_3(s)	CH_3(t)	CH_2(q)	CH_3(s)	CH_3(t)
I (1a)	-0.09	5.92	6.39	8.13	5.71	6.24	8.16
II (1b)†	-0.06	5.97	6.44	8.17	5.75	6.26	8.18
III (1c)	-0.09	5.89	6.35	8.13	5.72	6.23	8.15
IV (1d)	-0.09(1) -0.06(2) -0.04(1)	6.06 6.02	6.53 6.49	8.20 8.23			

**Meso*-proton signals masked by TFA resonance.

†The $CDCl_3$ spectrum of aetioporphyrin-II is actually that from the random mixture prepared using Fischer's method.[23] Isomerically pure aetioporphyrin-II was not sufficiently soluble in $CDCl_3$ for a satisfactory spectrum to be measured.

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‡Full discussion of the porphyrin syntheses would not be appropriate here; see Experimental section for full details of new synthetic approaches to particular type-isomers.

Table 3. Chemical shifts (τ) of mercury complexes (4) from aetioporphyrins and coproporphyrin tetramethyl esters in $CDCl_3$

Type isomer	Porphyrin series	*meso*-H[a]	CH_3	CH_2-CH_3	CH_2-CH_2-CO_2CH_3	$OCOCH_3$
I	Aetio	1.03	6.52 6.56	6.0(m), 8.32(t) 8.37(t)		10.24
	Copro[b]	0.93	6.33 6.35		5.60(m),7.02(t),6.42	10.40
II	Aetio	0.96 1.00	6.49	6.0(m), 8.30(t)		10.49
	Copro[b]	0.97 0.99	6.51		5.70(m),7.07(t),6.53	10.49
III	Aetio	0.82 0.93 1.12 1.18	6.40[c] 6.49 6.52 6.58	5.9(m), 8.35(m)		10.49
	Copro[b]	0.90 0.95 1.08 1.13	6.4- 6.8(m)		5.68(m),7.10(t), [d]	10.32
IV	Aetio	0.84(1) 1.13(2) 1.42(1)	6.54 6.71	6.2(m), 8.28(t) 8.47(t)		9.81
	Copro[b]	0.76(1) 0.99(2) 1.13(1)	6.40 6.53		5.70(m),6.96(t),6.43 7.10(t)	10.59

[a] Satellite peaks observed (see text) due to ^1H–^{199}Hg couplings. [b] Tetramethyl esters. [c] Additional fine structure observed. [d] Signals obscured by methyl group resonances. Numbers in parentheses refer to relative signal intensities.

dicarboxylic acid (6) in refluxing formic acid, gave a Hg(II) complex (4) which was identical by NMR spectroscopy with that from the random mixture of aetioporphyrin isomers obtained by the common monopyrrole polymerisation. This provided a dramatic demonstration that this type of pyrromethane dimerisation provides porphyrin mixtures due to random redistribution of the pyrromethane rings in acid prior to cyclisation and oxidation to give the porphyrin.

The NMR spectrum of the chelate (4) obtained from the highly unsymmetrical aetioporphyrin-III (1c) was complex and clearly displayed the asymmetry in the molecule; however, it showed four clear *meso*-proton resonances (Table 3).

It was expected that the aetioporphyrin-IV chelate (4) would show two sets of non-equivalent nuclear Me groups and also two sets of triplets from the Me portions of the Et groups. This multiplicity, we considered, might lead to confusion between aetioporphyrin-I and IV identification, but we hoped that the *meso*-protons in the type-IV isomer might appear as a 1:2:1 pattern compared with the singlet in the aetioporphyrin-I case. This was indeed observed (Table 3) and thus completed the full NMR differentiation between the aetioporphyrin isomers.

In order to ascertain that the method was not applicable only to the aetioporphyrins, and that the geometrical considerations were general, a study of the chelates (4) from the coproporphyrin tetramethyl esters (**2a–d**) was carried out. All of the results (Table 3) were in agreement with the trends observed in the aetioporphyrins, though the resonances from the methyl esters occasionally complicated the interpretation.† Again, coproporphyrin-II (**2b**) had to be prepared by the MacDonald type condensation of a 5,5′-diformylpyrromethane with a pyrromethane-5,5′-dicarboxylic acid; use of the Fischer method[24] with the pyrromethane-5,5′-dicarboxylic acid in hot formic acid gave a random mixture of coproporphyrin type isomers. Admittedly, the isomer differentiation in the coproporphyrin series is not such a difficult problem; the esters have well defined m.ps, they can be identified by NMR spectroscopy of the free bases or metal complexes,[14,25,26] and paper chromatographic separations have been described.[2] Nevertheless, the complete agreement within two series of primary type isomers illustrates that potential uses of the chelates (4) in structure determination.

As yet, crystals of the complex (4) from octaethylporphyrin (3) suitable for X-ray analysis have not been obtained. This is in part due to the relatively easy dissociation of this complex in solution, and as might be expected from double sandwich complexes of this type, compounds prepared from porphyrins with bulky substituents tend to be less stable than, for example, the aetioporphyrin derivatives, and also lower melting. Indeed, it is not possible to prepare[15] the chelate (4) from *meso*-tetraphenylporphyrin, presumably owing to adverse repulsions between the phenyl rings.

The complex (4) from octaethylporphyrin (3) dissociates readily in very dilute solution, and also in the presence of nucleophilic solvents such as methanol, tetrahydrofuran, 1,4-dioxan, and pyridine. Thus, on recrystallisation of 4 from methylene chloride–1,4-dioxan, a substance with the visible absorption spectrum (Fig. 1) resembling that of a normal 1:1 metalloporphyrin is obtained. Microanalytical data showed this compound to be aquo-octaethylporphyrinatomercury(II) (7).

When 7 was warmed with excess Hg(II) acetate in methylene chloride—tetrahydrofuran, the double sandwich complex 4 reformed, thus showing the reversibility of the dissociation process. When the complexes 4 or 7 were dissolved in pyridine, the solutions became deep red and gave electronic absorption spectra identical with that from the monopyridinate of octaethylporphyrinatomercury(II) (8) (*cf* Ref. 27). A spectrophotometric titration of 7 with pyridine revealed three isosbestic points (λ_{max} 410,

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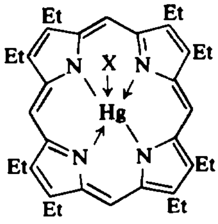
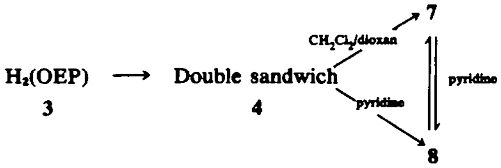
†However, esterification with 5% H_2SO_4 in CD_3OD (*cf* Ref. 14) can circumvent these difficulties.



7: X = H_2O
8: X = NC_5H_5

540 and 575 nm), showing that the aquo complex 7 and the pyridinate were the only two species involved. The reactions of the octaethylporphyrin Hg(II) complexes are summarised in Scheme 1.

We consider that one of the primary requirements for formation of the double sandwich structure is that the metal used must lie out of the plane of the porphyrin ring in the normal 1:1 complex. On this basis we have examined formation of metalloporphyrins under non-polar solvent conditions using metal ions of large ionic radius, such as Cd(II), Ba(II) and Pb(II). However, we have obtained no evidence of double sandwich complex formation with these metals; it is interesting that Tsutsui *et al.*[5] have obtained spectroscopic evidence for the formation of a bis-rhenium monomercury double sandwich (presumably) from treatment of a monohydrogen-rhenium complex with Hg(II) acetate. Hence, formation of these layered complexes (4) is probably associated with favourable interactions between ligand and metal orbitals producing stable complexes somewhere along or near the reaction coordinate for normal metal insertion to produce 1:1 metalloporphyrin complexes. A fuller discussion of the relevance of these compounds (4) to the mechanism of metal insertion into the porphyrin ligand will be published in due course (*cf* ref. 15).



Scheme 1

EXPERIMENTAL

M.ps were measured on a microscopic hot-stage apparatus. Unless otherwise stated, chromatographic purifications were carried out on Merck neutral alumina (Brockmann Grade III). Visible absorption spectra (solns in chloroform) were measured on a Unicam SP 800 spectrophotometer, and ^1H NMR spectra were determined (usually in $CDCl_3$ with TMS or chloroform as internal standard) with a Varian HA-100 instrument. Mass spectra (direct insertion probe, operating conditions 70 eV, 50 μA, source temperatures *ca.* 200°) were measured using an A.E.I. MS 12 spectrometer.

Aetioporphyrin-I,[28] aetioporphyrin-IV,[29] and the tetramethyl esters of coproporphyrin-I,[28] coproporphyrins-II and -III,[14] and coproporphyrin-IV,[30] were prepared according to literature methods.

Aetioporphyrin-II (**1b**). Compound **5**[31] (1·0 g) and **6**[31] (1·23 g, 1·1 equiv.) were stirred together in CH_2Cl_2 (600 ml) well protected (Al-foil) from light. Toluene *p*-sulphonic acid hydrate (4·35 g, 6 equivs) in hot methanol (7 ml) was added quickly to the stirred solution, which was set aside for 23 hr. Zinc(II) acetate (1 g) in MeOH (40 ml) was then added, and the mixture was stirred for another 48 hr before evaporation under reduced pressure. The residue was stirred with trifluoroacetic acid (20 ml) during 15 min and then poured into CH_2Cl_2 and water. $NaHCO_3$aq was added cautiously and then shaken. The organic phase was washed with water, dried (Na_2SO_4), concentrated to *ca.* 50 ml and then treated with an equal volume of MeOH. The crystalline porphyrin was filtered off and washed with hot MeOH until the washings were colourless, giving 520 mg (29%) of highly insoluble purple-red microcrystals, m.p. > 300°.

Aetioporphyrin-III (**1c**). 5′-t-Butoxycarbonyl-3,4′-diethyl-3′,4-dimethylpyrromethane-5-carboxylic acid[32] (1·15 g) was added to stirring trifluoroacetic acid (10 ml) under a stream of dry N_2. Stirring was continued for 1 hr before the soln was poured into CH_2Cl_2 and water. The acid was carefully neutralised with $NaHCO_3$aq, and the organic phase was washed with water, dried (Na_2SO_4), and evaporated to give a red-brown gum which was dissolved in CH_2Cl_2 (10 ml) and then added to a stirred soln of 3,3′-diethyl-5,5′-diformyl-4,4′-dimethylpyrromethane[31] (557 mg) in CH_2Cl_2 (500 ml). The mixture was kept in the dark, and toluene *p*-sulphonic acid hydrate (2·42 g, 6 equiv.) in a minimum volume of hot MeOH was added to the stirred soln. After stirring for 17 hr the mixture was poured into dil NaOAc aq and the organic layer was washed 3 times with water, dried (Na_2SO_4), and then evaporated to dryness. The residue was chromatographed, eluting with *hot* chloroform. The porphyrinic eluates were collected, evaporated, and the residue was crystallised from CH_2Cl_2–MeOH, giving 422 mg (42%) of purple-red microcrystals, m.p. > 300°.

Bis[*aetioporphyrinato*-I-*mercury*(II) *acetato*]*mercury*(II)† (**4** from **1a**). Mercuric acetate (174 mg, 2·6 equivs) was added to a stirred soln of aetioporphyrin-I (100 mg) in CH_2Cl_2 (35 ml) and THF (15 ml). Stirring was continued for a further 30 min, with occasional warming. Spectrophotometry, after this time, usually indicated that metal insertion was complete. The mixture was then stirred with Kieselgel G (3 g) during 15 min and filtered through a bed of the same silicagel, which was washed afterwards with CH_2Cl_2–THF. The combined filtrates were evaporated to dryness, and the residue was crystallised from CH_2Cl_2–n-hexane, giving 144 mg (81%) of purple-red crystals, m.p. > 300°. (Found; C, 48·78; N, 6·46. $C_{68}H_{78}Hg_3N_8O_4$ requires: C, 48·81; N, 6·36%). An independent flame ionisation Hg analysis gave Hg, 35·3 ± 1·0%; required: Hg, 35·97%). λ_{max} 406 (ϵ 158,000), 544 inf (9300), 570 (10,800) and 607 sh nm (4500), ν_{max} (KBr) C=O, 1580, 685 cm^{-1}, *m/e* (%), 676 (^{200}Hg; 0·6), 478 (100), 476 (3) and 239 (11).

In a similar manner, the following compounds were also prepared:

Bis[*aetioporphyrinato*-II-*mercury*(II) *acetato*]*mercury*(II), (**4** from **1b**), in 95% yield (170 mg scale), obtained as a red-purple crystalline solid from CH_2Cl_2–n-hexane, m.p. > 300°. (Found; C, 48·55; N, 6·34. $C_{68}H_{78}Hg_3N_8O_4$ requires; C, 48·81; N, 6·36%), λ_{max} 409 (ϵ 190,000), 548 inf (10,000), 572 (11,800) and 607 sh nm (4400), ν_{max} (KBr) C=O, 1585, 675 cm^{-1}, *m/e* (%), 676 (^{200}Hg, 100), 661 (25), 478 (55), 476 (10) and 338 (20).

Bis[*aetioporphyrinato*-III-*mercury*(II) *acetato*]*mercury*(II), (**4** from **1c**), in 95% yield (170 mg scale), obtained as red-purple microcrystals from CH_2Cl_2–n-hexane, m.p. > 300°. (Found: C, 48·95; N, 6·36. $C_{68}H_{72}Hg_3N_8O_4$ requires: C, 48·81; N, 6·36%), λ_{max} 408 (ϵ 170,000), 549 inf (10,100), 573 (11,400), and 610 sh nm (4400), ν_{max} (KBr) C=O 1585, 685 cm^{-1}, *m/e* (%), 676 (^{200}Hg, 32), 661 (9), 646 (5), 478 (100), 476 (25), 338 (7) and 239 (32).

Bis[*aetioporphyrinato*-IV-*mercury*(II) *acetato*]*mercury*(II), (**4** from **1d**), in 97% yield (170 mg scale), obtained in the form of the dihydrate as red-purple microcrystals from CH_2Cl_2–n-hexane, m.p.>300°. (Found: C, 47·68; N, 6·76. $C_{68}H_{82}Hg_3N_8O_6$ requires: C, 47·78; N, 6·56%), λ_{max} 410 (ϵ 163,000), 549 inf (7700), 576 (10,100) and 611 sh nm (3700), ν_{max} (KBr) C=O, 1570, 690 cm^{-1}, *m/e* (%), 735 (^{200}Hg, 0·3), 692 (0·1), 676 (10), 661 (2), 646 (1), 478 (100), 476 (6) and 239 (20).

Bis[*coproporphyrin*-I *tetramethyl esterato*-*mercury*(II) *acetato*]*mercury*(II), (**4** from **2a**), in 96% yield (150 mg scale),

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†As mentioned in the text, elemental analyses were complicated by distillation of mercury into the water absorption tube during burning. Thus, in general, only C and N figures are reported. If, however, the correct Hg percentage was assumed, back-calculations using the combined "Hg + H" figure, often afforded satisfactory figures for hydrogen content.

obtained in the form of the dihydrate as red-purple needles from CH_2Cl_2–n-hexane, m.p. 259–260°. (Found; C, 46·61; N, 5·16. $C_{84}H_{98}Hg_3N_8O_{22}$ requires: C, 46·41; N, 5·16%), λ_{max} 408 (ϵ 172,000), 546 inf (8900), 576 (12,100), and 607 sh nm (4300), ν_{max} (KBr), ester C=O 1725, acetate C=O 1560, 685 cm^{-1}, *m/e* (%), 908 (^{200}Hg, 2), 710 (100), 637 (31), 564 (8), and 355 (5), m* 571·5 ($710 \rightarrow 637$) and 499·3 ($637 \rightarrow 564$).

Bis[coproporphyrin-II *tetramethyl esterato-mercury*(II) *acetato]mercury*(II), (**4** from **2b**), in 85% yield (130 mg scale), obtained as red-purple microcrystals from CH_2Cl_2–n-hexane, m.p. 290–293°. (Found; C, 47·33; N, 5·20. $C_{84}H_{94}Hg_3N_8O_{20}$ requires: C, 47·21; N, 5·24%), λ_{max} 409 (ϵ 199,000), 549 inf (10,000), 576 (12,000), and 608 sh nm (4800), ν_{max} (KBr) ester C=O 1720, acetate C=O 1585, 675 cm^{-1}, *m/e* (%), 908 (^{200}Hg, 1), 710 (100), 637 (41), 564 (9), 355 (5), m* 571·5 ($710 \rightarrow 637$), 499·3 ($637 \rightarrow 564$) and 427·5 ($564 \rightarrow 491$).

Bis[coproporphyrin-III *tetramethyl esterato-mercury*(II) *acetato]mercury*(II), (**4** from **2c**), in 71% yield (120 mg scale), obtained as a purple amorphous powder from CH_2Cl_2–n-hexane, m.p. 76–80°. Attempts to obtain a satisfactory elemental analysis were unsuccessful, ν_{max} (KBr) ester C=O 1730, acetate C=O, 1570, 690 cm^{-1}, *m/e* (%), 908 (^{200}Hg, 0·5), 710 (100), 637 (23), 564 (6) and 355 (3), m* 571·5 ($710 \rightarrow 637$), 499·3 ($637 \rightarrow 564$) and 427·5 ($564 \rightarrow 491$).

Bis[coproporphyrin-IV *tetramethyl esterato-mercury*(II) *acetato]mercury*(II), (**4** from **2d**), in 90% yield (125 mg scale), obtained as purple-red microcrystals from CH_2Cl_2–n-hexane, m.p. 153–155°. (Found; C, 47·31; N, 5·13. $C_{84}H_{94}Hg_3N_8O_{20}$ requires: C, 47·21; N, 5·24%), λ_{max} 407 (ϵ 161,000), 548 inf (8500), 574 (11,000), and 605 sh nm (4200), ν_{max} (KBr) ester C=O 1725, acetate C=O 1580, 675 cm^{-1}, *m/e* (%), 908 (^{200}Hg, 0·6), 710 (100), 637 (69), 546 (16), and 355 (9), m* 571·5 ($710 \rightarrow 637$), 499·3 ($637 \rightarrow 564$) and 427·5 ($564 \rightarrow 491$).

Bis[octaethylporphyrinato-mercury(II) *acetato]mercury*(II), (**4** from **3**), in 92% yield (160 mg scale), obtained as the dihydrate in the form of red-purple prisms from CH_2Cl_2–n-hexane, m.p. > 300°. (Found; C, 50·31; N, 6·41. $C_{76}H_{98}Hg_3N_8O_6$ requires: C, 50·11; N, 6·15%), ν_{max} (KBr) C=O 1585 cm^{-1}.

Recrystallisation of this compound from CH_2Cl_2–1,4-dioxan gave red fluffy needles of a metalloporphyrin, characterised as *aquo octaethylporphyrinato-mercury*(II) **7**, and obtained in quantitative yield from the double sandwich compound. (Found; C, 57·82; N, 7·45. $C_{36}H_{46}HgO$ requires: C, 57·54; N, 7·45%), λ_{max} 409 (ϵ 308,000), 533 (11,000) and 563 nm (12,200), λ_{max} in pyridine, 424 (ϵ 178,000), 556 (14,800) and 587 nm (5400). NMR spectrum (in pyridine), τ, −0·3 (4 H, s *meso*-H), 5·94 (16 H, q $C\underline{H}_2CH_3$) and 8·14 (24 H, t $CH_2C\underline{H}_3$), *m/e* (%), 732 (^{200}Hg, 63), 717 (6), 702 (4), 687 (4), 672 (4), 657 (3), 632 (2), 534 (100), 532 (12), 366 (14) and 267 (19).

Attempted preparation of bis[aetioporphyrinato-I-mercury(II) *trifluoroacetato]mercury*(II). Mercury(II) trifluoroacetate (200 mg; 2·2 equivs) was added to a stirred soln of **1a** (100 mg) in dry CH_2Cl_2 (40 ml) and THF (30 ml). After 10 min, silicagel (2 g) was added and after 10 min further stirring the mixture was filtered through a bed of silicagel. The filtrate was evaporated to dryness under reduced pressure and the gummy residue was crystallised slowly from CH_2Cl_2–n-hexane, giving a purple microcrystalline powder (90 mg; 48%), m.p. 140–142°. A satisfactory elemental analysis was not obtained for this compound, presumably owing to partial hydrolysis of the apical ligands. ν_{max} (KBr) C=O 1675 cm^{-1}.

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