

## Synthesis and Properties of Thallium(III) Porphyrin Chelates<sup>1</sup>

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Treatment of porphyrins with thallium(III) acetate or trifluoroacetate affords the corresponding thallium(III) chelates, which suffer ligand exchange during chromatography on alumina to furnish the aquoporphinatothallium(III) hydroxides [*e.g.* (2c)]; other examples of ligand exchange are presented. The aquo-hydroxides are obtained directly when porphyrins are metallated with thallium(III) nitrate trihydrate. Demetallation is readily accomplished with acids, by reduction ( $Tl^{III} \rightarrow Tl^I$ ), or by a combination of both of these methods.

Information on metal-ligand interactions is obtained from the <sup>1</sup>H n.m.r. spectra; thallium-proton couplings are reported and are shown to occur *via* a predominantly  $\pi$ -bond mechanism for the *meso*-protons, but through a  $\sigma$ -bond mechanism for the peripheral protons. The visible absorption spectra indicate no major distortion of the porphyrin ring by the metal atom, and together with n.m.r. evidence, this suggests strongly that the metal atom is situated out of the plane of the porphyrin ring. The mass spectra of thallium(III) porphyrins show several anomalous features, the most notable being extrusion of the metal atom to give the free porphyrin ion, which is often the base peak in the spectra.

ALTHOUGH the chemistry of a wide variety of metallo-porphyrins has been studied in detail,<sup>2</sup> thallium(III) porphyrins have received little attention. Those reports which have been published treated thallium as a relatively insignificant member within a whole series of metals under investigation; as a result, an inadequate, and sometimes misleading account of the chemistry of these complexes is available.

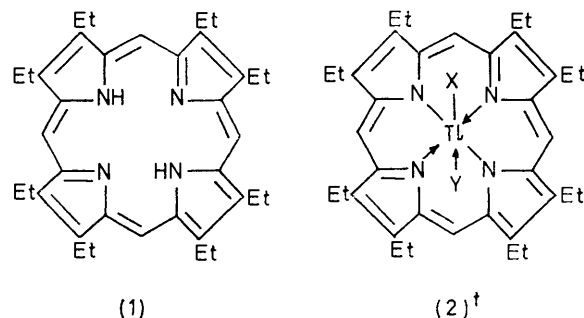
In 1929, Fischer and Putzer<sup>3</sup> prepared a thallium complex of protoporphyrin-IX and deduced that the product contained one thallium atom per porphyrin ligand. Later, Haurowitz<sup>4</sup> obtained red and green chelates of mesoporphyrin-IX with a species thought to be thallium(II). Thallium(I) and thallium(III) complexes of tetraphenylporphyrin were reported by Rothmund,<sup>5</sup> but as with the other investigations, these compounds were inadequately characterised.

We now report an investigation of the synthesis and physical properties (particularly n.m.r.) of thallium(III) porphyrins. The n.m.r. investigation was prompted by the large nuclear moment of thallium, which allows this technique to be used as a probe for metal-ligand interactions in metalloporphyrins. The crystal ionic radius<sup>6</sup> (*r*) of thallium(III) (*r* 0.95 Å) is reasonably compatible with the formation of 'stable' complexes, whereas thallium(I) (*r* 1.47 Å) would not be expected to give normal chelates. However, in view of the claims<sup>5</sup> of Rothmund, and the recent characterisation<sup>7</sup> of unstable lead(II) (*r* 1.20 Å) chelates, the existence of thallium(I) porphyrins cannot be excluded.

**Synthesis and Ligand Exchange.**—Treatment of porphyrins [*e.g.* (1)] with 1 equiv., or an excess, of thallium(III) salts affords the corresponding chelates [*e.g.*

† For simplicity, the chelates bearing axial ligands (X and Y) are depicted as octahedral species, though it is not certain that the water molecule is co-ordinated to the metal atom. Assignment of a precise geometry to these complexes awaits the results of an X-ray study, which is in hand. The chelates (2a, d, and e) were crystallised from dry solvents [unlike (2b and c)] and do not appear to possess axial water ligands (elemental analysis and mass spectra where applicable). It is not clear whether or not this is an inherent property of these chelates, or whether a more labile ligand was present, but was lost during drying (usually 0.1 mmHg; 100 °). Thermal removal of metalloporphyrin axial ligands is not uncommon (see ref. 8).

(2a—c)],† which can be isolated by passage of the reaction mixture through a bed of Kieselgel G to remove the excess of thallium salts. For example, with thallium(III) trifluoroacetate or acetate, the trifluoroacetate (2a) or aquo-acetate (2b) can be obtained, and these have



a; X = O·CO·CF<sub>3</sub>, Y absent  
 b; X = O·CO·CH<sub>3</sub>, Y = H<sub>2</sub>O  
 c; X = OH, Y = H<sub>2</sub>O  
 d; X = I, Y absent  
 e; X = CN, Y absent

been completely characterised. However, with thallium(III) nitrate, the aquo-hydroxide (2c) is isolated directly, presumably because the thallium reagent is used as the trihydrate. Chromatography of (2a) or (2b) resulted in ligand exchange with water from the deactivated alumina support, and the aquo-hydroxide (2c) was obtained in high yield.<sup>9</sup> The ligands in (2c) were

<sup>1</sup> Preliminary communication, K. M. Smith, *Chem. Comm.*, 1971, 540.

<sup>2</sup> Cf. J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964.

<sup>3</sup> H. Fischer and B. Putzer, *Z. physiol. Chem.*, 1926, **154**, 39.

<sup>4</sup> F. Haurowitz, *Ber.*, 1935, **68**, 1795.

<sup>5</sup> P. Rothmund and A. R. Menotti, *J. Amer. Chem. Soc.*, 1948, **70**, 1808.

<sup>6</sup> 'Handbook of Chemistry and Physics,' Chemical Rubber Co., 47th edn., 1966, p. F-124.

<sup>7</sup> D. G. Whitten, J. C. Yau, and F. A. Carrol, *J. Amer. Chem. Soc.*, 1971, **93**, 2291.

<sup>8</sup> *E.g.* A. Yamamoto, L. K. Phillips, and M. Calvin, *Inorg. Chem.*, 1968, **7**, 847.

<sup>9</sup> We have already reported the synthesis and n.m.r. spectra of the thallium(III) coproporphyrins: R. J. Abraham, G. H. Barnett, E. S. Bretschneider, and K. M. Smith, *Tetrahedron*, 1973, **29**, 553.

further modified; for example, treatment with potassium iodide in acetone afforded the iodide (2d), and with sodium cyanide in methanol, the cyanide (2e) was produced.

*N.m.r. Spectra.*—The +1 and +3 oxidation states of thallium are diamagnetic, and both isotopes [203 (29.5% abundance) and 205 (70.5)] have a nuclear spin of  $\frac{1}{2}$ . A number of thallium-proton couplings have been reported<sup>10</sup> and in a detailed study by Evans and his co-workers<sup>11-13</sup> it was noted that only for very large couplings were the isotopic splittings resolved, owing to the similarity of the magnetic moments of the <sup>203</sup>Tl and

of hydrogen with methyl in model aromatic systems.<sup>14,15</sup> For  $\pi$ -bond transmission, the X-<sup>1</sup>H coupling is equal in magnitude, but opposite in sign, to the X-Me coupling, whereas for  $\sigma$ -bond transmission, the X-Me coupling is much smaller than the X-<sup>1</sup>H coupling. We have used this technique in our analyses of the thallium(III) porphyrin spectra.

The proton resonance spectra of porphyrins have been well documented; in particular, the large concentration dependence of the shifts has been extensively investigated and interpreted.<sup>9,16-18</sup> Two types of behaviour have been put forward as explanations for the

TABLE I  
Proton chemical shifts ( $\delta$ ) and thallium-proton couplings (Hz) of thallium(III) porphyrins

Thallium(III) porphyrin (ligands in parentheses)	<i>meso</i> -H	Proton chemical shifts					<i>meso</i> -H	Tl-H couplings		
		$\beta$ -Substituents						$\beta$ -Substituents		
		H	CH <sub>3</sub>	CH <sub>2</sub> ·CH <sub>3</sub>	CH <sub>2</sub> ·CH <sub>2</sub> ·CO <sub>2</sub> ·CH <sub>3</sub>	Others		H	CH <sub>3</sub>	CH <sub>2</sub> (CH <sub>3</sub> )
Octaethyl (OH, H <sub>2</sub> O) (2c)	10.32			4.23, 1.95 4.17			44.4			6.1 18.1
Octaethyl (OAc, H <sub>2</sub> O) (2b)	10.30			ca. 4.1, 1.92		O·CO·CH <sub>3</sub> , 0.05	46.0			<i>a</i>
Octaethyl (O·CO·CF <sub>3</sub> ) (2a)	10.34			ca. 4.1, 1.94		CO·CF <sub>3</sub> , $\phi^*$ 75.43	49.0			<i>a</i>
Octaethyl (I) (2d)	10.32			ca. 4.1, 1.91			45.0			<i>a</i>
Octaethyl (CN) (2e)	10.24			ca. 4.1, 1.93			32.0			<i>a</i>
Aetio-I (OH, H <sub>2</sub> O) (3a)	10.10		3.52	3.96, 1.82			46.2	8.0		11.8 <sup>b</sup>
Aetio-II (OH, H <sub>2</sub> O) (3b)	10.29		3.61	ca. 4.1, 1.90			45.5		8.5	<i>a</i>
Aetio-IV (OH, H <sub>2</sub> O) (3c) <sup>c</sup>	10.27(1) 10.24(2) 10.21(1)		3.64 3.60	4.08, 1.92			46.0 45.0 45.0	8.0		<i>a</i>
Aetio-I (O·CO·CF <sub>3</sub> )	10.22		3.49	ca. 4.1, 1.83		CO·CF <sub>3</sub> , $\phi^*$ 75.29 <sup>e</sup>	51.0		9.0	<i>a</i>
Copro-I (OAc, H <sub>2</sub> O)	10.15		3.62		4.35, 3.26, 3.64	O·CO·CH <sub>3</sub> , -0.05	46.5	8.0		<i>d</i>
Pyrro-XV (OH, H <sub>2</sub> O) (6a)	10.19 10.15 10.08 10.03	9.17	3.72(1) 3.58(1) 3.54(2)	ca. 4.2, 1.84	4.0—4.4, 3.19, 3.63		47.0 46.8 44.6 44.0	70.0	9.5 9.0 8.5	
Tetraphenyl (OH, H <sub>2</sub> O) (4a)		9.05				{ Ph: o, 8.36, 8.10 m, p, 7.75		65.4		
Tetraphenyl (OAc, H <sub>2</sub> O) (4b)		9.02				{ Ph: o, 8.31, 8.08 m, p, 7.73 O·CO·CH <sub>3</sub> , -0.03		64.0		

<sup>a</sup> Methylene protons diastereotopic; a full analysis was not carried out [but cf. (2c)]. <sup>b</sup> Slight non-equivalence. <sup>c</sup> Shifts were concentration dependent; values are quoted for ca. 0.1M-solution. <sup>d</sup> Not observed, owing to overlapping with propionate methylene resonances. <sup>e</sup> See ref. 25 for details of  $\phi^*$ .

<sup>205</sup>Tl isotopes. In all of the porphyrins studied herein, only one type of thallium coupling was observed, and for simplicity these will be referred to as Tl-<sup>1</sup>H couplings. Maher and Evans<sup>13</sup> have also drawn attention to the fact that for thallium(III) compounds, the magnitude of the Tl-<sup>1</sup>H coupling is approximately 30 times that of the corresponding <sup>1</sup>H-<sup>1</sup>H coupling. The mechanism of Tl-<sup>1</sup>H couplings in aromatic systems was also investigated by these workers, using the method of replacement

shifts; that most commonly mentioned is the attractive interaction between porphyrin rings which results in a stacking arrangement of the molecules in solution.<sup>9,16,17</sup> The second type of phenomenon is the specific complexing between metal atoms (*e.g.* magnesium<sup>18</sup> and zinc<sup>19</sup>) on the one hand with co-ordinating ligands in the porphyrin side-chains on the other.

The main features of the proton n.m.r. spectra of a number of thallium(III) porphyrins are collected in

<sup>10</sup> J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' vol. 2, Pergamon, Oxford, 1966.

<sup>11</sup> J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, 1961, 208; 1963, 176; *J. Chem. Soc.*, 1963, 5534.

<sup>12</sup> J. P. Maher, M. Evans, and M. Harrison, *J.C.S. Dalton*, 1972, 188.

<sup>13</sup> J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1965, 637.

<sup>14</sup> C. Banwell and N. Sheppard, *Discuss. Farad. Soc.*, 1962, 34, 115.

<sup>15</sup> R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, 1961, 16, 563.

<sup>16</sup> R. J. Abraham, P. A. Burbidge, A. H. Jackson, and D. B. MacDonald, *J. Chem. Soc. (B)*, 1966, 620.

<sup>17</sup> R. J. Abraham and P. F. Swinton, *J. Chem. Soc. (B)*, 1969, 903.

<sup>18</sup> G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Amer. Chem. Soc.*, 1963, 85, 3809.

<sup>19</sup> R. J. Abraham, G. H. Barnett, G. E. Hawkes, and K. M. Smith, unpublished results.

Table 1, and the fairly typical spectrum of aquo-octaethylporphinatoothallium(III) hydroxide (2c) is shown in Figure 1. The assignments of the resonances in the spectrum of (2c) are obvious; the chemical shift of the *meso*-protons is fairly normal for a metalloporphyrin (e.g. ref. 20), and suggests that there is no major distortion of the porphyrin ring by the large metal atom. (Such distortion would be expected to reduce the ring current and cause an upfield shift of the *meso*-proton

ethylporphyrin. In all these chelates, the metal is almost certainly out of the plane of the porphyrin ring, and the asymmetric environment above and below the plane of the macrocycle could account for the pronounced non-equivalence of the methylene protons. In the spectra of the thallium(III) tetraphenylporphyrins (4), the *ortho*-protons of the phenyl groups have different chemical shifts (Table 1), no doubt as a result of the different environment experienced by the *ortho*-proton

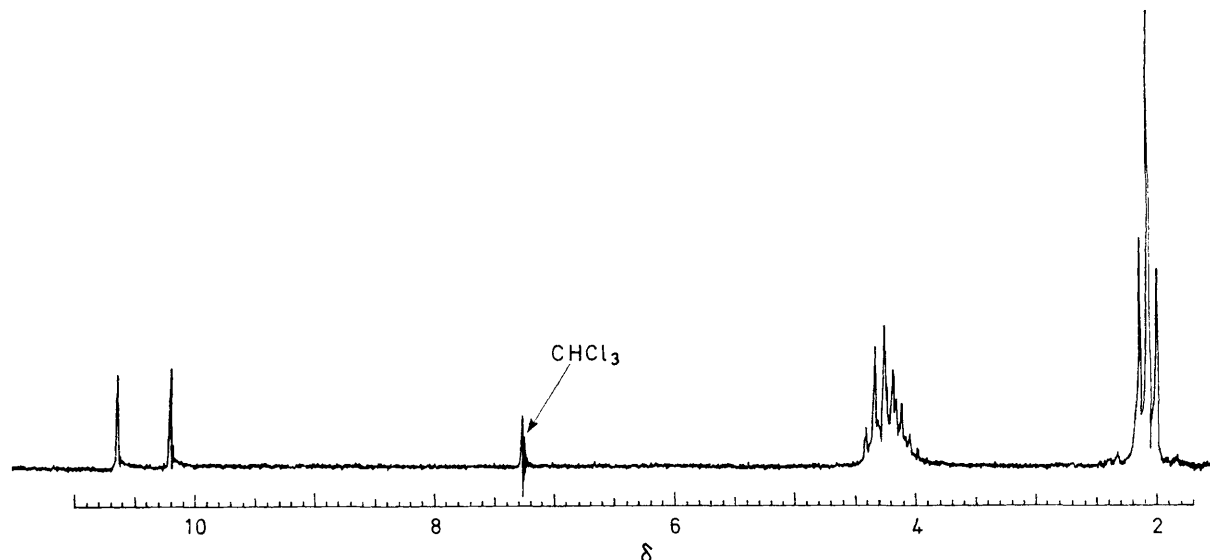
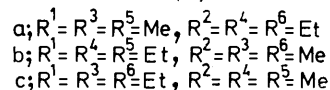
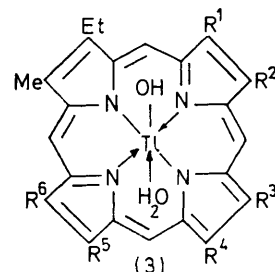


FIGURE 1 Proton n.m.r. spectrum of aquo-octaethylporphinatoothallium(III) hydroxide (2c) in  $\text{CDCl}_3$

resonances.) The most striking feature of the spectrum shown in Figure 1 is the large thallium coupling (44.4 Hz) to the *meso*-protons; the observation of thallium couplings through nitrogen is unusual, but these are probably observed on account of the enforced rigidity of the metalloporphyrin system. No measurable couplings between the thallium and the methyls of the ethyl functions was observed, and this has been found to be general in that protons which are three or more bonds removed from the porphyrin nucleus do not couple with the chelating thallium atom. The final, and important feature to be found in the spectrum of (2c) is the complex and unsymmetrical pattern of the methylene protons of the ethyl side-chains. We have already investigated and analysed<sup>21</sup> this pattern as an  $\text{ABXR}_3$  spectrum\* in which the diastereotopic methylene protons (A,B) have very different thallium couplings (6.1 and 18.1 Hz). The methylene protons of the trifluoroacetate (2a), aquo-acetate (2b), iodide (2d), and cyanide (2e) were also non-equivalent, as were those of thallium aetioporphyris-II and -IV [(3b) and (3c), respectively] and to a much lesser extent, thallium aetioporphyrin-I (3a). Such non-equivalence has also been observed in the lead(II),<sup>7</sup> tin(II),<sup>7</sup> and scandium(III)<sup>20</sup> chelates of octa-

above the ring plane from that situated below<sup>22</sup> (Figure 2). In contradistinction, the observation of



\* Strictly speaking, this spectrum is of the type  $\text{ABC}_3\text{X}$ , since the methyl protons should not be considered as a different nucleus. However, the  $J:\delta$  ratio is sufficiently small for this argument to be valid. Note the absence of asymmetry in the methyl group.

different chemical shifts for *ortho*-protons in some indium(III) tetraphenylporphyrin chlorides [e.g. (5)] has been interpreted<sup>23</sup> in terms of 'non-equivalence of phenyls in pairs, presumably, across the porphine ring' (our italics). We consider this explanation to be in

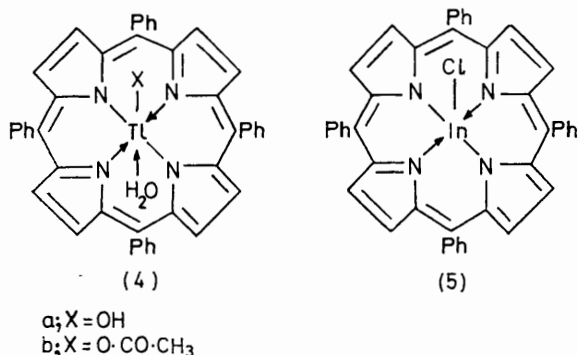
<sup>20</sup> E.g. J. W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H. H. Schneehage, and D. Weck, *Annalen*, 1971, **745**, 135.

<sup>21</sup> R. J. Abraham and K. M. Smith, *Tetrahedron Letters*, 1971, 3335.

<sup>22</sup> No rotation of phenyl groups occurs below ca. 60°: G. N. LaMar, G. R. Eaton, R. H. Holm, and F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **95**, 63.

<sup>23</sup> M. Bhatti, W. Bhatti, and E. Mast, *Inorg. Nucl. Chem. Letters*, 1972, **8**, 133.

error, since the metal atom in the indium(III) chelate must introduce asymmetry about the porphyrin ring



plane, thereby causing non-equivalence of the *ortho*-protons within each phenyl group. Furthermore, it is difficult to imagine a suitable distortion which would allow the phenyls to be non-equivalent in diagonal pairs.

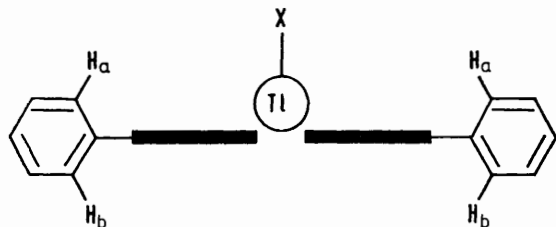


FIGURE 2 Schematic end-on view of a section through structure (4), indicating the different environments experienced by the phenyl *ortho*-protons H<sub>a</sub> and H<sub>b</sub>.

A further point of note in the spectrum of (2c) is the absence of any signal due to the axial hydroxy and water ligands; the spectrum was recorded over the range  $\pm 6$  kHz from tetramethylsilane, and no signal was detected (see later for discussion of i.r. results). The chemical and spectroscopic evidence for the presence of the ligands in (2c) is definitive, and the absence of the expected resonances could be explained in terms of broadening, due to exchange or hydrogen bonding. If there was also some residual Tl-<sup>1</sup>H coupling, then this would add to the difficulty in observation of the resonances. In the thallium(III) coproporphyrins, the distance between porphyrin rings in the aggregated dimer is very near to that calculated for the metal-free porphyrin;<sup>9</sup> this is surprising when one considers the extra space that the out-of-plane metal atom and its axial ligands would occupy. Intermolecular hydrogen bonding within the dimer would reduce the internuclear space requirement, while affording an additional attractive force between the rings; this would also account for the ligand protons not being observed in the proton n.m.r. spectra. Buchler<sup>20,24</sup> has also commented

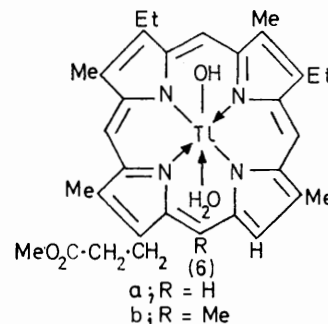
<sup>24</sup> J. W. Buchler, L. Puppe, and H. H. Schneehage, *Annalen*, 1971, **749**, 134; J. W. Buchler, personal communication.

<sup>25</sup> R. J. Abraham and D. F. Wileman, *J.C.S. Perkin II*, 1973, 1521.

<sup>26</sup> D. Doddrell and W. S. Caughey, *J. Amer. Chem. Soc.*, 1972, **94**, 2510.

upon the difficulty of observing hydroxy ligands of metalloporphyrins and has referred to the phenomenon as 'ligand uncertainty.' However, the protons of the acetate ligands are observed in the n.m.r. spectra; in both the thallium(III) octaethylporphyrin (2b) and tetraphenylporphyrin (4b) cases a three-proton singlet was observed near  $\delta$  0 (Table 1). The <sup>19</sup>F n.m.r. spectrum of the trifluoroacetate (2a) showed a sharp singlet 6.67 p.p.m. downfield from CF<sub>3</sub>·CCl<sub>3</sub> (*i.e.* at  $\phi^*$  75.43).<sup>25</sup>

*The Tl-<sup>1</sup>H Couplings.*—The data in Table 1 allow deductions to be made about the nature of the mechanism of transmission of the couplings. Replacement of a  $\beta$ -hydrogen with a methyl group results in a reduction of the coupling from *ca.* 70 to *ca.* 9 Hz [in the pyrroloporphyrin-XV methyl ester chelate (6a)]. This large difference implies strongly that the  $\beta$ -<sup>1</sup>H coupling is transmitted *via* a  $\sigma$ -mechanism; this is reinforced by the observation of a near planar zig-zag pathway<sup>14</sup> between the coupling nuclei. The effect of substituting a methyl group for a *meso*-hydrogen atom is to reduce the thallium coupling from *ca.* 45 to *ca.* 28 Hz [in the  $\gamma$ -phyloporphyrin-XV methyl ester thallium(III) chelate (6b)]. This suggests far more  $\pi$ -contribution to the transmission mechanism than in the case of the  $\beta$ -substituents. Considerable support from other physical measurements of porphyrins is available; the <sup>13</sup>C n.m.r. shifts of the  $\beta$ -carbon atoms of porphyrins have been shown<sup>26</sup> to be typically olefinic, whereas those of the *meso*-carbon atoms have been compared with shifts of the  $\beta$ -carbon atoms of pyrrole rings. Thus, Doddrell and Caughey<sup>28</sup> have suggested that this provides evidence for the '16-membered inner-pathway'<sup>27</sup> for delocalisation of the porphyrin  $\pi$ -electrons. More substantial evidence is



provided by the e.s.r. spectrum of the  $\pi$ -cation radical of zinc tetraphenylporphyrin, in which the hyperfine splitting of the  $\beta$ -hydrogens ( $a_{\beta-H}$  0.25 G) is much smaller than the *meso*-hydrogen splitting ( $a_{meso-H}$  1.48 G) in the  $\pi$ -cation radical of, for example, magnesium octaethylporphyrin;<sup>28</sup> this indicates a much smaller amount of electron spin density on the  $\beta$ -carbons.

The smaller Tl-<sup>1</sup>H coupling of the *meso*-protons in the

<sup>27</sup> L. E. Webb and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1965, **87**, 667.

<sup>28</sup> R. H. Felton, D. Dolphin, D. C. Borg, and J. Fajer, *J. Amer. Chem. Soc.*, 1969, **91**, 196; J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *ibid.*, 1970, **92**, 3451.

cyanide (2e) ( $J$  32 Hz) compared with the hydroxide (2c) ( $J$  44.4 Hz) presumably reflects both the withdrawal of electrons from the metal by the cyanide and increased  $\pi$ -contribution to the bonding.

**Concentration Effects.**—Unlike the metal-free porphyrins, most of the thallium(III) porphyrins described here showed only small concentration dependence of their n.m.r. spectra. For example, compound (2c) exhibited no appreciable change in the chemical shifts of its resonances over a 30-fold range in dilution from a saturated solution (*ca.* 0.1M in  $\text{CDCl}_3$ ). However, thallium(III) aetioporphylin-IV (3c) did show concentration effects similar to those found for the coproporphyrin-IV tetramethyl ester chelate.<sup>9</sup>

**Visible Absorption Spectra.**—The electronic spectra of thallium(III) porphyrins are of the normal two-banded type (Figure 3) typical of many metalloporphyrins.

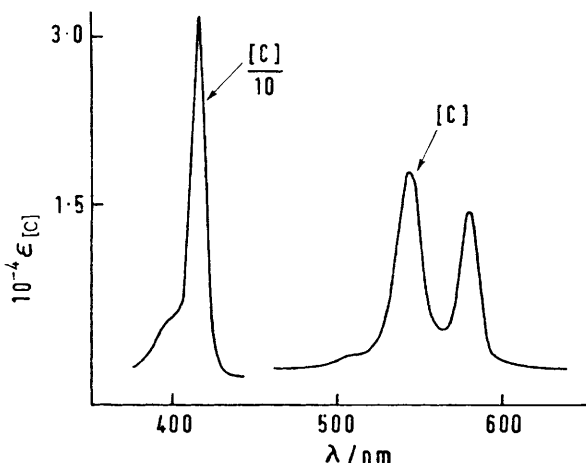


FIGURE 3 Visible absorption spectrum of compound (2c) in  $\text{CH}_2\text{Cl}_2$

It is apparent that there is no major distortion of the macrocyclic ring and that the large metal atom is situated above, rather than in, the plane of the porphyrin ring. The similarity of the visible absorption spectra of thallium porphyrins to those of normal divalent metal complexes may well have led Haurowitz<sup>4</sup> to formulate his compounds as derivatives of thallium(II). Visible absorption spectra are often used to obtain a rough estimate of the stability of a particular metalloporphyrin within a series;<sup>29</sup> for example, those chelates with the  $\alpha$  or  $\beta$  satellite bands at lowest wavelength, or with the greater numerical value for the ratio of the intensities of the  $\beta$  to  $\alpha$  bands, are considered to be most stable. Table 2 shows the wavelengths and  $\beta : \alpha$  band intensity ratios for some common chelates of octaethylporphyrin. The data indicate that thallium(III) porphyrins should be approximately as stable as magnesium porphyrins. However, this is demonstrably incorrect, since demetallation by acids occurs at a rate comparable with the behaviour of zinc(II) porphyrins, though thallium(III)

porphyrins are extremely susceptible to reductive demetallation. A perfect correlation in Table 2 would be unexpected, because trivalent thallium is being compared with a series of divalent metal chelates.

TABLE 2

Wavelengths and extinction ratios of  $\alpha$  and  $\beta$  bands in the visible absorption spectra of some metal chelates of octaethylporphyrin in  $\text{CH}_2\text{Cl}_2$

Metal	$\lambda_{\text{max}}$ , nm		Extinction ratio ( $\beta/\alpha$ )
	$\alpha$ band	$\beta$ band	
Nickel(II)	515	552	2.96
Copper(II)	525	563	1.94
Zinc(II)	532	571	1.39
Magnesium(II)	543	582	0.84
Thallium(III)	543	581	0.77

Variation of the axial ligands in the chelates (2) does not effect any great change in the electronic spectra, though minor changes are apparent (Experimental section).

**I.r. Spectra.**—A puzzling feature in the n.m.r. spectra of the aquo-hydroxides [*e.g.* (2c)] was the inability of the technique to detect the axial ligands. An obvious alternative physical method for investigation of these ligands was i.r. spectroscopy, but only very broad and weak OH bands ( $3580$ – $3700$   $\text{cm}^{-1}$ ) were observed for KBr discs or solutions in chloroform. Dilution of the chloroform solutions led to sharpening of the bands, indicating that intermolecular hydrogen bonding might account for the broadness.

The trifluoroacetate (2a) showed a strong band (KBr) at  $1665$   $\text{cm}^{-1}$  (C=O) with a weaker, but sharper band at  $790$   $\text{cm}^{-1}$  (OCO). Similarly, the aquo-acetate (2b) featured a broad band at  $1565$  with another at  $680$   $\text{cm}^{-1}$ . These results with the acetate (2b) are in accord with the data for other metallo-octaethylporphyrin acetates [*e.g.* scandium(III),  $1570$ ; zirconium(IV),  $1560$  and  $690$ ; <sup>21</sup> and mercury(II),  $1580$   $\text{cm}^{-1}$  <sup>30</sup>].

**Mass Spectra.**—Mass spectrometry has been used widely in the porphyrin area;<sup>31</sup> the main advantage of the technique is that it usually affords a reliable method for the determination of porphyrin and metalloporphyrin molecular weights, since in the absence of very labile side-chains, the base peak is often the molecular ion. However, thallium(III) porphyrins are unusual<sup>32</sup> in that the base peak is usually the metal-free porphyrin ligand ( $\text{PH}_2$ ); this provides an easy method for identification of the porphyrin constituent of the chelate. An ion corresponding to the directly demetallated ligand (P) is also apparent, as is a doublet at  $m/e$  203/205 (Tl) due to free thallium. A consequence of this last observation is the presence of anomalous ions corresponding to a high mass adduct between two thallium atoms and one porphyrin ligand lacking axial ligands ( $\text{Tl}_2\text{P}$ ), and the constitution of these ions has been confirmed<sup>32</sup> by high

<sup>31</sup> *E.g.* A. H. Jackson, G. W. Kenner, K. M. Smith, R. T. Aplin, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, 1965, **21**, 2913; D. R. Hoffmann, *J. Org. Chem.*, 1965, **30**, 3512; H. Budzikiewicz, F. v.d. Haar, and H. H. Inhoffen, *Annalen*, 1967, **701**, 23.

<sup>32</sup> K. M. Smith, *Org. Mass Spectrometry*, 1972, **6**, 1401.

<sup>29</sup> Ref. 2, pp. 34, 76.

<sup>30</sup> M. F. Hudson and K. M. Smith, unpublished results.

resolution mass measurement. These anomalous ions are presumably formed by ion-molecule collisions<sup>33</sup> in the source of the mass spectrometer (note the high pressure of thallium present). One example in which the ion  $\text{PH}_2$  is (marginally) not the base peak, is the iodide (2d) [TIP(I)]; here the base peak is the ion TIP, and high intensity peaks corresponding to TII and I are also observed. The mass spectrum shows no evidence of a water ligand.

**Demetallation of Thallium(III) Porphyrins.**—We have found that thallium(III) can be removed from porphyrins with acid at about the same rate (measured spectroscopically) as zinc from the same ligand; this suggests that the former metal may be a good masking function for porphyrin NH groups. With trifluoroacetic acid, thallium(III) porphyrins are demetallated almost instantaneously, but small quantities of oxophlorins are also produced, presumably because the liberated thallium(III) forms the trifluoroacetate, which is known to give<sup>34</sup> oxophlorins with metalloporphyrins in the presence of trifluoroacetic acid. A better procedure for demetallation is to pass a small quantity of sulphur dioxide through a methylene chloride-tetrahydrofuran solution of the thallium(III) porphyrin before addition of a small quantity of concentrated hydrochloric acid; the thallium(III) is reduced rapidly to thallium(I) and a precipitate of thallium(I) chloride is soon apparent. Other reductive methods have also proved satisfactory; the metal is removed slowly by hydrogenation in tetrahydrofuran over 10% palladised charcoal, but almost instantaneously with sodium borohydride in methanol-methylene chloride. It appears that a whole variety of reducing agents are effective, but we have not made an exhaustive study, in view of the efficiency of the acid-sulphur dioxide procedure.

#### EXPERIMENTAL

M.p.s were measured on a microscopic hot-stage apparatus. All chromatographic separations were carried out with Merck neutral alumina (Brockmann Grade III). Visible absorption spectra (solutions in methylene chloride) were measured with a Unicam SP 800 spectrophotometer, and <sup>1</sup>H n.m.r. spectra were determined (solutions in deuteriochloroform with tetramethylsilane as internal standard) with a Varian HA-100 instrument. Mass spectra (direct insertion probe, operating conditions 70 eV, 50  $\mu\text{A}$ , source temperatures 200–220°) were measured with an A.E.I. MS 12 spectrometer.

Thallium(III) acetate,<sup>35</sup> trifluoroacetate,<sup>36</sup> and nitrate,<sup>37</sup> were prepared from thallic oxide (B.D.H.) by following established literature procedures.

**Aquo-1,2,3,4,5,6,7,8-octaethylporphyrinatothallium(III) Hydroxide (2c)** [*Thallium(III) Octaethylporphyrin (OH, H<sub>2</sub>O)*].—Octaethylporphyrin (1 g) was dissolved with heating in tetrahydrofuran (25 ml) and methylene chloride (25 ml);

after cooling, thallium(III) trifluoroacetate (1.1 g) in tetrahydrofuran (20 ml) was added and the solution was set aside for 5 min with occasional swirling before being poured into methylene chloride (250 ml) and then washed with water (500 ml). The organic phase was washed with dilute aqueous sodium hydrogen carbonate solution and water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to dryness. The residue was chromatographed, initially with chloroform containing 2% ethanol as eluant (this assists the ligand exchange on the column) and then with methylene chloride. The porphyrinic eluates were collected, evaporated to dryness, and the residue was crystallised from methylene chloride-methanol to give the *thallium(III) chelate*, m.p. >300° (1.31 g, 91%) (Found: C, 55.75; H, 6.0; N, 7.2.  $\text{C}_{36}\text{H}_{47}\text{N}_4\text{O}_2\text{Tl}$  requires C, 56.0; H, 5.75; N, 7.25%),  $\lambda_{\text{max}}$  415 ( $\epsilon$  327,000), 543 (18,200), and 581 nm (14,200), *m/e*<sup>32</sup> 942 (11%), 940 (9), 938 (2.5), 772 (55), 770 (20), 737 (12), 735 (5), 534 (100), 532 (15), 205 (7), and 203 (3).

The following compounds were prepared in an analogous manner.<sup>9</sup>

**Aquo-2,4,6,8-tetraethyl-1,3,5,7-tetramethylporphyrinatothallium(III) hydroxide (3a)** [*thallium(III) aetioporphyrin-I (OH, H<sub>2</sub>O)*] (88%; 178 mg scale) had m.p. >300° (Found: C, 53.4; H, 5.4; N, 7.5.  $\text{C}_{32}\text{H}_{39}\text{N}_4\text{O}_2\text{Tl}$  requires C, 53.7; H, 5.5; N, 7.8%),  $\lambda_{\text{max}}$  415 ( $\epsilon$  290,000), 542 (17,000), and 580 nm (12,200), *m/e* 886 (14%), 884 (11), 882 (3), 716 (9), 714 (3), 681 (9), 679 (4), 478 (100), 463 (28), 358 (2), 239 (19), 205 (21), and 203 (9).

**Aquo-2,3,6,7-tetraethyl-1,4,5,8-tetramethylporphyrinatothallium(III) hydroxide (3b)** [*thallium(III) aetioporphyrin-II (OH, H<sub>2</sub>O)*] (90%; 350 mg scale) had m.p. >300° (Found: C, 53.55; H, 5.3; N, 7.75.  $\text{C}_{32}\text{H}_{39}\text{N}_4\text{O}_2\text{Tl}$  requires C, 53.7; H, 5.5; N, 7.8%),  $\lambda_{\text{max}}$  415 ( $\epsilon$  366,000), 542 (20,000), and 580 nm (14,500), *m/e* 886 (5%), 884 (4), 882 (1), 716 (17), 714 (8), 681 (15), 679 (6), 478 (100), 463 (25), 239 (12), 205 (10), and 203 (4).

**Aquo-2,3,5,8-tetraethyl-1,4,6,7-tetramethylporphyrinatothallium(III) hydroxide (3c)** [*thallium(III) aetioporphyrin-IV (OH, H<sub>2</sub>O)*] (83%; 37 mg scale) had m.p. >300° (Found: C, 53.8; H, 5.4; N, 7.5.  $\text{C}_{32}\text{H}_{39}\text{N}_4\text{O}_2\text{Tl}$  requires C, 53.7; H, 5.5; N, 7.8%),  $\lambda_{\text{max}}$  415 ( $\epsilon$  337,000), 542 (18,500), and 580 nm (14,000), *m/e* 886 (2%), 884 (2), 882 (1), 716 (20), 714 (7), 681 (10), 679 (4), 478 (100), 463 (35), 358 (3), 239 (19), 205 (8), and 203 (3).

**Aquo-2,4-diethyl-7-(2-methoxycarbonylethyl)-1,3,5,8-tetramethylporphyrinatothallium(III) hydroxide (6a)** [*thallium(III) pyrroporphyrin-XV methyl ester (OH, H<sub>2</sub>O)*] (85%; 80 mg scale) had m.p. 241–244° (Found: C, 51.8; H, 4.65; N, 7.4.  $\text{C}_{32}\text{H}_{37}\text{N}_4\text{O}_4\text{Tl}$  requires C, 51.5; H, 5.0; N, 7.5%),  $\lambda_{\text{max}}$  415 ( $\epsilon$  237,000), 543 (12,600), and 580 nm (7300), *m/e* 916 (4%), 914 (4), 912 (1), 746 (15), 744 (7), 711 (8), 709 (3), 508 (100), 205 (16), and 203 (6).

**Aquo-2,4-diethyl-7-(2-methoxycarbonylethyl)- $\gamma$ -1,3,5,8-pentamethylporphyrinatothallium(III) hydroxide (6b)** [*thallium(III)  $\gamma$ -phylloporphyrin-XV methyl ester (OH, H<sub>2</sub>O)*] (87%; 108 mg scale) had m.p. 253–256° (Found: C, 51.8; H, 4.85; N, 7.4.  $\text{C}_{33}\text{H}_{39}\text{N}_4\text{O}_4\text{Tl}$  requires C, 52.1; H, 5.15; N, 7.4%),  $\lambda_{\text{max}}$  420 ( $\epsilon$  322,500), 549 (15,400), 579 (3500), and 591 nm (3000), *m/e* 930 (1%), 928 (1), 926 (0.5), 760 (5),

<sup>33</sup> E. G. J. H. Beynon, 'Mass Spectrometry and its Applications to Organic Chemistry,' Elsevier, Amsterdam, 1960, p. 275.

<sup>34</sup> S. W. McCombie and K. M. Smith, *Tetrahedron Letters*, 1972, 2463; G. H. Barnett, M. F. Hudson, S. W. McCombie, and K. M. Smith, *J.C.S. Perkin I*, 1973, 691.

<sup>35</sup> L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, vol. 1, 1967, p. 1150.

<sup>36</sup> A. McKillop, J. D. Hunt, M. J. Zelesko, J. S. Fowler, E. C. Taylor, G. McGillivray, and F. Kienzle, *J. Amer. Chem. Soc.* 1971, **93**, 4841.

<sup>37</sup> A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Letters*, 1970, 5275.

758 (2), 725 (2), 723 (1), 522 (100), 261 (4), 205 (16), and 203 (7). This compound was only slightly soluble in  $\text{CDCl}_3$ , but the n.m.r. spectrum showed a three-proton doublet ( $\tau$  5.26;  $J$  28 Hz) assigned to the  $\gamma$ -methyl group.

*Aquo- $\alpha\beta\gamma\delta$ -meso-tetra-phenylporphinatothallium(III) hydroxide* (4a) (85%; 52 mg scale) had m.p.  $>300^\circ$  (Found: C, 61.8; H, 3.5; N, 6.35.  $\text{C}_{44}\text{H}_{31}\text{N}_4\text{O}_2\text{Tl}$  requires C, 62.0; H, 3.7; N, 6.6%),  $\lambda_{\text{max}}$  433 ( $\epsilon$  525,500), 567 (18,500), and 607 nm (10,000),  $m/e$  1022 (2%), 1020 (2), 1018 (1), 852 (1), 850 (0.5), 817 (2), 815 (1), 614 (100), 307 (20), 205 (18), and 203 (8).

*Aquo- $\alpha\beta\gamma\delta$ -meso-tetra-phenylporphinatothallium(III) acetate* (4b), prepared (71%; 116 mg scale) according to the method of Rothmund and Menotti,<sup>5</sup> had m.p.  $>300^\circ$  (Found: C, 62.2; H, 4.0; N, 6.0.  $\text{C}_{46}\text{H}_{33}\text{N}_4\text{O}_3\text{Tl}$  requires C, 61.8; H, 3.7; N, 6.3%),  $\lambda_{\text{max}}$  433 ( $\epsilon$  524,500), 567 (20,000), and 607 nm (10,500),  $m/e$  1022 (2%), 1020 (2), 1018 (1), 894 (1), 892 (0.5), 876 (1), 874 (0.5), 817 (2), 815 (1), 614 (100), 307 (17), 205 (15), and 203 (6),  $\nu_{\text{max}}$  (KBr) 1570  $\text{cm}^{-1}$  (C=O).

*Aquo-octaethylporphinatothallium(III) Acetate* (2b).—Octaethylporphyrin (100 mg) was dissolved in methylene chloride (50 ml) and tetrahydrofuran (10 ml) and treated with thallium(III) acetate (214 mg, *ca.* 3 equiv.) in tetrahydrofuran (5 ml). The mixture was heated during 16 h at  $40^\circ$ , then evaporated to dryness, and the residue was taken up in methylene chloride (25 ml). The solution was passed through a bed of Kieselgel G, which was washed with a small quantity of methylene chloride. The eluate was evaporated to dryness and the *thallium(III) porphyrin* (120 mg, 80%) was crystallised from methylene chloride–*n*-hexane; m.p.  $233\text{--}234^\circ$  (Found: C, 56.5; H, 6.0; N, 7.0.  $\text{C}_{38}\text{H}_{47}\text{N}_4\text{O}_3\text{Tl}$  requires C, 56.2; H, 5.8; N, 6.9%),  $\lambda_{\text{max}}$  415 ( $\epsilon$  349,500), 544 (18,100), 580 nm (13,500),  $m/e$  942 (60%), 940 (53), 938 (15), 796 (25), 794 (10), 737 (50), 735 (24), 534 (100), 267 (14), 205 (23), 203 (10), and 60 (15),  $\nu_{\text{max}}$  (KBr) 1565 and 680  $\text{cm}^{-1}$  (C=O).

*Aquo-2,4,6,8-tetrakis-(2-methoxycarbonylethyl)-1,3,5,7-tetra-methylporphinatothallium(III) acetate* [*thallium(III) coproporphyrin-I tetramethyl ester (OAc, H<sub>2</sub>O)*], similarly prepared (82%; 121 mg scale), had m.p.  $>300^\circ$  (Found: C, 51.2; H, 5.25; N, 5.5.  $\text{C}_{42}\text{H}_{49}\text{N}_4\text{O}_{11}\text{Tl}$  requires C, 50.95; H, 5.0; N, 5.7%),  $\lambda_{\text{max}}$  416 ( $\epsilon$  383,000), 544 (20,000), and 581 nm (13,000),  $m/e$  1118 (5%), 1116 (3), 1114 (0.5), 1045 (1), 1043 (1), 972 (1), 970 (1), 710 (100), 637 (40), 565 (10), 491 (5), 355 (5), 334 (9), 205 (15), and 203 (7),  $\nu_{\text{max}}$  (KBr) 1565 and 680  $\text{cm}^{-1}$  (C=O).

*Octaethylporphinatothallium(III) Trifluoroacetate* (2a).—Octaethylporphyrin (111 mg) was dissolved in methylene chloride (40 ml) and treated with thallium trifluoroacetate (125 mg) in tetrahydrofuran (20 ml). After stirring during 5 min, the solution was divided; 40 ml was subjected to the usual aqueous work-up and chromatography, and afforded the aquo-hydroxide (2c) (98 mg; 94%). The remaining 20 ml was passed through thoroughly dried

Kieselgel G (which was washed with dry methylene chloride) and the eluates were evaporated to dryness. Crystallisation from dry methylene chloride–*n*-hexane gave the *chelate* (43 mg, 76%), m.p.  $>300^\circ$  (Found: C, 53.7; H, 5.5; N, 6.7.  $\text{C}_{38}\text{H}_{44}\text{F}_3\text{N}_4\text{O}_2\text{Tl}$  requires C, 53.7; H, 5.2; N, 6.6%),  $\lambda_{\text{max}}$  412 ( $\epsilon$  272,000), 541 (16,000), and 578 nm (13,600),  $m/e$  942 (16%), 940 (14), 938 (4), 850 (2), 848 (1), 737 (5), 735 (2), 534 (100), 267 (17), 205 (10), and 203 (4),  $\nu_{\text{max}}$  (KBr) 1667 and 790  $\text{cm}^{-1}$  (C=O).

*2,4,6,8-Tetraethyl-1,3,5,7-tetramethylporphinatothallium(III) trifluoroacetate* [*thallium(III) aetioporphyrin-I (O·CO·CF<sub>3</sub>)*] was prepared similarly except that the reaction mixture was not divided; yield 70% (58 mg scale), m.p.  $>300^\circ$  (Found: C, 51.7; H, 5.05; N, 7.1.  $\text{C}_{34}\text{H}_{36}\text{F}_3\text{N}_4\text{O}_2\text{Tl}$  requires C, 51.4; H, 4.6; N, 7.1%),  $\lambda_{\text{max}}$  414 ( $\epsilon$  351,000), 542 (19,100), and 580 nm (14,200),  $m/e$  886 (35%), 884 (30), 882 (7), 794 (1), 792 (0.5), 681 (20), 679 (10), 478 (100), 463 (31), 239 (19), 205 (26), and 203 (11).

*Octaethylporphinatothallium(III) Iodide* (2d).—Aquo-octaethylporphinatothallium(III) hydroxide (50 mg) was dissolved in absolute acetone (20 ml) and dry tetrahydrofuran (5 ml), and dry powdered potassium iodide (1 g) was added. The mixture was heated under reflux during 48 h before removal of the excess of potassium iodide by filtration through dry Celite. The solution was evaporated to dryness, methylene chloride (10 ml) was added, and potassium iodide was filtered off. The filtrate was evaporated and the residue crystallised from methylene chloride–dry methanol to give the *chelate* (56 mg, 91%), m.p.  $>300^\circ$  (Found: C, 50.1; H, 5.4; N, 6.2.  $\text{C}_{36}\text{H}_{44}\text{I}\text{N}_4\text{Tl}$  requires C, 50.05; H, 5.1; N, 6.5%),  $\lambda_{\text{max}}$  421 ( $\epsilon$  290,000), 546 (18,000), and 584 nm (12,500),  $m/e$  942 (12%), 940 (9), 938 (3), 864 (27), 862 (13), 737 (100), 735 (42), 534 (85), 332 (6), 330 (3), 267 (12), 205 (8), 203 (4), and 127 (3).

*Octaethylporphinatothallium(III) Cyanide* (2e).—Aquo-octaethylporphinatothallium(III) hydroxide (36 mg) was dissolved in methylene chloride (15 ml) and stirred during 3 days with sodium cyanide (100 mg) in methanol (10 ml). The excess of sodium cyanide was filtered off on a bed of Celite and the filtrate was evaporated to dryness. Methylene chloride was added to the residue and sodium cyanide was removed by filtration; evaporation of the filtrate and crystallisation of the residue from methylene chloride–dry methanol gave the *chelate* (33 mg, 95%), m.p. *ca.*  $280^\circ$  (decomp.) (Found: C, 58.2; H, 5.8; N, 9.0.  $\text{C}_{37}\text{H}_{44}\text{N}_5\text{Tl}$  requires C, 58.2; H, 5.8; N, 9.2%),  $\lambda_{\text{max}}$  416 ( $\epsilon$  365,000), 545 (18,500), and 583 nm (12,000),  $m/e$  942 (6%), 940 (5), 938 (2), 763 (3), 761 (1), 737 (2), 735 (1), 534 (100), 267 (25), 205 (5), and 203 (2).

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