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Molecular Structures of Methyl-5,10,15,20-tetraphenylporphinatothallium(III) and Chloro-5,10,15,20-tetraphenylporphinatothallium(III)

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Methyl-5,10,15,20-tetraphenylporphinatothallium(III), CH_3TlTPP, and methyl-2,3,7,8,12,13,17,18-octaethylporphinatothallium(III), CH_3TlOEP, are obtained by the reaction of diacetatomethylthallium(III) with $TPPH_2$ and $OEPH_2$, respectively. The molecule CH_3TlTPP displays a square-pyramidal coordination geometry for the thallium atom and crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.046$ (2), $b = 16.244$ (3), $c = 23.373$ (5) Å, $\beta = 115.5$ (1)°, and $Z = 4$. The compound previously assumed to be aquohydroxy-5,10,15,20-tetraphenylporphinatothallium(III), $(H_2O)\cdot OHTlTPP$ is isomorphous with CH_3TlTPP and is shown by x-ray analysis to be chloro-5,10,15,20-tetraphenylporphinatothallium(III), ClTlTPP, $a = 10.064$ (2), $b = 16.177$ (2), $c = 23.354$ (5) Å, and $\beta = 115.3$ (1)°. Measurement of diffracted intensities employed θ–2θ scans with graphite-monochromated Mo Kα radiation on a four-circle diffractometer. The structures were solved using the heavy-atom technique. Full-matrix least-squares refinement gave a final value of 0.045 (0.046) [for CH_3TlTPP(ClTlTPP)] for the conventional unweighted residual, R, for 2751 (2782) unique reflections having $I \geq 3\sigma(I)$. In these isomorphous complexes there are significant differences in coordination geometry, notably the displacement of the thallium atom from the porphyrin mean plane. CH_3TlTPP: $C_t\cdots Tl$, 0.979; Tl–N, 2.29 (1); Tl–C, 2.147 (12) Å. ClTlTPP: $C_t\cdots Tl$, 0.737; Tl–N, 2.21 (1); Tl–Cl, 2.420 (4) Å. The ^{13}C and ^1H NMR spectra of CH_3TlTPP and CH_3TlOEP show marked differences in the ^{205}Tl–^{13}C and ^{205}Tl–^1H coupling constants when compared with their chlorothallium porphyrin analogues, ClTlTPP and ClTlOEP.

The interpretation of NMR parameters of complexes containing heavy metals is of considerable current interest.[1] A knowledge of molecular structures in solution is a prerequisite for any detailed analysis of the factors influencing these parameters. For example, it has been established[2–4] that the coupling constants of several heavy-metal organometallic derivatives are dependent on solvent–complex interactions. As an extension of a program to establish the nature of these solvent interactions in organothallium complexes,[3,4] coordination environments have been sought which either preclude coordination of solvent molecules or allow exchange of solvent at a single site only. Alkylthallium porphyrins were selected for study and we report here unexpected results which were obtained with methyl-5,10,15,20-tetraphenylporphinatothallium(III), CH_3TlTPP, and methyl-2,3,7,8,12,13,17,18-octaethylporphinatothallium(III), CH_3TlOEP.

Experimental Section

^{13}C NMR spectra were obtained at 22.63 MHz on a Bruker HX-90E spectrometer and ^1H NMR spectra were obtained at 60 MHz in lock mode on a Perkin-Elmer R12B spectrometer and at 220 MHz on a Varian HR-220 spectrometer. All spectra were run in saturated deuteriochloroform solutions with tetramethylsilane as internal standard, and signal multiplicities are reported as d = doublet, t = triplet, and m = multiplet. Except where noted, by reference to a specific isotope of thallium, separate coupling to ^{205}Tl and ^{203}Tl ($I = {}^1/_2$, natural abundance 70.5 and 29.5%, respectively, $\gamma_{205}/\gamma_{203} = 1.0097$) was not resolved and is indicated by omission of the mass number. Microanalysis data were determined on a Perkin-Elmer Elemental Analyzer 240 within this Department, and by the Butterworth Microanalytical Service.

Methyl-5,10,15,20-tetraphenylporphinatothallium(III), CH_3TlTPP. Tetraphenylporphyrin ($TPPH_2$) (610 mg, 1.0 mmol) was dissolved with heating in chloroform (50 mL); excess diacetatomethylthallium(III)[5] (370 mg, 1.1 mmol) in chloroform (25 mL) was added to the cooled solution and the solution was set aside for 30 min. The green solution was concentrated to ca. 5 mL and left to stand at −5 °C overnight. The crystals produced were collected by filtration and air dried to give CH_3TlTPP, as deep blue prisms, mp >300 °C (730 mg, 91%). Anal. Calcd for $C_{45}H_{31}N_4Tl$: C, 64.9; H, 3.7; N, 6.7. Found: C, 65.0; H, 4.1; N, 6.6. ^1H NMR: δ −3.49 (d, CH_3–Tl, $^2J(^{205}Tl–^1H) = 724 \pm 2$ Hz), 7.73 (m, meta and para H), 8.18 (m, ortho H),[6] 8.91 ppm (d, β-H, $^4J(Tl–^1H) = 16.4$ Hz). ^{13}C NMR: δ 121.5 (d, meso C, $^3J(Tl–^{13}C) = 56.4$ Hz), 126.4 (s, C_3), 127.5 (s, C_4), 131.8 (d, β-C, $^3J(Tl–^{13}C) = 27.6$ Hz), 134.7 (s, C_2), 142.9 (s, C_1), 150.2 ppm (d, α-C, $^2J(Tl–^{13}C) = 33.5$ Hz). Low solubility precluded observation of the ^{13}C resonance due to $\mathit{C}H_3$–Tl.

Methyl-2,3,7,8,12,13,17,18-octaethylporphinatothallium(III), CH_3TlOEP, was prepared from octaethylporphyrin ($OEPH_2$) in an analogous manner to that for CH_3TlTPP. Red crystals of CH_3TlOEP were obtained from chloroform (87%), mp >300 °C. Anal. Calcd for $C_{37}H_{47}N_4Tl$: C, 59.1; H, 6.3; N, 7.4. Found: C, 58.9; H, 6.2; N, 7.8. ^1H NMR: δ −3.89 (d, $C\mathit{H}_3$–Tl, $^2J(^{205}Tl–^1H) = 715 \pm 3$ Hz), 1.89 (t, $C\mathit{H}_3$–CH_2), 4.13 (m, $C\mathit{H}_2$–CH_3),[7] 10.15 ppm (d, meso H, $^4J(Tl–^1H) = 7.8$ Hz). ^{13}C NMR: δ −0.86 (d, $\mathit{C}H_3$–Tl, $^1J(^{205}Tl–^{13}C) = 5835 \pm 3$ Hz), 18.5 (s, $\mathit{C}H_3$–CH_2), 19.9 (s, CH_3–$\mathit{C}H_2$), 97.5 (d, meso C, $^3J(Tl–^{13}C) = 52$ Hz), 142.1 (d, β-*C*, $^3J(Tl–^{13}C) = 24.4$ Hz), 147.5 ppm (d, α-*C*, $^2J(Tl–^{13}C) = 29.4$ Hz).

Chloro-5,10,15,20-tetraphenylporphinatothallium(III), ClTlTPP, was obtained by the reaction of $TPPH_2$ with trifluoroacetatothallium(III) followed by chromatography on alumina with chloroform (2% ethanol), under conditions used by Abraham,[8] for the synthesis of the compound presumed to be aquohydroxy-5,10,15,20-tetraphenylporphinatothallium(III), $(H_2O)OHTlTPP$. Crystals of ClTlTPP suitable for diffraction studies were grown from chloroform/methanol. The ^1H NMR spectrum of ClTlTPP was in agreement with that of the compound reported to be $(H_2O)OHTlTPP$.[8] Anal. Calcd for $C_{44}H_{28}N_4ClTl$: C, 62.0; H, 3.3; N, 6.6; Cl, 4.2. Found: C, 61.8; H, 3.5; N, 6.4; Cl 4.7. Calcd for $C_{44}H_{31}N_4O_2Tl$: C, 62.0; H, 3.6; N, 6.6.

Chloro-2,3,7,8,12,13,17,18-octaethylporphinatothallium(III), ClTlOEP, was prepared by a method analogous to that for ClTlTPP. The ^1H NMR spectrum of ClTlTPP was in agreement with that of the compound reported to be $(H_2O)OHTlOEP$.[8] Anal. Calcd for $C_{36}H_{44}N_4ClTl$: C, 55.9; H, 5.7; N, 7.3; Cl, 4.6. Found: C, 55.9; H, 5.1; N, 6.2; Cl, 5.7. Calcd for $C_{36}H_{47}N_4O_2Tl$: C, 56.0; H, 6.1; N, 7.3.

Crystallography. Weissenberg photographs used to determine the probable space group indicated for both CH_3TlTPP and ClTlTPP monoclinic, $2/m$, symmetry. The systematically absent reflections were those uniquely required by the centrosymmetric space group $P2_1/c$.

Unit-cell calibration was carried out for each sample by a least-squares fit of the angular parameters for 25 reflections with 2θ ca. 20° centered in the counter aperture of a Philips PW1100 automatic four-circle diffractometer using graphite monochromatized Mo Kα radiation (λ 0.7107 Å). A θ–2θ scan mode was used for data collection and reflections with $3.0 < \theta < 30.0°$ were examined. Weak reflections which gave $I_{top} - 2(I_{top})^{1/2} < I_{back}$ on the first scan were not further examined (I_{top} is the intensity at the top of the reflection peak and I_{back} is the mean of two preliminary 5-s background measurements on either side of the peak). Of the remaining reflections those for which the total intensity recorded in the first scan of the peak (I_{int}) was <500 counts were scanned twice to increase their accuracy. A constant scan speed of 0.05° s^{-1} and a variable scan width of $(0.8 + 0.1 \tan \theta)°$ were used, with a background measuring time proportional to I_{back}/I_{int}. Three standard reflections were measured every 5 h during data collection and showed no significant variations in intensity. See Table I for pertinent crystal information and details of data collection.

Table I. Summary of Crystal Data and Intensity Collection

Compd	CH_3TlTPP	ClTlTPP
Formula weight, amu	832.1	852.6
Formula	$C_{45}H_{31}N_4Tl$	$C_{44}H_{28}N_4ClTl$
Space group	$P2_1/c$	$P2_1/c$
a, Å	10.046 (2)	10.046 (2)
b, Å	16.244 (3)	16.177 (3)
c, Å	23.373 (5)	23.354 (5)
β, deg	115.5 (1)	115.3 (1)
Space group[a]	$P2_1/n$	$P2_1/n$
c, Å	21.095 (5)	21.172 (5)
β, deg	90.0 (1)	90.5 (4)
V, Å^3	3442.4	3443.6
Z	4	4
F(000)	1640	1672
Crystal dimensions, mm	0.15 × 0.15 × 0.15	0.20 × 0.07 × 0.20
μ, cm^{-1}	45.25	45.97
Final no. of variables	164	164
Unique data used $I > 3\sigma(I)$	2751	2782

[a] The monoclinic space group $P2_1/n$ was used in the data collection and refinement and the atomic coordinates (Table II) are given in this space group.

Reflections in two quadrants (5142) were measured after the preliminary test (see above) for CH_3TlTPP, and 3032 reflections were measured in one quadrant for ClTlTPP. The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer.[9] The variance of the intensity, *I*, was calculated as the sum of the variance due to counting statistics and $(0.03I)^2$, where the term in I^2 was introduced to allow for other sources of error.[10] *I* and $\sigma(I)$ were corrected for Lorentz and polarization factors and reflections for which $I < 3\sigma(I)$ were rejected. The transmission factors estimated, for the crystal of ClTlTPP, along the nonequivalent edge lengths were 0.725 and 0.400. The transmission factor estimated for the near cubic crystal of CH_3TlTPP was 0.507 along the crystal edge length. No absorption corrections were applied. Equivalents were averaged to give 2751 and 2782 unique reflections for CH_3TlTPP and ClTlTPP, respectively.

Both structures were solved by the heavy-atom method and refined by full-matrix least squares. The hydrogen atom coordinates were estimated geometrically (assuming C–H = 1.08 Å) and for the refinement allowed to ride on their respective carbon atom coordinates. For both structures the phenyl rings were refined as rigid bodies (with C–C = 1.395 Å) and for the final stages of refinement the thallium atom in each case was allowed to assume anisotropic thermal parameters (together with the chlorine atom in ClTlTPP). In the final cycle of refinement no parameter shift in each compound exceeded 0.12σ. For CH_3TlTPP *R* was 0.045 and $R' = 0.043$ and for ClTlTPP $R = 0.046$ and $R' = 0.044$ ($R' = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$, where $w = m(\sigma^2|F_o| + n \times 10^{-4}|F_o|^2)^{-1}$, and for CH_3TlTPP $m = 1.0471$, $n = 2.3$, and for ClTlTPP $m = 1.108$, $n = 0.59$). Neutral atom scattering factors were used,[11] those for Tl and Cl being corrected for anomalous dispersion effects ($\Delta f'$, $\Delta f''$).[12] Computation was carried out using the "Shelx" system[13] and ORTEP2.[14] A listing of the observed and calculated structure amplitudes for the data used in the refinements is available.[15]

Results and Discussion

The reaction of chloroform solutions of $TPPH_2$ and $OEPH_2$ with a slight excess of diacetatomethylthallium(III)[5] at room temperature gave >90% of CH_3TlTPP or CH_3TlOEP after

Table II. Atomic Fractional Cell Coordinates (Tl × 10^5, others × 10^4) for the Tetraphenylporphinatothallium Compounds CH_3TlTPP and ClTlTPP[d]

Atom type[a]	x^b	y^b	z^b
Tl	18631 (5) [16219 (5)]	19042 (4) [18281 (3)]	34512 (2) [34785 (3)]
N_{a1}	251 (9) [218 (10)]	2793 (6) [2793 (6)]	3798 (4) [3799 (5)]
N_{b1}	433 (8) [408 (9)]	1884 (6) [1889 (7)]	2607 (4) [2604 (4)]
N_{c1}	1790 (9) [1747 (9)]	515 (6) [497 (6)]	3248 (4) [3255 (5)]
N_{d1}	1498 (9) [1486 (10)]	1402 (6) [1382 (7)]	4450 (4) [4460 (5)]
C_{a1}	135 (10) [92 (12)]	3070 (8) [3070 (8)]	4408 (5) [4399 (5)]
C_{a2}	−632 (12) [−599 (13)]	3815 (8) [3833 (8)]	4409 (6) [4406 (7)]
C_{a3}	−961 (12) [−944 (13)]	3977 (8) [3992 (8)]	3800 (6) [3791 (6)]
C_{a4}	−438 (11) [−414 (12)]	3321 (7) [3352 (8)]	3422 (5) [3419 (6)]
C_{a5}	−624 (10) [−594 (12)]	3237 (7) [3263 (8)]	2756 (5) [2764 (6)]
C_{a6}	−1431 (8) [−1351 (9)]	3884 (5) [3937 (5)]	2441 (4) [2424 (4)]
C_{b1}	−210 (11) [−231 (12)]	2571 (7) [2583 (8)]	2390 (5) [2397 (6)]
C_{b2}	−491 (11) [−451 (12)]	2470 (7) [2490 (8)]	1716 (5) [1718 (6)]
C_{b3}	−10 (11) [25 (12)]	1732 (7) [1743 (9)]	1548 (6) [1539 (6)]
C_{b4}	587 (11) [549 (12)]	1350 (7) [1353 (8)]	2102 (5) [2101 (6)]
C_{b5}	1123 (11) [1119 (12)]	579 (7) [566 (8)]	2118 (5) [2132 (6)]
C_{b6}	1062 (7) [1043 (9)]	65 (5) [63 (5)]	1521 (3) [1528 (4)]
C_{c1}	1682 (10) [1628 (12)]	171 (7) [156 (8)]	2651 (5) [2664 (6)]
C_{c2}	2145 (11) [2044 (13)]	−667 (8) [−696 (8)]	2680 (6) [2692 (6)]
C_{c3}	2444 (12) [2355 (14)]	−822 (8) [−871 (9)]	3297 (6) [3304 (6)]
C_{c4}	2241 (11) [2170 (12)]	−89 (8) [−123 (8)]	3647 (6) [3666 (6)]
C_{c5}	2395 (12) [2354 (12)]	−14 (8) [−36 (8)]	4313 (6) [4309 (6)]
C_{c6}	2902 (8) [2911 (9)]	−739 (4) [−759 (5)]	4671 (3) [4673 (4)]
C_{d1}	2024 (12) [2022 (13)]	674 (8) [656 (8)]	4663 (6) [4673 (6)]
C_{d2}	2109 (11) [2098 (12)]	729 (8) [707 (8)]	5353 (6) [5357 (6)]
C_{d3}	1591 (11) [1595 (12)]	1460 (8) [1448 (8)]	5328 (6) [5527 (6)]
C_{d4}	1225 (10) [1219 (11)]	1894 (8) [1895 (8)]	4962 (5) [4974 (5)]
C_{d5}	609 (12) [593 (12)]	2664 (7) [2662 (8)]	4959 (6) [4947 (6)]
C_{d6}	361 (7) [357 (9)]	3044 (5) [3039 (6)]	5588 (3) [5587 (3)]
C_{a7}	−889[c] [−868]	2949 [2914]	5867 [5876]
C_{a8}	−1115 [−1061]	3234 [3176]	6481 [6496]
C_{a9}	−90 [−28]	3616 [3562]	6817 [6827]
C_{a10}	1160 [1196]	3711 [3687]	6539 [6539]
C_{a11}	1385 [1389]	3426 [3425]	5925 [5919]
C_{b7}	−853 [−715]	4618 [4651]	2236 [2214]
C_{b8}	−1639 [−1451]	5225 [5283]	1955 [1930]
C_{b9}	−3003 [−2824]	5098 [5200]	1880 [1856]
C_{b10}	−3581 [−3461]	4364 [4486]	2085 [2066]
C_{b11}	−2795 [−2724]	3757 [3855]	2366 [2350]
C_{c7}	−182 [−190]	−204 [−220]	1314 [1312]
C_{c8}	−288 [−278]	−666 [−677]	759 [754]
C_{c9}	852 [867]	−860 [−850]	412 [412]
C_{c10}	2096 [2100]	−591 [−566]	619 [627]
C_{c11}	2202 [2188]	−128 [−110]	1174 [1185]
C_{d7}	2096 [2136]	−1137 [−1163]	5115 [5120]
C_{d8}	2601 [2678]	−1794 [−1806]	5467 [5478]
C_{d9}	3910 [3995]	−2053 [−2046]	5375 [5389]
C_{d10}	4716 [4770]	−1656 [−1643]	4932 [4941]
C_{d11}	4212 [4228]	−999 [−999]	4580 [4583]
Methyl C	3789 (11)	2433 (8)	3282 (6)
Chlorine	[3776 (3)]	[2430 (2)]	[3272 (2)]

[a] Each symbol for an atom of the thallium tetraphenylporphyrins carries a literal subscript to identify its particular subunit (a, b, c, or d) and a numerical subscript that follows the numbering schemes used in Figure 1 to distinguish atoms of the same element within the same subunit. [b] The atomic coordinates are given for the nonstandard space group $P2_1/n$. [c] The phenyl substituents were refined as rigid bodies pivoting on the atom bonding to the porphyrin ring system, and the fractional cell coordinates for atoms C_7–C_{11} are dependent on atoms C_6. [d] Methylthallium values are given first followed by the chlorothallium values in square brackets. Least-squares esd values are given in parentheses.

partial removal of solvent. The ^1H NMR spectra of these compounds showed coupling to $^{203,205}Tl$ but showed negligible solvent dependency and provided no evidence for coordination of pyridine over the temperature range −60 to 35 °C. This result was surprising in view of reported adduct formation in other metalloporphyrins[16] and the suggested six-coordination for thallium in complexes assumed to be the aquohydroxythallium(III) derivatives $(H_2O)OHTlTPP$ and $(H_2O)OHTlOEP$.[8,17] An x-ray structure determination of CH_3TlTPP provided an explanation for this anomaly.[18]

Final coordinates and isotropic thermal parameters for all atoms except hydrogen atoms are listed in Tables II and III, respectively. The numbering scheme used to designate atoms of the $Tl(NC_{11}H_7)_4$ moiety is as follows. Each symbol for an atom of the porphyrin carries a literal subscript to identify the particular 2-methylenepyrrole subunit (a, b, c, or d) and a numerical subscript to distinguish between atoms of the same element within the subunit. Numerical subscripts for atoms are assigned in the same way for each subunit. The view of the molecule CH_3TlTPP in Figure 1 is nearly parallel to the methyl–thallium bond and perpendicular to the mean plane of the macrocycle.

The thallium atom in CH_3TlTPP is displaced from the plane defined by the porphyrin ring system by 1.11 Å. A shortening of the Tl–N bonds from an average of 2.29 Å or a major distortion from planarity of the N_4^{2-} donor set would be required before the Tl atom would lie close enough to the porphyrin to allow the approach of a second axial ligand.

A tilting of adjacent pyrrole rings by 9.4 ± 0.60° with respect to each other is apparently required to allow the Tl

Table III. Thermal Parameters (×10³ Å²) for the Tetraphenylporphinatothallium Compounds, CH_3TlTPP and ClTlTPP[c]

Atom type[a]	U	Atom type[a]	U
Methyl C	47 (3)	C_{d3}	42 (3) [43 (3)]
N_{a1}	34 (3) [46 (3)]	C_{d4}	36 (2) [44 (3)]
N_{b1}	33 (2) [42 (2)]	C_{d5}	38 (3) [45 (4)]
N_{c1}	35 (2) [43 (3)]	C_{d6}	39 (3) [46 (3)]
N_{d1}	38 (2) [45 (3)]	C_{a7}	55 (4) [70 (5)]
C_{a1}	38 (3) [40 (3)]	C_{a8}	63 (4) [84 (5)]
C_{a2}	46 (3) [53 (4)]	C_{a9}	59 (4) [79 (5)]
C_{a3}	44 (3) [50 (4)]	C_{a10}	56 (4) [88 (5)]
C_{a4}	35 (3) [42 (3)]	C_{a11}	46 (4) [71 (5)]
C_{a5}	33 (3) [42 (3)]	C_{b7}	67 (4) [57 (4)]
C_{a6}	37 (3) [46 (4)]	C_{b8}	75 (5) [58 (4)]
C_{b1}	35 (3) [48 (4)]	C_{b9}	69 (4) [69 (5)]
C_{b2}	41 (3) [49 (3)]	C_{b10}	75 (5) [74 (5)]
C_{b3}	34 (3) [44 (3)]	C_{b11}	69 (4) [66 (4)]
C_{b4}	35 (3) [42 (3)]	C_{c7}	44 (3) [61 (4)]
C_{b5}	29 (3) [56 (4)]	C_{c8}	51 (3) [71 (4)]
C_{b6}	47 (3) [47 (4)]	C_{c9}	59 (4) [64 (4)]
C_{c1}	48 (3) [45 (3)]	C_{c10}	57 (4) [72 (5)]
C_{c2}	42 (3) [47 (4)]	C_{c11}	55 (4) [64 (4)]
C_{c3}	42 (3) [49 (4)]	C_{d7}	45 (3) [73 (5)]
C_{c4}	40 (3) [47 (3)]	C_{d8}	60 (4) [73 (4)]
C_{c5}	42 (3) [37 (3)]	C_{d9}	65 (4) [65 (4)]
C_{c6}	42 (3) [49 (4)]	C_{d10}	71 (4) [66 (4)]
C_{d1}	40 (3) [45 (3)]	C_{d11}	61 (4) [64 (5)]
C_{d2}	42 (3) [44 (3)]		

	U_{11}[b]	U_{22}[b]	U_{33}[b]	U_{12}[b]	U_{13}[b]	U_{23}[b]
Tl in CH_3TlTPP	41 (3)	39 (3)	32 (3)	−1.6 (4)	−3.3 (2)	1.3 (4)
Tl in ClTlTPP	46 (0)	41 (0)	33 (0)	−2.7 (4)	−3.7 (2)	4.6 (4)
Cl in ClTlTPP	51 (2)	72 (3)	66 (3)	8 (2)	2 (2)	−9 (2)

[a] The atom numbering system follows that used in Table II. [b] Anisotropic parameters (×10³ Å²). [c] Methylthallium values are given first followed by the chlorothallium values in square brackets. Least-squares esd values are given in parentheses.

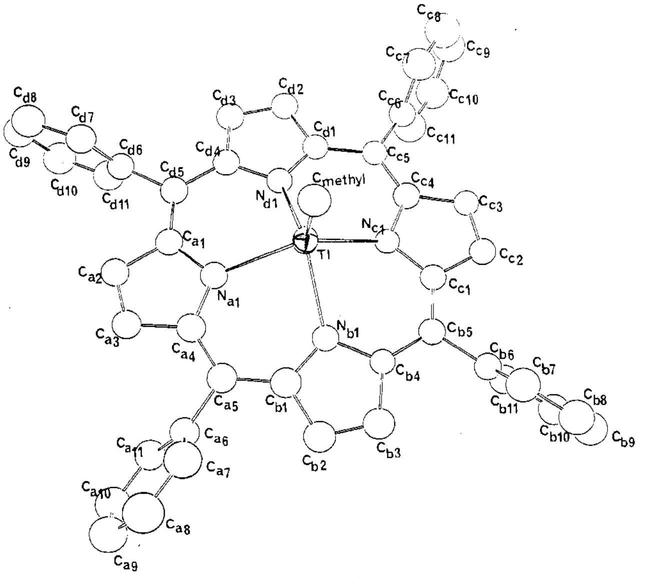


Figure 1. Model in perspective of the CH_3TlTPP molecule. The view is offset 5° from the perpendicular to the mean plane of the molecule.

atom to be coordinated at such an unusually large distance from the N_4 plane and to relieve "radial strain"[21] in the core of the metalloporphyrin. "Radial strain" is minimal when the metal to coordinated nitrogen distance is only ~2.01 Å.[21] This structure determination is the first reported for a mono-organothallium(III) compound and the first alkylmetalloporphyrin structure.

The $^{205}Tl-^{13}C$ couplings in the methyl compounds CH_3TlTPP and CH_3TlOEP are similar but differ markedly from those reported for the aquohydroxy complexes $(H_2O)OHTlTPP$[17] and $(H_2O)OHTlOEP$[22] (Table IV). The nature of the axial ligands appears to have minimal effect on ^{13}C chemical shifts. In an effort to determine the part played by structural differences, in particular coordination number and geometry, on the $Tl-^1H$ and $Tl-^{13}C$ couplings to the porphyrin ring in these complexes, a structural investigation was undertaken of the compound presumed to be $(H_2O)OHTlTPP$ and prepared by the method of Smith.[8] The structural determination and analytical results (vide infra) showed the original formulation[8] to be in error and that the product was ClTlTPP.

Table IV. ^{13}C NMR Data[a] for the Porphine Skeleton in the Thallium(III) Porphyrin Complexes, CH_3TlTPP, CH_3TlOEP, ClTlTPP, and ClTlOEP

	δ, ppm ($J(Tl-^{13}C)$, Hz)		
Compd	Meso C	β-Pyrrole C	α-Pyrrole C
CH_3TlTPP	121.5 (56)	131.8 (28)	150.2 (34)
CH_3TlOEP	97.5 (52)	142.1 (24)	147.5 (30)
ClTlTPP[b]	121.6 (115)	132.1 (110)	149.3 (7)
ClTlOEP[c]	97.7 (147)	142.7 (104)	146.8 (18)

[a] In $CDCl_3$ with $(CH_3)_4Si$ as internal standard. [b] Values from ref 17. [c] Values from ref 22.

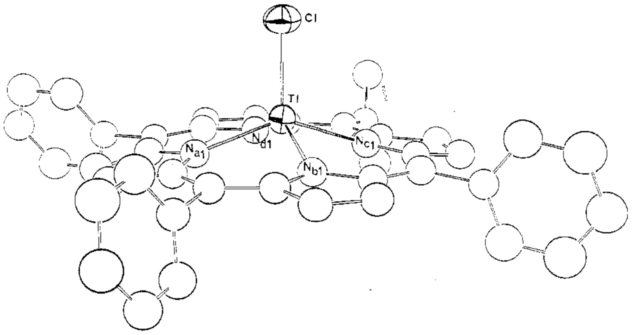


Figure 2. Model in perspective of the ClTlTPP molecule. The view is 90° away from that of Figure 1 and is essentially 5° from the normal to the axis of the chloro–thallium bond.

Final coordinates and isotropic thermal parameters for all atoms except hydrogen atoms for ClTlTPP are listed in Tables II and III, respectively. The numbering scheme follows that used for CH_3TlTPP. The view of the molecule ClTlTPP in Figure 2 is nearly perpendicular to the Cl–Tl bond. The Tl–N bond distance 2.21 (1) Å and Tl–Cl is 2.420 (4) Å. The pyrrole rings are tilted with respect to each other by 8.7 ± 0.7°. Coordinate bond lengths, polyhedral edge lengths, and the angles subtended at the thallium atom for CH_3TlTPP and ClTlTPP are given with their estimated standard deviations in Table V. In both molecules the coordination polyhedra are square pyramidal. Bond lengths and angles within the macrocycle are given with their estimated standard deviations in Table VI[15] for each molecule. There is no significant alternation of bond lengths around the porphine skeleton.[23] Using the numbering scheme outlined in Table II the average values for bond lengths in the porphine skeleton for CH_3TlTPP [ClTlTPP] are: N_1-C_1 = 1.373 (6) [1.373 (12)]; C_1-C_2 = 1.440 (10) [1.436 (14)]; C_2-C_3 = 1.351 (7) [1.359 (6)]; C_4-C_5 = 1.409 (19) [1.399 (8)]; C_5-C_6 = 1.490 (13) [1.509 (3)] Å. The deviation from the mean bond lengths (in units of 0.001 Å, in parentheses) is in each case less than the mean of the estimated standard deviations for the individual bond lengths (Table VI).[15] The agreement in the bond angles of a given chemical type in the core is equally close with average values as follows for CH_3TlTPP [ClTlTPP]: $C_1N_1C_4$ = 107.3 (8) [108.1 (8)]; $N_1C_1C_2$ = 108.9 (7) [108.4 (10)]; $C_1C_2C_3$ = 107.4 (4) [107.5 (6)]; $N_1C_4C_5$ = 125.9 (12) [125.6 (6)]; $C_3C_4C_5$ =

Table V. Molecular Dimensions in the Coordination Group of CH_3TlTPP and ClTlTPP[a]

(a) Distances, A			
Tl–C_m|Cl|	2.147 (12) [2.420 (4)]	Tl–N_{c1}	2.298 (10) [2.208 (10)]
Tl–N_{a1}	2.290 (9) [2.215 (10)]	Tl–N_{d1}	2.290 (10) [2.206 (10)]
Tl–N_{b1}	2.287 (9) [2.211 (9)]		
(b) Angles, deg			
N_{a1}–Tl–C_m|Cl|	115.9 (5) [110.3 (3)]	N_{a1}–Tl–N_{b1}	79.4 (3) [82.9 (4)]
N_{b1}–Tl–C_m|Cl|	116.3 (4) [108.6 (3)]	N_{b1}–Tl–N_{c1}	79.7 (3) [84.0 (4)]
N_{c1}–Tl–C_m|Cl|	113.0 (4) [107.5 (3)]	N_{d1}–Tl–N_{a1}	79.4 (3) [83.5 (4)]
N_{d1}–Tl–C_m|Cl|	116.1 (4) [111.4 (3)]	N_{d1}–Tl–N_{a1}	79.3 (3) [84.1 (4)]
		N_{a1}–Tl–N_{c1}	131.0 (3) [142.2 (4)]
		N_{b1}–Tl–N_{d1}	127.7 (3) [139.9 (4)]
(c) Polyhedral Edge Lengths, A			
N_{a1}–C_m|Cl|	3.76 [3.80]	N_{a1}–N_{b1}	2.92 [2.93]
N_{b1}–C_m|Cl|	3.77 [3.76]	N_{b1}–N_{c1}	2.94 [2.96]
N_{c1}–C_m|Cl|	3.71 [3.73]	N_{c1}–N_{d1}	2.93 [2.96]
N_{d1}–C_m|Cl|	3.77 [3.82]	N_{d1}–N_{a1}	2.93 [2.94]

[a] The methyl values are given first followed by the chloro values in square brackets. Least-squares esd's are given in parentheses. The atom numbering scheme follows that used in Table II.

125.4 (10) [125.9 (5)]; $C_4C_5C_{x1}$ = 125.8 (5) [127.1 (3)]; $C_4C_5C_6$ = 115.8 (16) [116.3 (12)]°.

The corresponding averaged bond lengths and angles in the porphine skeleton for CH_3TlTPP and ClTlTPP are in excellent agreement and show only one significant difference from the corresponding values found for Cl_2SnTPP,[20] although the esd's for bond parameters in the two thallium structures are large enough to make such a comparison difficult. Thus, for Cl_2SnTPP N_1–C_1, C_1–C_2, C_2–C_3, and C_4–C_5 values are 1.370, 1.446, 1.380, and 1.409 Å, respectively. The C_2–C_3 distances in CH_3TlTPP (1.351 Å) and ClTlTPP (1.359 Å) agree more closely with the value of 1.353 Å which is an average from seven structure determinations of iron–TPP complexes.[24a]

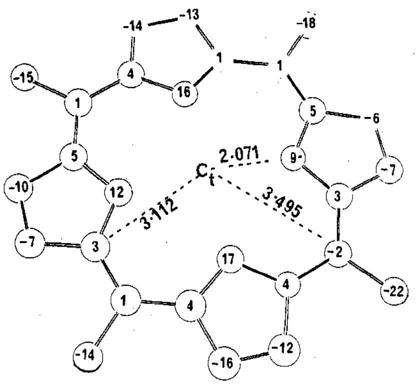
The $C_t\cdots N$ distances for CH_3TlTPP and ClTlTPP are 2.071 and 2.083 Å, respectively, and are close to the value of 2.098 Å found for Cl_2SnTPP. Figure 3 shows the structural radii, $C_t\cdots C(\alpha)$ and $C_t\cdots C(\text{meso})$.

The displacements of the carbon and nitrogen atoms in the porphine skeletons from the mean plane of the cores[15] are displayed in Figure 3, which is drawn in the same orientation as Figure 1. Each labeled atom of Figure 1 has been replaced by its out-of-plane displacement in units of 0.01 Å. Both structures show marked "doming"[24b] in that the least-squares planes[15] defined by the nitrogen atoms, the α-carbon atoms, the meso-carbon atoms, and the β-carbon atoms are all nearly parallel and are separated by successive values of 0.10 (0.09), 0.03 (0.01), and 0.11 (0.12) Å for CH_3TlTPP (ClTlTPP), respectively. The "doming" found here is in contrast to the conformation adopted in pyZnOEP[24c] where one pyrrole ring is approximately parallel to the plane of the four nitrogen atoms and the other three pyrrole planes tilt away from the metal atom. Also in the two structures described here the mean planes defined respectively by the four nitrogen atoms and the entire $C_{20}N_4$ porphine skeleton in CH_3TlTPP [ClTlTPP] are separated by 0.14 [0.12] Å, compared to ~0.01 Å in other porphyrins, NOCoTPP,[24d] for example.

The dihedral angles between the mean plane of the porphine skeleton and the planes of the four phenyl groups are 80.0, 83.3, 70.4, and 64.3° for CH_3TlTPP and 85.1, 82.6, 64.5, and 72.1° for ClTlTPP. The axial Tl–C methyl bond in CH_3TlTPP is tipped only 1.2° from the normal to the mean skeletal plane and the corresponding Tl–Cl angle in ClTlTPP is 2.0°. Consequently both molecules deviate little from C_{4v} symmetry.

The presence of chlorine in the compounds ClTlTPP and ClTlOEP was confirmed by satisfactory chlorine analyses, and the anisotropic thermal parameters of the chlorine atom in ClTlTPP assumed physically impossible values when it was assigned as an oxygen atom. The published mass spectrum[8] of ClTlOEP is consistent with the formulation as a chloro compound. The calculated ratio[25] of the molecular ion, peaks *m/e* 772/770, was found to be 2.48 for $(H_2O)OHTlOEP$ and 2.79 for ClTlOEP. The observed value was 2.75.[8] If the compound was the aquohydroxy compound this would represent an error of 11% in peak height measurements, whereas

(a) ; CH_3TlTPP



(b) ; ClTlTPP

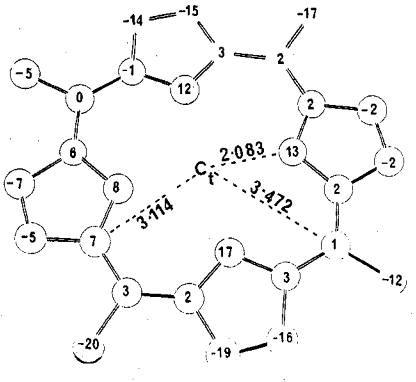


Figure 3. Formal diagram of the porphinato core with the same relative orientation as Figure 1. Each atom symbol of (a) CH_3TlTPP and (b) ClTlTPP has been replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphinato core. Also shown are the values for the structural radii, $C_t\cdots N$, $C_t\cdots C_\alpha$, and $C_t\cdots C_{meso}$.

the error calculated from the $[M^{+\cdot}\text{–axial ligand(s)}]^+$ peaks *m/e* 737/735 (in the same spectrum) was 2.5% (calcd ratio of *m/e* 737/735 = 2.47, found 2.40). The source of chlorine in the synthesis is presumably the chloroform solvent used as eluent of the product from the reaction of $(CF_3COO)_3Tl$ with $TPPH_2$ on an alumina column. It appears that thallium has a remarkable ability to abstract a chlorine atom from the solvent molecule. A similar situation to the chloro, aquohydroxy case found here has been encountered for ClFeTPP which was at first believed to be (H_2O)OHFeTPP.[26] Analogously, compounds described as (H_2O)OHTl porphyrins,[8,17,22] and prepared by similar procedures, may also contain chloro rather than hydroxy ligands.

^{13}C NMR Spectra. The NMR data presented in Table IV can be examined on the basis of the solid state structures of CH_3TlTPP and ClTlTPP. The ^{13}C NMR spectra of the ClTlTPP, CH_3TlTPP and ClTlOEP, CH_3TlOEP pairs show some minor differences in chemical shifts. The $J(\text{Tl–}^{13}\text{C})$ coupling constants of the two chloro compounds, ClTlTPP and ClTlOEP, are similar but substantially different from the values found for the analogous methyl compounds, CH_3TlTPP and CH_3TlOEP, both in their absolute magnitudes and in the ratio of the two bond to three bond couplings. The differences found for $J(\text{Tl–}^{13}\text{C})$ in the TPP complexes are not readily attributable to structural differences between the two molecules CH_3TlTPP and ClTlTPP.

The structures of CH_3TlTPP and ClTlTPP do show substantially different displacements of the metal atom out of the porphyrin plane; $C_t\cdots Tl$ is 0.979 and 0.737 Å, respectively. Other structural features involving spin–spin coupled atoms, however, are found to be very similar; for example, the Tl–N–C_α angles for ClTlTPP and CH_3TlTPP were 124.9 (8) and 123.9 (8)°, respectively. The Tl–N bond length is shortened by only 0.08 Å in ClTlTPP compared to CH_3TlTPP. However, the possibility that $J(\text{Tl–}^{13}\text{C})$ may be extremely sensitive to bond and angle deformations cannot be excluded (as are $^2J(^{13}\text{C–}^1\text{H})$ and $^3J(^{13}\text{C–}^1\text{H})$ couplings).[27]

The values of $J(\text{Tl–}^{13}\text{C})$ obtained for CH_3TlTPP and CH_3TlOEP are comparable to those obtained for dimethylthallium(III) 4,4′-diethoxycarbonyl-3,3′,5,5′-tetramethyldipyrromethene.[28] The extent of π delocalization is reduced in the dipyrromethene case compared to that in the thallium(III) porphyrin derivatives and the similarity of the couplings casts doubt upon the reliability of using $J(\text{Tl–}^{13}\text{C})$ as a probe of the π-electron pathway.[8,22]

If it were assumed[22] that these couplings are dominated by the Fermi contact term,[29] the increases in $^3J(\text{Tl–}^{13}\text{C}_\beta)$ and $^3J(\text{Tl–}^{13}\text{C}_{\text{meso}})$ after substitution of methyl for chlorine may be ascribable to the greater electronegativity of the chlorine atom.[31] However, the corresponding decrease observed for $^2J(\text{Tl–}^{13}\text{C})$ is less readily explained and illustrates the need for basic studies on substituent effects before useful information about electronic structure can be deduced from coupling constants.

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Registry No. CH_3TlTPP, 63848-50-0; ClTlTPP, 63848-51-1; CH_3TlOEP, 63848-52-2; ClTlOEP, 58167-68-3; diacetatomethylthallium(III), 14774-85-7; (H_2O)OHTlTPP, 51475-96-8; (H_2O)OHTlOEP, 33339-93-4.

Supplementary Material Available: Tables of molecular dimensions in the porphyrin skeleton (Table VI), equations of least-squares planes in the porphyrin skeleton (Table VII), and observed and calculated structure amplitudes (42 pages). Ordering information is given on any current masthead page.

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