

BIS-THALLIUM(I) PORPHYRIN COMPLEXES

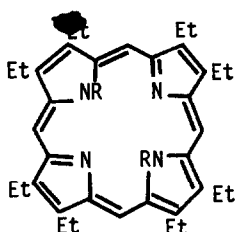
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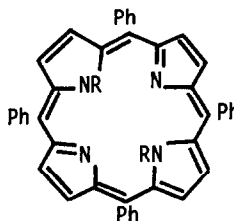
Summary: Treatment of octaethylporphyrin (1) or tetraphenylporphyrin (2) with more than two equiv of thallium(I) ethoxide gives the corresponding stable bis[thallium(I)] porphyrin complexes (5) and (6), respectively; these thallium(I) porphyrins are shown to have very different chemical and spectroscopic properties than do the corresponding thallium(III) porphyrin complexes.

Complexes of porphyrins with most metals in the periodic table, and often in several different oxidation states for the same metal, have been described.¹ For example, treatment of porphyrins such as octaethylporphyrin (1) and tetraphenylporphyrin (2) with thallium(III) salts gives the corresponding thallium(III) complexes (3) and (4), respectively, which have been thoroughly investigated, particularly by NMR spectroscopy on account of the nuclear spin of thallium.² However, apart from a brief report by Rothmund,³ thallium(I) porphyrins have not been studied, and have been said to be unstable.³ In this Letter we describe the synthesis and properties of thallium(I) complexes [(5) and (6), respectively] of octaethylporphyrin (1) and tetraphenylporphyrin (2). Thallium(I) porphyrins are of particular current interest in the broad field of metalloporphyrin chemistry because they have been predicted⁴ to have the novel "Hyper" type of electronic absorption spectrum; the comparative chemistry of thallium(I) and thallium(III) porphyrins is also of interest.

Our early attempts to prepare thallium(I) porphyrins centered on reduction of thallium(III) porphyrins with sodium borohydride (which was totally fruitless⁵), and treatment of porphyrins with thallium(I) acetate in pyridine. The latter approach gave, as Rothmund reported,³ green solutions of unstable chelates. However, we have now found that treatment of octaethylporphyrin (1) with more than 2 equiv of thallium(I) ethoxide in tetrahydrofuran as solvent gives an immediate precipitate of stable, and analytically pure bis[thallium(I)] complex, (5), mp >300°C. [Found: C, 45.70; H, 4.89; N, 5.88. $C_{36}H_{44}N_4Tl_2$ requires: C, 45.92; H, 4.71; N, 5.95%]. The



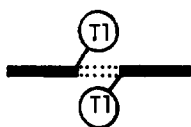
- (1) R = H
 (3) R₂ = Tl-X
 (5) R = Tl



- (2) R = H
 (4) R₂ = Tl-X
 (6) R = Tl

tetraphenylporphyrin complex (6) [Found: C, 52.24; H, 2.75; N, 5.09. C₄₄H₂₈N₄Tl₂ requires: C, 51.73; H, 2.76; N, 5.49%. Mp >300°C] was similarly obtained from tetraphenylporphyrin, (2).

The NMR spectra of the new complexes were remarkably similar to those of the free bases, except that in (5) the meso protons were broadened and the NH protons were absent, and in (6) the β -protons were slightly broadened and the NH protons were again absent. This NMR behavior



(7)

contrasts with that of the corresponding thallium(III) complexes (3) and (4) which showed² significant couplings to these protons [$J_{\text{meso-H-Tl}} = 46$ Hz (3) and $J_{\beta\text{-H-Tl}} = 65$ Hz (4)]. Furthermore, the ortho-phenyl protons in the tetraphenyl complex (6) showed no

evidence of non-equivalence, suggesting that the thallium(I) ions are symmetrically disposed on either side of the porphyrin plane, as shown in (7).

The electronic absorption spectra of the thallium(I) complexes (5) and (6) are shown in Figures 1 and 2, respectively. They are clearly of the "Hyper" type, being similar to those of the analogous Sn(II) and Pb(II) complexes, and substantiate in all respects the proposals of Gouterman.⁴ Bis-thallium(I) porphyrins are green in solution, but on standing evidence of partial demetalation is apparent spectrophotometrically. Upon treatment with 2,3-dichloro-5,6-dicyano-benzoquinone, the thallium(I) chelates are oxidized to their thallium(III) counterparts.

Mass spectrometry of the complexes (5) and (6) showed no evidence of chelation of the two thallium ions, the free-base molecular ion being the base peak. However, prominent peaks at m/e 203 and 205 (Tl) were observed; these observations are closely paralleled in the mass spectra of the corresponding thallium(III) porphyrins,⁶ in which demetalation to give free-base porphyrin is always a major fragmentation pathway. An added feature of the mass spectra was the ease with which other metal ions were scavenged by the bis-dethallated species from the spectrometer source.

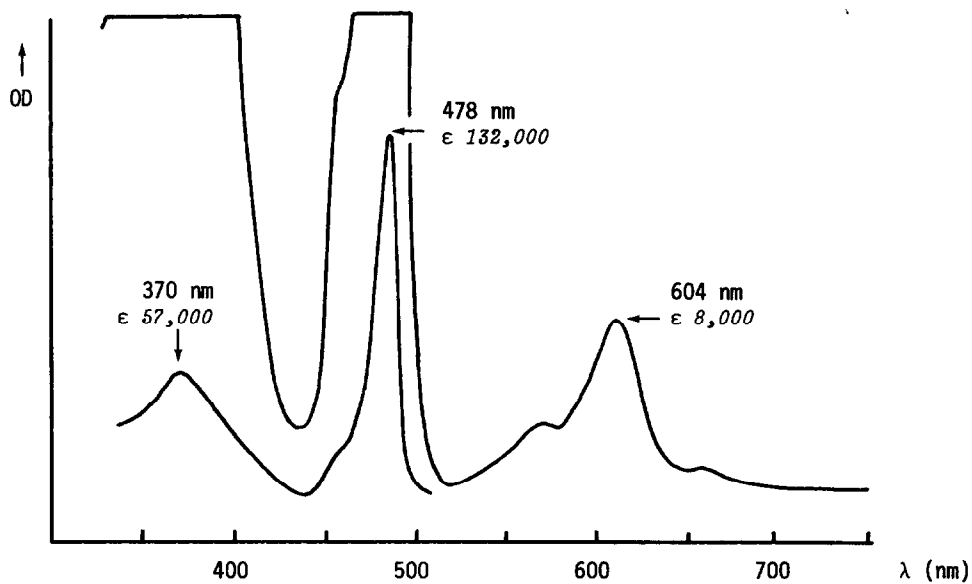


FIGURE 1: Electronic Absorption Spectrum, in CH_2Cl_2 , of TL_2OEP (5).

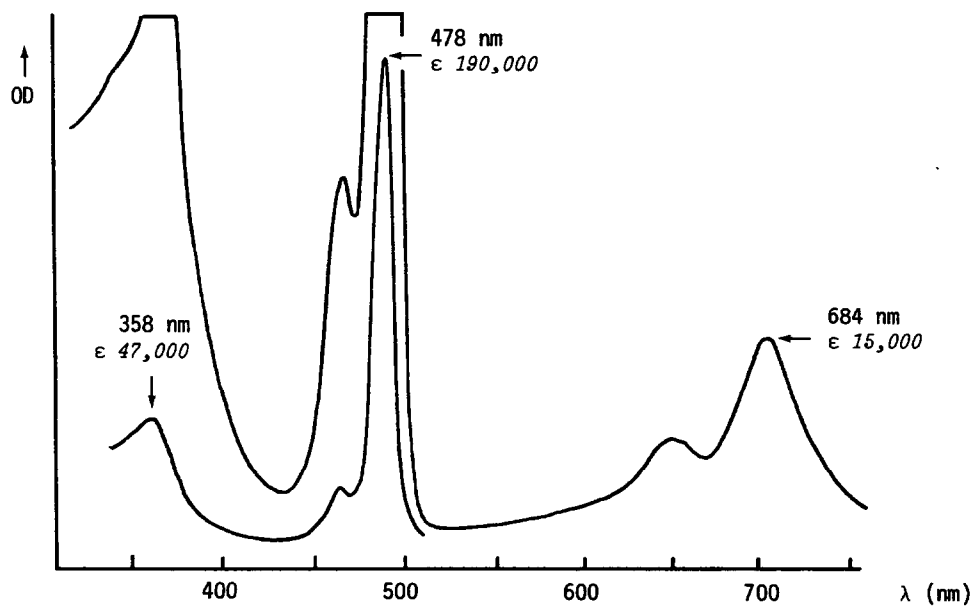
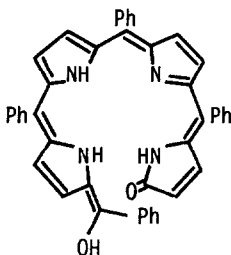


FIGURE 2: Electronic Absorption Spectrum, in CH_2Cl_2 , of TL_2TPP (6).

In methylene chloride solution, the thallium(I) complex (6) of tetraphenylporphyrin was photo-oxidized to give the open-chain compound (8). This same compound has already been obtained via the isoporphyrin cation of zinc(II) tetraphenylporphyrin,⁷ and from photo-oxygenation of magnesium(II) tetraphenylporphyrin,^{8,9} or photo-oxygenation of cadmium(II) tetraphenylporphyrin.¹⁰ The ready photocleavage of (6) suggests that it possesses a fairly low oxidation potential, comparable with MgTPP and CdTPP, but considerably lower than Tl(III)TPP ($E_{1/2}^1 = \underline{\text{ca.}}$



(8)

1 Volt at Pt vs. sce).¹¹

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References and Notes:

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