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Porphyrins and Large Metal Ions. Crystal and Molecular Structure of 2,3,7,8,12,13,17,18-Octaethylporphinatochlorothallium(III)

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The structure of 2,3,7,8,12,13,17,18-octaethylporphinatochlorothallium(III), $C_{36}H_{44}N_4TlCl$, has been determined from three-dimensional diffractometer data. A total of 8776 independent reflections were measured. The compound crystallizes in the triclinic space group $P\bar{1}$ with a unit cell of $a = 14.063$ (3) Å, $b = 14.983$ (6) Å, $c = 10.202$ (5) Å, $\alpha = 99.05$ (4)°, $\beta = 104.07$ (2)°, $\gamma = 66.92$ (3)°. There are two molecules in the unit cell. The structure was solved by heavy-atom methods and refined by least-squares techniques to a final conventional R index of 0.053 for the 5553 reflections having $I \geq 2\sigma_I$. Molecules of solvation included in the solid state consist of one dichloromethane molecule and one water molecule per formula unit. The metalloporphyrin is a square-pyramidal complex with a chlorine atom as the axial ligand. The average Tl–N bond length is 2.212 (6) Å, while the Tl–Cl distance is 2.449 (3) Å. The metal ion is located 0.69 Å out of the mean plane of the four pyrrole nitrogen atoms. The porphinato core is highly expanded with an average radius of 2.10 Å. The macrocycle shows some deviation from planarity, exhibiting a net doming toward the metal ion.

Introduction

In recent years thallium salts have become increasingly more important as reagents in organic syntheses.[1,2] Thallic salts are powerful but selective oxidizing agents due to the ease of reduction from the +3 to the +1 oxidation state. Several reactions between porphyrins and thallic salts have been reported; for example, treatment of 2,3,7,8,12,13,17,18-octaethylporphine (H_2(OEP)) with thallium(III) trifluoroacetate (TTFA) gave[3,4] a metalloporphyrin characterized as in Figure 1. In the absence of trifluoroacetic acid the thallium(III) porphyrin was stable toward oxidation by excess TTFA,[4] presumably owing to the high oxidation potential ($E^1{}_{1/2} = 1.00$ V vs. SCE)[5] of the macrocycle containing a thallium ion. However, addition of acid[3,6] or treatment of zinc(II) porphyrins ($E^1{}_{1/2} = 0.63$ V) with TTFA[7] causes formation of oxophlorins, dioxoporphodimethenes, and other meso (methine) oxygenated macrocycles. On the other hand, porphyrins protected from methine oxidation by formation by their thallium(III) complexes are susceptible to efficient modification of labile side chains[8,9] using thallium reagents.

In addition to its role as a reagent, thallium presents interesting steric properties because of its size. Here we report the steric arrangement obtained when a large metal ion is complexed with the porphyrin moiety. The radius of the porphinato core has been found to contract to 1.93 Å to accommodate a small ion like Ni(II)[10] or expand to ~2.09 Å to accommodate a large ion like Sn(IV).[11,12] The complexation of a very large metal like Tl(III) might be expected to have a significant effect on the geometry of the porphyrin, as well as on its chemical reactivity. The original formulation (Figure 1) suggested a six-coordinate complex, though it was stressed that there was no evidence for coordination of the water molecule to the metal atom.[4] We wished to determine whether or not the porphyrin core would be able to expand enough to form a six-coordinate complex or whether the metal ion would lie significantly out of the plane of the macrocycle, as is found for high-spin iron(II) metalloporphyrins.[13] The latter possibility would probably result in a five-coordinate complex. There have been very few x-ray structure determinations reported for thallium complexes;[14-16] relatively little is known about their stereochemistry. For these reasons a study of thallium(III) octaethylporphyrin was begun.

Table I. Crystal Data for $(C_{36}H_{44}N_4)TlCl{\cdot}CH_2Cl_2{\cdot}H_2O$[a]

$a = 14.063$ (3) Å
$b = 14.983$ (6) Å
$c = 10.202$ (5) Å
$\alpha = 99.05$ (4)°
$\beta = 104.07$ (2)°
$\gamma = 66.92$ (3)°
$V = 1913.4$ Å^3
Fw 875.6
$Z = 2$
$d_{\text{calcd}} = 1.52$ g/cm^3
$\mu = 44.87$ cm^{-1} (Mo Kα radiation)
Systematic absences: none
Space group $P\bar{1}$

[a] Estimated standard deviation of least significant figures shown in parentheses.

Experimental Section

Crystals of the title compound almost always proved to be twinned. However, the nature of the twinning was such that it was possible to distinguish the members of the twins by morphology. A large crystal was grown slowly over a period of several months from a mixture of dichloromethane, methanol, and dioxane. Due to the apparent formation of hydrogen chloride in this mixture, the hydroxide ligand originally present was replaced by chloride; similar substitutions with cyanide and iodide have also been reported.[4] It was possible to cleave the crystal and separate the twins. The reflections measured during the data collection were unquestionably single peaks, indicating a clean separation of the twins. The fragment used for intensity measurements was a reddish plate. Except for the {010} planes, which are the prominent faces of the plate, the crystal faces were not well defined. However the other faces were approximated by the following indices (number following indices is the distance in millimeters from an arbitrary point inside the crystal): $(\bar{1}\bar{1}0)$ (0.205), (110) (0.198), $(3\bar{2}0)$ (0.158), $(\bar{3}20)$ (0.164), (001) (0.262), $(00\bar{1})$ (0.285), and $(\bar{2}\bar{1}1)$ (0.219).

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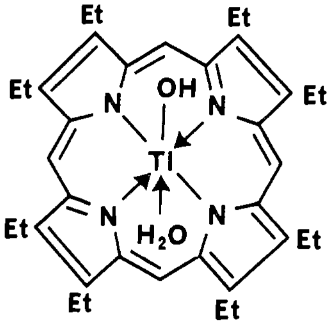

Figure 1. Proposed structure for the aquo–hydroxy adduct of thallium(III) octaethylporphyrin.

The $(0\bar{1}0)$ and (010) planes were each 0.009 mm from the origin point. The crystal was mounted in a glass capillary[17] at an arbitrary orientation, but with the c axis very roughly parallel to the spindle axis.

Cell data are summarized in Table I. Cell dimensions were determined by least-squares calculations, minimizing the differences between observed and calculated 2θ values (measured at both $+2\theta$ and -2θ) for 15 reflections in the range $38° < 2\theta < 41°$. The $K\alpha_1$–$K\alpha_2$ doublet was partially resolved so the wavelength for Mo $K\alpha_1$ radiation (λ 0.709 26 Å) was used. The ambient temperature was 17 °C. Cell constant data and subsequent intensity data were measured on a Datex-Syntex automated diffractometer. The radiation was monochromatized by pyrolitic graphite. The choice of the centric space group $P\bar{1}$ was confirmed by the successful solution of the structure.

Data were collected by the θ–2θ scan method, monitoring the intensity scale by remeasuring a group of five standard reflections periodically. A Mo $K\alpha$ wavelength of 0.710 69 Å was assumed for the intensity measurements. The intensities of these standard reflections decreased systematically during data collection. The appearance of the crystal also changed, indicating partial crystal decomposition, possibly from the loss of solvent molecules from the crystal lattice. Intensities of reflections were measured in sets and corrected by a factor calculated from the weighted mean of the intensities of the check reflections. The maximum correction factor was 1.21. The scan rate was 2°/min. The scan range was 2°. Backgrounds at either end of the scan range were collected for half the scan time. Independent reflections (8776) were measured out to a $(\sin\theta)/\lambda$ value of 0.65 $Å^{-1}$ or 27.5° in θ. Of these, 5553 had a net intensity greater than $2\sigma_I$ and were used in the analysis. The standard deviation σ_I was defined in terms of the statistical variances of the counts as $\sigma_I^2 = \sigma_I^2(\text{count}) + K^2(S + B_1 + B_2)^2$ where S, B_1, and B_2 are the observed counts for the scan and two backgrounds, respectively. $\sigma_I^2(\text{count})$ is the variance determined solely from counting statistics. A value of 0.02 was used for K.

The intensities were corrected for coincidence[18] ($\tau = 1.67 \times 10^{-7}$ counts^{-1}). The data were corrected for absorption by means of a Gaussian integration method (8 × 6 × 8 grid). The transmission coefficients varied from 0.20 to 0.44. Structure factors were calculated in the usual way, assuming an ideally imperfect monochromator for the polarization factor.

Determination and Refinement of Structure

Because there are two molecules in the unit cell of space group $P\bar{1}$, all atoms lie in general positions. The position of the thallium ion was found from an unsharpened Patterson synthesis. The rest of the 46 nonhydrogen atoms were found from a series of difference syntheses. As mentioned earlier, the hydroxide ion in the original sample had been replaced by a chloride ion and this was clearly evident as the electron density was more appropriate for a chloride ion than for an oxygen atom. Two solvent molecules were present in the crystal lattice. From the peak heights and interatomic distances, one was clearly dichloromethane. No evidence of disorder was noted for this solvent molecule. On the other hand the other solvent molecule was much less clearly defined. There were two peaks located ~1 Å apart. These were located close to a center of inversion, which places one peak 2.3 Å away from a symmetry-related peak. This is an impossibly close distance. These peaks were interpreted as a disordered water molecule with two major sites. Hence these two peaks were refined as oxygen atoms. Even though they had somewhat different heights, indicating the position further away from the inversion center was favored, no attempt was made to refine occupancy factors and each position was given an occupancy factor of 0.5.

Least-squares refinement using block-diagonal and finally full-matrix methods was carried out. The function minimized was $\sum w(F_o - F_c)^2$ where $w = 1/\sigma_F^2$. Initially isotropic temperature factors were used, but in the final refinement all nonhydrogen atoms except those on the solvent molecules were varied assuming anisotropic thermal motion. Thermal parameters for the solvent molecule atoms were refined isotropically throughout. The positions of hydrogen atoms were not discernible from ΔF maps; hence the positions of all but the hydrogens on the water solvent molecule were calculated and their contributions included in the structure factor calculations assuming an isotropic thermal parameter, B, of 4.0 $Å^2$. A staggered configuration was assumed for the hydrogen atoms of the terminal carbon atoms of the ethyl groups. The hydrogen atom positions were not refined in the least-squares procedure, but prior to the final cycles of refinement, their positions were recalculated. The refinement converged with $R = \sum\|F_o| - |F_c\|/\sum|F_o| = 0.053$ and $R_w = (\sum w\|F_o| - |F_c\|^2/\sum wF_o^2)^{1/2} = 0.061$.

A correction for anomalous dispersion was made for the thallium ion ($\Delta f' = -3.56$, $\Delta f'' = 9.66$) and chlorine atoms ($\Delta f' = 0.13$, $\Delta f'' = 0.16$).[19] Scattering factors were from ref 20. The thallium and chlorine atoms were assumed to be in the zero ionization state. No evidence of secondary extinction was found.

In the last cycle of refinement all shifts were less than 1 standard deviation with the exception of the positional parameters of the sites for the oxygen atom of the disordered water molecule. These positional parameters appeared to have been oscillating somewhat. Because the largest shift in the porphyrin molecule was 0.19 standard deviation, with most shifts being of the order of 0.05 standard deviation, refinement was terminated. The final value of the standard deviation of an observation of unit weight, defined as $[\sum w\|F_o| - |F_c\|^2/(N_o - N_v)]^{1/2}$, was 1.46 for $N_o = 5553$ reflections and $N_v = 399$ parameters.

The structure was solved and most of the refinement performed on the IBM 360/65 and its successor at Texas A&M,[21] the Amdahl 470 v/6. The final refinement and calculations were performed on a PDP 11/45 computer using the Enraf-Nonius structure determination package (SDP). Several local data-handling programs were also used as well as the autoindexing and least-squares cell parameter and refinement programs written by Sparks for the NOVA computer.[22] Data collection programs used were those written by Stanford for the Varian 620i. Use was made of the PDP 11/40-Vector General graphics system which is part of the CRYSNET network.[23,24]

The final positional and thermal parameters for nonhydrogen atoms are given in Table II. The final calculated positions of the hydrogen atoms are given in Table III. Tables IV and V contain the root-mean-square components of thermal displacement along the principal axes of the thermal ellipsoids and the observed and calculated structure factors, respectively. Tables III–V are available as supplementary material.

Discussion

The structure of 2,3,7,8,12,13,17,18-octaethylporphinatomonochlorothallium (III), ClTl(OEP), is shown in Figure 2. This figure also shows the numbering system used. A stereoview of the molecule is shown in Figure 3. Bond lengths and angles are listed in Table VI. The complex is a five-coordinate square-pyramidal metalloporphyrin with a chlorine atom as the axial ligand. The thallium ion is 0.69 Å out of the plane of the four pyrrole nitrogen atoms in the direction of the chlorine atom. This displacement of the metal ion from the porphyrin plane is consistent with the interpretation of the NMR and visible absorption spectra.[4] Except for the eight-coordinate $(OAc)_2Hf(OEP)$ and $(OAc)_2Zr(OEP)$ complexes,[25] in which the displacement is 1.01–1.02 Å, and the four-coordinate $Bi(OEP)^+NO_3^-$, which has a displacement of 1.09 Å,[26] this displacement is the largest found for any simple metalloporphyrin. The displacement is approximately that estimated by Perutz for the high-spin iron ion in deoxyhemoglobin.[27]

The structures of only a limited number of thallium(III) complexes have been reported.[14-16] From these it would appear that the favored coordination is octahedral. The structure of a square-pyramidal thallium(III) complex, (1,10-phenan-

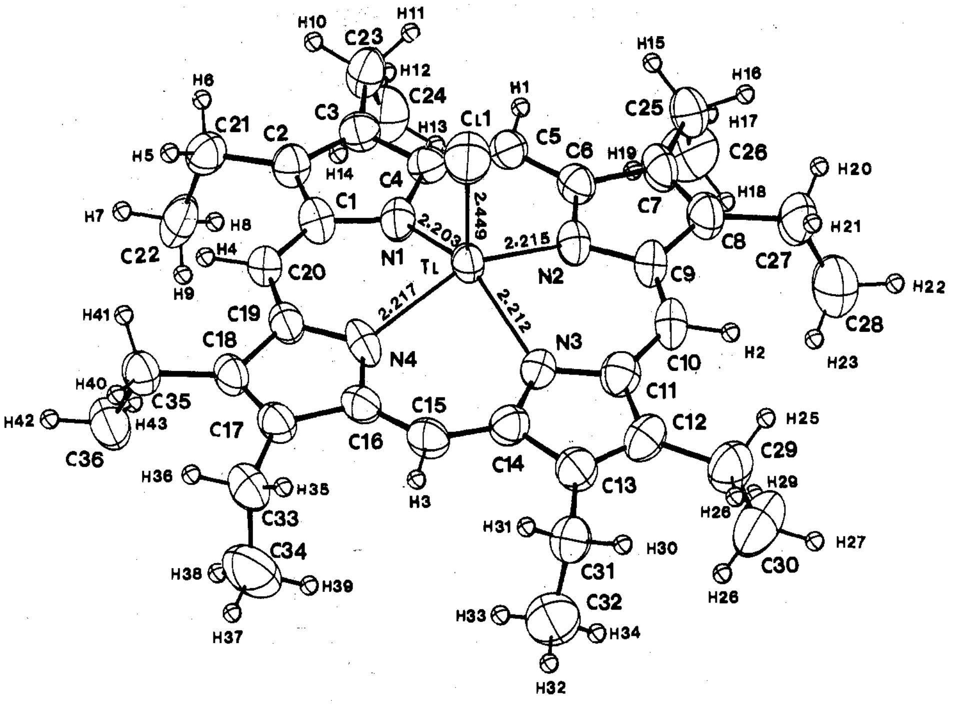

Figure 2. ORTEP[40] drawing of the structure 2,3,7,8,12,13,17,18-octaethylporphinatochlorothallium(III), ClTl(OEP). Numbering scheme and bond distances involving Tl are shown. The thermal ellipsoids are drawn for 50% probability, except those of the hydrogen atoms which are not drawn to scale. H(24) and H(44) are hidden behind C(28) and C(36), respectively.

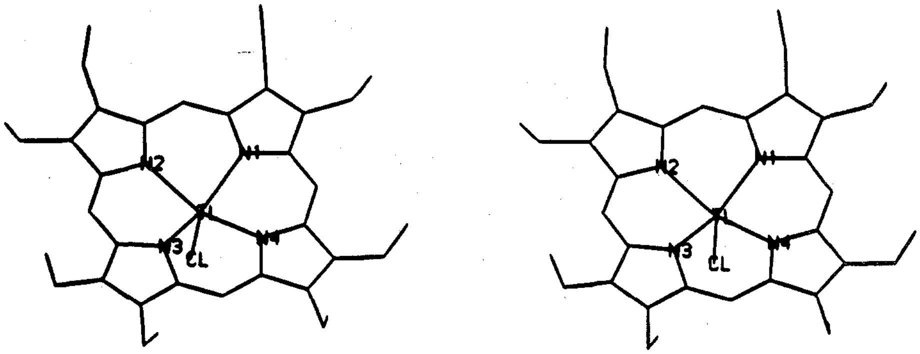

Figure 3. Stereoview of a single molecule of ClTl(OEP). Hydrogens have been omitted.

throline)trichlorothallium(III), (phen)$TlCl_3$, which will be particularly germane to the subsequent discussion, has been reported.[28] Even this compound is pseudooctahedral as it forms a weak dimer with a centrosymmetrically related molecule. A chlorine atom from this molecule occupies the other apical site with a Tl–Cl distance of 3.236 (4) Å. The metal ion is 0.44 Å from the mean plane of the four basal ligand atoms.

When the structure of ClTl(OEP) is compared with those of other metalloporphyrins and also that of (phen)$TlCl_3$, several features are seen which can be attributed to the complexation of a very large metal ion like Tl(III) to the relatively rigid porphyrin ligand. It has been estimated that the optimum size of the "hole" in a metalloporphyrin is 2.01 Å.[29] Large metal ions, particularly those which are weak complexing ions, will not fit into the macrocycle and must therefore lie out of the macrocyclic plane. Interesting exceptions are the dichlorotin(IV) complexes of octaethylporphyrin (Cl_2Sn(OEP))[11] and tetraphenylporphyrin (Cl_2-Sn(TPP)).[12] The strongly complexing Sn(IV) ion lies in the porphyrin plane with an Sn–N distance of 2.08–2.09 Å. This is a very short separation for Sn–N bonds, which are normally ~2.18 Å. However it represents a large expansion of the porphinato core. On the other hand the weakly complexing Zn(II) ion in the monopyridine adduct of zinc octaethylporphyrin (pyZn(OEP))[30] is 0.31 Å out of the plane of the four pyrrole nitrogen atoms. The average Zn–N distance is 2.067 Å, a normal Zn–N distance. The radius of the porphinato core expands to 2.04 Å.

The case of ClTl(OEP) is intermediate between the above examples. The average Tl–N distance is 2.212 (6) Å. This is much shorter than any other reported Tl–N distance. For example in (phen)$TlCl_3$[28] the Tl–N distances are 2.35 and 2.38 Å. The Tl–Cl distance of 2.449 (2) Å agrees well with the values found in (phen)$TlCl_3$. In the dichlorotin(IV) porphyrin complexes,[11,12] the Sn–Cl distance was longer than in nonmacrocyclic complexes.

Another effect of the complexation of the large Tl(III) ion is the size of the porphinato core, as represented by the separation between diagonally situated pyrrole nitrogen atoms. These distances are 4.179 (10) and 4.221 (9) Å corresponding to an average radius of 2.10 Å.

Table VII compiles data for several metalloporphyrins which have a significant out-of-plane displacement of the metal ion. One criterion for inclusion in this table is the absence of another ligand on the same side of the metal ion as the porphyrin. The other criterion is that there be no crystallographic disorder which makes it difficult to determine whether or not the metal ion lies in the porphyrin plane. There

Table II. Fractional Coordinates and Thermal Motion Parameters Derived from the Least-Squares Refinement[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl	0.130 92 (2)	0.173 51 (2)	0.237 76 (3)	366 (1)	425 (1)	381 (1)	−363 (1)	−2 (2)	69 (2)
Cl(1)	0.231 0 (2)	0.119 0 (2)	0.054 6 (2)	73 (1)	90 (1)	59 (1)	−81 (2)	54 (2)	−21 (2)
N(1)	0.114 2 (5)	0.048 3 (5)	0.304 2 (7)	45 (3)	57 (3)	36 (4)	−59 (5)	26 (6)	−13 (6)
N(2)	0.243 7 (5)	0.166 3 (5)	0.433 6 (7)	44 (3)	57 (4)	36 (4)	−56 (5)	0 (6)	0 (7)
N(3)	0.088 4 (5)	0.332 7 (5)	0.276 5 (8)	44 (3)	40 (3)	45 (4)	−35 (5)	9 (7)	−7 (7)
N(4)	−0.038 1 (5)	0.212 9 (5)	0.141 6 (8)	30 (3)	74 (4)	46 (4)	−49 (5)	−3 (6)	17 (8)
C(1)	0.043 6 (6)	0.007 4 (6)	0.240 6 (9)	43 (4)	58 (5)	40 (5)	−49 (6)	4 (8)	16 (8)
C(2)	0.075 5 (6)	−0.088 2 (6)	0.286 3 (9)	49 (4)	45 (4)	44 (5)	−43 (6)	9 (8)	15 (8)
C(3)	0.168 7 (6)	−0.105 1 (6)	0.378 0 (10)	42 (4)	37 (4)	51 (5)	−22 (6)	6 (8)	22 (8)
C(4)	0.193 5 (6)	−0.018 7 (6)	0.389 4 (9)	41 (4)	39 (4)	37 (5)	−15 (7)	7 (8)	13 (8)
C(5)	0.278 9 (6)	−0.001 0 (6)	0.473 7 (9)	40 (4)	43 (4)	36 (5)	−21 (7)	−2 (8)	6 (8)
C(6)	0.304 0 (6)	0.081 8 (6)	0.495 5 (9)	40 (4)	49 (4)	33 (5)	−32 (6)	5 (7)	5 (8)
C(7)	0.391 5 (7)	0.095 4 (7)	0.591 6 (10)	44 (4)	71 (5)	37 (5)	−54 (7)	−2 (8)	3 (9)
C(8)	0.383 8 (7)	0.188 0 (7)	0.579 8 (10)	48 (4)	68 (5)	44 (6)	−53 (7)	0 (9)	−6 (10)
C(9)	0.289 0 (6)	0.233 4 (6)	0.479 2 (10)	50 (4)	54 (4)	47 (6)	−58 (6)	0 (8)	−6 (9)
C(10)	0.247 4 (7)	0.328 3 (7)	0.442 0 (11)	53 (4)	70 (5)	54 (6)	−80 (6)	3 (9)	−6 (10)
C(11)	0.154 2 (7)	0.375 8 (6)	0.352 7 (10)	53 (4)	53 (5)	48 (5)	−50 (7)	25 (8)	4 (9)
C(12)	0.112 7 (7)	0.476 4 (6)	0.323 5 (10)	71 (5)	47 (4)	57 (6)	−62 (7)	33 (9)	0 (9)
C(13)	0.023 4 (7)	0.490 9 (6)	0.225 8 (11)	49 (5)	43 (4)	76 (7)	−37 (7)	12 (9)	22 (10)
C(14)	0.007 9 (7)	0.399 7 (6)	0.197 2 (10)	49 (4)	39 (4)	50 (6)	−30 (7)	11 (8)	5 (9)
C(15)	−0.075 3 (7)	0.381 5 (6)	0.110 6 (10)	41 (4)	39 (4)	57 (6)	−13 (7)	−6 (9)	32 (9)
C(16)	−0.098 9 (6)	0.299 2 (6)	0.085 7 (10)	34 (4)	44 (4)	57 (6)	−14 (7)	7 (8)	18 (9)
C(17)	−0.191 1 (6)	0.283 9 (6)	−0.003 7 (10)	36 (4)	53 (5)	44 (5)	−24 (7)	0 (8)	9 (9)
C(18)	−0.184 2 (6)	0.193 1 (6)	0.005 8 (9)	35 (4)	59 (5)	35 (5)	−36 (7)	3 (7)	−8 (9)
C(19)	−0.085 3 (6)	0.146 5 (6)	0.100 3 (9)	36 (4)	55 (4)	40 (5)	−41 (6)	13 (7)	−4 (8)
C(20)	−0.047 2 (6)	0.051 6 (6)	0.143 9 (9)	43 (4)	45 (4)	46 (5)	−44 (6)	13 (8)	−7 (8)
C(21)	0.013 5 (7)	−0.153 9 (6)	0.244 3 (11)	57 (5)	38 (4)	57 (6)	−36 (7)	3 (9)	9 (9)
C(22)	−0.074 6 (8)	−0.126 8 (8)	0.324 2 (13)	83 (6)	87 (6)	89 (8)	−104 (8)	50 (11)	−3 (12)
C(23)	0.231 7 (7)	−0.192 1 (6)	0.456 2 (11)	70 (5)	51 (4)	54 (6)	−65 (7)	−1 (10)	10 (9)
C(24)	0.206 9 (9)	−0.179 8 (8)	0.594 4 (12)	82 (6)	74 (6)	70 (7)	−64 (9)	−9 (12)	54 (11)
C(25)	0.472 0 (7)	0.023 2 (7)	0.687 9 (10)	51 (5)	68 (5)	47 (6)	−55 (7)	−14 (9)	19 (10)
C(26)	0.434 0 (10)	0.025 5 (9)	0.811 9 (12)	108 (8)	84 (7)	47 (6)	−57 (12)	14 (12)	33 (11)
C(27)	0.460 3 (8)	0.237 3 (8)	0.655 2 (12)	66 (6)	73 (6)	57 (7)	−63 (9)	−25 (11)	0 (11)
C(28)	0.427 5 (10)	0.302 6 (10)	0.771 4 (15)	79 (7)	124 (9)	96 (10)	−92 (12)	−3 (15)	−42 (17)
C(29)	0.158 9 (8)	0.549 7 (7)	0.396 1 (12)	76 (6)	49 (5)	84 (8)	−58 (8)	4 (12)	23 (11)
C(30)	0.120 4 (11)	0.587 3 (9)	0.534 8 (16)	141 (9)	85 (7)	114 (11)	−136 (11)	53 (17)	−51 (16)
C(31)	−0.050 9 (7)	0.585 3 (7)	0.163 6 (12)	58 (5)	54 (5)	92 (8)	−62 (7)	31 (11)	−10 (11)
C(32)	−0.142 3 (9)	0.636 8 (8)	0.231 0 (16)	76 (7)	61 (6)	135 (12)	−40 (11)	18 (16)	26 (15)
C(33)	−0.278 8 (7)	0.360 0 (8)	−0.080 5 (12)	42 (5)	68 (6)	76 (8)	−34 (8)	−7 (11)	11 (12)
C(34)	−0.358 3 (9)	0.427 1 (9)	0.003 2 (16)	54 (7)	94 (8)	133 (12)	−15 (12)	0 (15)	76 (16)
C(35)	−0.259 9 (7)	0.144 2 (7)	−0.063 6 (10)	41 (4)	62 (5)	48 (6)	−38 (7)	−4 (9)	10 (10)
C(36)	−0.334 6 (7)	0.146 0 (8)	0.023 3 (12)	48 (4)	93 (6)	63 (7)	−71 (8)	14 (9)	−5 (12)
C(37)	0.391 8 (10)	0.255 7 (10)	0.168 5 (15)	80 (3)					
Cl(2)	0.498 9 (3)	0.248 8 (3)	0.291 6 (5)	111 (1)					
Cl(3)	0.323 4 (4)	0.370 7 (4)	0.116 4 (6)	140 (1)					
O(1)	0.430 8 (9)	0.512 7 (9)	−0.385 6 (13)	41 (2)					
O(2)	0.494 4 (14)	0.473 9 (13)	−0.411 6 (20)	83 (5)					

[a] In this and subsequent tables estimated standard deviations for the least significant figure are in parentheses. The Debye-Waller factor is defined as $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{33}b^*c^*kl)]$. The values for U have been multiplied by 10^3, except for those of Tl which have been multiplied by 10^4. For those atoms refined isotropically, the values for B (multiplied by a factor of 10) are given in the column labeled U_{11}. Isotropic temperature factors are defined by $T = \exp[-B(\sin^2\theta)/\lambda^2]$.

are several metalloporphyrins, generally tetraphenylporphyrin complexes, which exhibit this type of disorder.[31] As can be seen from Table VII, the average radius in ClTl(OEP) is the largest of any five-coordinate out-of-plane metalloporphyrin. This is about the same radius found for the tin(IV) metalloporphyrin and also for four-coordinate Mn(TPP) (2.082 Å),[32] so it is apparent that this is approximately the upper limit for the expansion of the porphinato core. (Mn(TPP) exhibits the type of disorder mentioned above and is not included in Table VII.) It should be noted from this table that there is no definite correlation between the out-of-plane displacement of the metal ion and C_t–N distance (C_t = center of plane of four pyrrole nitrogen atoms). Indeed, except for ClTl(OEP), most of the metalloporphyrins in Table VII which have large out-of-plane displacements of the metal ion also have porphinato cores which are only slightly or moderately expanded.

The observation that the porphinato core in ClTl(OEP) is much more expanded than most metalloporphyrins which similarly push the metal ion out of the macrocyclic plane would seem to indicate that there is a strong tendency for Tl(III) to form an octahedral complex or at least a pseudooctahedral complex like (phen)$TlCl_3$ with a smaller out-of-plane displacement of the metal ion than found in ClTl(OEP). However either the tendency is not as strong as in the Sn(IV) case or the thallium ion cannot contract enough to fit in the hole of the porphyrin. The macrocycle blocks the addition of another axial ligand.

It might be expected that the macrocycles in metalloporphyrins which have the metal ion significantly out of the plane would show a C_{4v} distortion from planarity. This type of distortion can be described as a "doming" of the macrocycle toward the metal ion. Two parameters can be used to describe this type of distortion from planarity. One is the difference between the displacement of the metal ion from the mean plane of the pyrrole nitrogen atoms (the P_n plane) and the mean plane of the 24 atom porphyrin skeleton (the P_c plane). For a planar macrocycle this difference should be zero. It should also be zero or very small for a nonplanar macrocycle which approximates D_{2d}, S_4, or C_{2v} symmetry. However there are cases such as the perchloratotetraphenylporphinatozinc radical ($ClO_4Zn(TPP)$)[33] in which the difference is large even though the distortion from planarity is definitely not of the C_{4v} type.

Table VI. Bond Lengths (A) and Angles (deg)[a]

Bond Lengths		
Tl-Cl(1)	2.452 (3)	
Tl-N(1)	2.203 (7)	Tl-N = 2.212 (6)
Tl-N(2)	2.215 (6)	
Tl-N(3)	2.212 (7)	
Tl-N(4)	2.217 (6)	
N(1)-C(1)	1.349 (10)	N-C_a = 1.364 (13)
N(1)-C(4)	1.390 (10)	
N(2)-C(6)	1.373 (10)	
N(2)-C(9)	1.351 (10)	
N(3)-C(11)	1.356 (10)	
N(3)-C(14)	1.364 (10)	
N(4)-C(16)	1.363 (10)	
N(4)-C(19)	1.363 (10)	
C(1)-C(2)	1.440 (12)	C_a-C_b = 1.448 (12)
C(3)-C(4)	1.448 (11)	
C(6)-C(7)	1.437 (11)	
C(8)-C(9)	1.462 (12)	
C(11)-C(12)	1.436 (12)	
C(13)-C(14)	1.439 (12)	
C(16)-C(17)	1.458 (12)	
C(18)-C(19)	1.466 (11)	
C(1)-C(20)	1.404 (11)	C_a-C_m = 1.390 (12)
C(4)-C(5)	1.388 (11)	
C(5)-C(6)	1.389 (11)	
C(9)-C(10)	1.384 (12)	
C(10)-C(11)	1.395 (12)	
C(14)-C(15)	1.377 (11)	
C(15)-C(16)	1.376 (12)	
C(19)-C(20)	1.410 (11)	
C(2)-C(3)	1.370 (11)	C_b-C_b = 1.362 (13)
C(7)-C(8)	1.370 (13)	
C(12)-C(13)	1.365 (12)	
C(17)-C(18)	1.342 (12)	
C(2)-C(21)	1.506 (11)	C_b-C_{aet} = 1.499 (20)
C(3)-C(23)	1.482 (12)	
C(7)-C(25)	1.499 (12)	
C(8)-C(27)	1.528 (12)	
C(12)-C(29)	1.497 (13)	
C(13)-C(31)	1.515 (13)	
C(17)-C(33)	1.464 (12)	
C(18)-C(35)	1.501 (11)	
C(21)-C(22)	1.534 (14)	C_{aet}-C_{bet} = 1.498 (27), 1.521 (28)*
C(21)-C(22)*	1.560 (19)	
C(23)-C(24)	1.497 (14)	
C(23)-C(24)*	1.509 (19)	
C(25)-C(26)	1.476 (14)	
C(25)-C(26)*	1.502 (19)	
C(27)-C(28)	1.453 (16)	
C(27)-C(28)*	1.482 (20)	
C(29)-C(30)	1.526 (17)	
C(29)-C(30)*	1.561 (21)	
C(31)-C(32)	1.483 (15)	
C(31)-C(32)*	1.499 (19)	
C(33)-C(34)	1.497 (16)	
C(33)-C(34)*	1.518 (19)	
C(35)-C(36)	1.519 (13)	
C(35)-C(36)*	1.534 (18)	
N(1)-N(2)	2.972 (9)	$(N-N)_{adj}$ = 2.970 (3)
N(1)-N(4)	2.973 (10)	
N(2)-N(3)	2.968 (10)	
N(3)-N(4)	2.968 (10)	
N(1)-N(3)	4.179 (10)	$(N-N)_{op}$ = 4.200 (29)
N(2)-N(4)	4.221 (10)	
C(5)-C(15)	6.831 (12)	C-C = 6.842 (15)
C(10)-C(20)	6.852 (12)	
C(37)-Cl(2)	1.689 (13)	C-Cl = 1.698 (12)
C(37)-Cl(3)	1.701 (13)	

Bond Angles		
Cl(1)-Tl-N(1)	109.8 (2)	Cl-Tl-N = 108.3 (13)
Cl(1)-Tl-N(2)	108.3 (2)	
Cl(1)-Tl-N(3)	107.8 (2)	
Cl(1)-Tl-N(4)	107.2 (2)	
N(1)-Tl-N(2)	84.5 (3)	$(N-Tl-N)_{adj}$ = 84.3 (2)
N(1)-Tl-N(4)	84.6 (3)	
N(2)-Tl-N(3)	84.2 (3)	
N(3)-Tl-N(4)	84.2 (3)	
N(1)-Tl-N(3)	142.4 (3)	$(N-Tl-N)_{op}$ = 143.4 (10)
N(2)-Tl-N(4)	144.5 (3)	
Tl-N(1)-C(1)	125.6 (6)	Tl-N-C_a = 124.0 (8)
Tl-N(1)-C(4)	123.9 (5)	
Tl-N(2)-C(6)	123.2 (5)	
Tl-N(2)-C(9)	123.2 (6)	
Tl-N(3)-C(11)	124.4 (6)	
Tl-N(3)-C(14)	124.1 (6)	
Tl-N(4)-C(16)	124.2 (6)	
Tl-N(4)-C(19)	123.4 (6)	
C(1)-N(1)-C(4)	107.6 (7)	C_a-N-C_a = 109.2 (12)
C(6)-N(2)-C(9)	109.6 (7)	
C(11)-N(3)-C(14)	108.7 (7)	
C(16)-N(4)-C(19)	110.5 (7)	
N(1)-C(1)-C(2)	109.9 (8)	N-C_a-C_b = 108.1 (12)
N(1)-C(4)-C(3)	108.6 (7)	
N(2)-C(6)-C(7)	109.0 (8)	
N(2)-C(9)-C(8)	107.0 (8)	
N(3)-C(11)-C(12)	108.6 (8)	
N(3)-C(14)-C(13)	108.4 (8)	
N(4)-C(16)-C(17)	106.4 (8)	
N(4)-C(19)-C(18)	107.2 (8)	
N(1)-C(1)-C(20)	124.9 (8)	N-C_a-C_m = 124.7 (7)
N(1)-C(4)-C(5)	123.9 (8)	
N(2)-C(6)-C(5)	124.5 (7)	
N(2)-C(9)-C(10)	125.1 (8)	
N(3)-C(11)-C(10)	124.7 (8)	
N(3)-C(14)-C(15)	124.2 (8)	
N(4)-C(16)-C(15)	124.5 (8)	
N(4)-C(19)-C(20)	126.1 (8)	
C(2)-C(1)-C(20)	125.2 (8)	C_b-C_a-C_m = 127.0 (11)
C(3)-C(4)-C(5)	127.4 (8)	
C(5)-C(6)-C(7)	126.3 (8)	
C(8)-C(9)-C(10)	127.7 (8)	
C(10)-C(11)-C(12)	126.6 (9)	
C(13)-C(14)-C(15)	127.4 (9)	
C(15)-C(16)-C(17)	129.1 (9)	
C(18)-C(19)-C(20)	126.7 (8)	
C(1)-C(2)-C(3)	107.3 (7)	C_a-C_b-C_b = 107.3 (9)
C(2)-C(3)-C(4)	108.6 (7)	
C(6)-C(7)-C(8)	106.0 (8)	
C(7)-C(8)-C(9)	108.3 (8)	
C(11)-C(12)-C(13)	107.2 (8)	
C(12)-C(13)-C(14)	107.0 (8)	
C(16)-C(17)-C(18)	108.9 (8)	
C(17)-C(18)-C(19)	106.9 (7)	
C(1)-C(2)-C(21)	125.3 (8)	C_a-C_b-C_{aet} = 124.9 (3)
C(4)-C(3)-C(23)	125.4 (8)	
C(6)-C(7)-C(25)	126.3 (9)	
C(9)-C(8)-C(27)	124.5 (9)	
C(11)-C(12)-C(29)	124.3 (9)	
C(14)-C(13)-C(31)	125.2 (9)	
C(16)-C(17)-C(33)	124.0 (8)	
C(19)-C(18)-C(35)	124.2 (8)	
C(3)-C(2)-C(21)	127.3 (8)	C_b-C_b-C_{aet} = 127.7
C(2)-C(3)-C(23)	127.9 (8)	
C(8)-C(7)-C(25)	127.6 (8)	
C(7)-C(8)-C(27)	127.2 (9)	
C(13)-C(12)-C(29)	128.4 (9)	
C(12)-C(13)-C(31)	127.7 (9)	
C(18)-C(17)-C(33)	126.9 (8)	
C(17)-C(18)-C(35)	129.0 (8)	
C(4)-C(5)-C(6)	130.3 (8)	C_a-C_m-C_a = 129.6 (13)
C(9)-C(10)-C(11)	129.4 (8)	
C(14)-C(15)-C(16)	130.8 (8)	
C(1)-C(20)-C(19)	127.8 (8)	
C(2)-C(21)-C(22)	112.2 (8)	C_b-C_{aet}-C_{bet} = 113.1 (9)
C(3)-C(23)-C(24)	112.5 (9)	
C(7)-C(25)-C(26)	112.0 (9)	
C(8)-C(27)-C(28)	114.9 (10)	
C(12)-C(29)-C(30)	113.2 (9)	
C(13)-C(31)-C(32)	112.9 (10)	
C(17)-C(33)-C(34)	113.3 (10)	
C(18)-C(35)-C(36)	113.7 (8)	
Cl(2)-C(37)-Cl(3)	112.5 (8)	

[a] Some nonbonded distances of interest are also given. Figures in parentheses for the averaged values are the root-mean-square standard deviations of the least significant figure. Asterisks indicate corrections for thermal motion.

Table VII. Selected Metalloporphyrins with Significant Out-of-Plane Displacement of the Metal Ion[a]

	$(\mathrm{M-N})_{\mathrm{av}}$	$(\mathrm{C_t-N})_{\mathrm{av}}$[b]	Metal ion displacement[c]	Δ[d]	$\mathrm{C_b}$ displacement[e]	Ref
$\mathrm{Bi(OEP)^+}$	2.32	2.047	1.09	0.13	−0.15, −0.46	*f*
$\mathrm{(OAc)_2Zr(OEP)}$	2.268, 2.259	2.024, 2.014	1.02, 1.02	0.17, 0.21	−0.20, −0.35 −0.23, −0.55	*g*
$\mathrm{(OAc)_2Hf(OEP)}$	2.257	2.016	1.01	0.13	−0.07, −0.22	*g*
ClTl(OEP)	2.212	2.10	0.69	0.06	0.01, −0.29	*h*
OV(OEP)	2.101	2.030	0.54	0.06	0.11, −0.36	*i*
(1-MeIm)Mn(TPP)	2.128	2.065	0.52	0.04	*z*	*j*
$\mathrm{O[Fe(TPP)]_2}$	2.087	2.027	0.50	0.04	0.20, −0.46	*k*
(SCN)Fe(TPP)	2.065	2.01	0.49	0.07	*z*	*l*
ClFe(proto-IX)	2.062	2.007	0.48	0.06	0.03, −0.30	*m*
(MeO)Fe(meso-IX-DME)	2.073	2.022	0.46	0.03	−0.04, −0.09	*n*
$\mathrm{(O_2NC_6H_4S)Fe}$(proto-IX-DME)	2.07	2.017	0.43	0.02	0.13, −0.16	*o*
(2-MeIm)Fe(TPP)	2.086	2.044	0.42	0.13	0.03, −0.52	*p*
(py)Zn(TpyP)	2.073	2.047	0.33	0.04	0.08, −0.22	*q*
(py)Zn(OEP)	2.067	2.043	0.31	0.09	0.0, −0.27	*r*
ClMn(TPP)	2.008	1.989	0.27	0.0	0.50, −0.51	*s*
$\mathrm{(ClO_4)Zn(TPP)}$	2.076	2.046	0.25	0.09	0.34, −0.53	*t*
$\mathrm{N_3Mn(TPP)}$	2.005	1.992	0.23	*z*	*z*	*u*
$\mathrm{(1,2\text{-}Me_2Im)Co(TPP)}$	1.984	1.979	0.15	0.03	0.17, −0.28	*v*
$\mathrm{(3,5\text{-}Me_2py)Co(TPP)}$	2.000	1.995	0.14	0.03	0.01, −0.16	*w*
(1-MeIm)Co(OEP)	1.955	1.950	0.13	0.03	0.04, −0.16	*x*
(1-MeIm)Co(TPP)	1.977	1.973	0.13	0.01	0.38, −0.28	*y*

[a] All values in Å. See text for criteria used to determine inclusion in this table. Abbreviations: OAc, acetate; Im, imidazole; Me, methyl (usually preceded by a number indicating its point of substitution on the ring); py, pyridine; MeO, methoxy; DME, dimethyl ester; OEP, octaethylporphyrin dianion; TPP, tetraphenylporphyrin dianion; proto-IX, protoporphyrin IX dianion; meso-IX, mesoporphyrin IX dianion, TpyP, tetra(4-pyridyl)porphyrin dianion. [b] $\mathrm{C_t}$ is the center of the plane of the four pyrrole nitrogen atoms ($\mathrm{P_n}$). [c] Displacement of the metal ion from the $\mathrm{P_n}$ plane. Table is listed in order of decreasing displacement. [d] Δ is the difference between the displacement of the metal ion from the $\mathrm{P_n}$ plane and the displacement of the same ion from the plane of the porphyrin skeleton ($\mathrm{P_c}$). A positive displacement indicates the $\mathrm{P_c}$ plane lies on the opposite side of the $\mathrm{P_n}$ plane from the metal ion. [e] Displacement of the $\mathrm{C_b}$ atoms from the $\mathrm{P_n}$ plane. A negative displacement indicates the atoms are on the other side of the plane from the metal ion. Minimum and maximum deviations are given. A large positive deviation is considered a minimum. [f] Reference 26. [g] Reference 25. There are two crystallographically independent molecules in $\mathrm{(OAc)_2Zr(OEP)}$. [h] This work. [i] F. Molinaro and J. A. Ibers, *Inorg. Chem.*, 15, 2278 (1976). [j] Reference 32. [k] A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *J. Am. Chem. Soc.*, 94, 3620 (1972). [l] Reference 31; J. L. Hoard, private communication. [m] D. F. Koenig, *Acta Crystallogr.*, 18, 663 (1965). [n] J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Am. Chem. Soc.*, 87, 2312 (1965). [o] S. C. Tang, S. Koch, G. C. Papaefthymiou, S. Foner, R. B. Frankel, J. A. Ibers, and R. H. Holm, *ibid.*, 98, 2414 (1976). [p] Reference 13. [q] Reference 29. [r] Reference 30. [s] B. M. L. Chen and A. Tulinsky, private communication. [t] Reference 33. [u] V. W. Day, B. R. Stults, E. L. Tasset, R. S. Marianelli, and L. J. Boucher, *Inorg. Nucl. Chem. Lett.*, 11, 505 (1975). Sufficient information is not given to describe deviations quantitatively from planarity. However the macrocycle is described as having S_4 symmetry. [v] P. N. Dwyer, P. Madura, and W. R. Scheidt, *J. Am. Chem. Soc.*, 96, 4815 (1974). [w] W. R. Scheidt and J. A. Ramunja, *Inorg. Chem.*, 14, 2643 (1975). [x] R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, 96, 4452 (1974). [y] W. R. Scheidt, *ibid.*, 96, 90 (1974). [z] Information not available.

The second parameter is the deviation of the β-pyrrole carbon atoms ($\mathrm{C_b}$) from the $\mathrm{P_n}$ plane. If the distortion is of the C_{4v} type, all of these atoms should be on the opposite side of the $\mathrm{P_n}$ plane from the metal ion. In actuality there are several cases which show a net doming, yet the $\mathrm{C_b}$ atoms on one ring may be in or slightly above the $\mathrm{P_n}$ plane.

The difference between the displacements of the metal ion from the $\mathrm{P_n}$ and $\mathrm{P_c}$ planes, Δ, and the minimum and maximum deviations of $\mathrm{C_b}$ atoms from the $\mathrm{P_n}$ plane are given for the metalloporphyrins included in Table VII. Inspection of this table shows that while the C_{4v} distortion is common for metalloporphyrins with an out-of-plane displacement of the metal ion it is by no means universal. The complexes which have the largest displacement of the metal ion are those most clearly exhibiting this type of distortion. Most of the metalloporphyrins in Table VII bear out Hoard's observation that the net doming is more likely to be <0.05 Å than >0.05 Å.[31]

It should also be noted that most of the compounds having large C_{4v} deformations have only slightly expanded porphinato cores. Hoard has calculated[34] that a C_{4v} type of distortion is inefficient in relieving strain in an expanded core, thus explaining the extremely small degree of nonplanarity found in the tin(IV) porphyrins. Therefore it is felt that a C_{4v} deformation is not dependent on excessive expansion or contraction of the core but rather on bonding interactions with the metal ion.[31]

Other external factors such as crystal packing may have a profound effect on the observed geometry of the macrocycle.[31] It is interesting to note that $\mathrm{(ClO_4)Zn(TPP)}$,[33] (py)Zn(TpyP),[29] and (py)Zn(OEP)[30] all have similar coordination geometries, yet only the third has a molecular geometry approximating C_{4v}. The other two approximate C_{2v} symmetry. Inspection of Table VII indicates that a C_{4v} type of deformation is more common for β-pyrrole-substituted porphyrins than meso-substituted porphyrins.

The specific case of ClTl(OEP) bears out the above points. Table VIII lists the deviations from various least-squares planes of interest. The molecule can be described very roughly as having the C_{4v} type of distortion. The $\mathrm{P_n}$ and $\mathrm{P_c}$ planes are separated by ~0.06 Å, which, while larger than found for most of the metalloporphyrins in Table VII, is not a particularly large separation, certainly not when compared to the large separations found in $\mathrm{(OAc)_2M(OEP)}$ (M = Zr, Hf)[25] and $\mathrm{Bi(OEP)^+NO_3^-}$.[26] In view of the above discussion this relatively small amount of doming might be expected for the highly expanded porphinato core in ClTl(OEP). The NMR spectrum indicated there was no major distortion of the porphyrin ring.[4]

The four pyrrole rings, which are individually planar, show different degrees of doming. Deviations from various least-squares planes of interest are given in Table VIII. This can be seen by comparing the angles between the plane of the individual pyrrole ring and the $\mathrm{P_n}$ plane and by observing the deviation of the β-carbon atoms (from the $\mathrm{P_n}$ plane). Ring I (N(1), C(1)–C(4)) and ring III (N(3), C(11)–C(14)) each form an angle of 4.7° with the $\mathrm{P_n}$ plane. The $\mathrm{C_b}$ atoms are

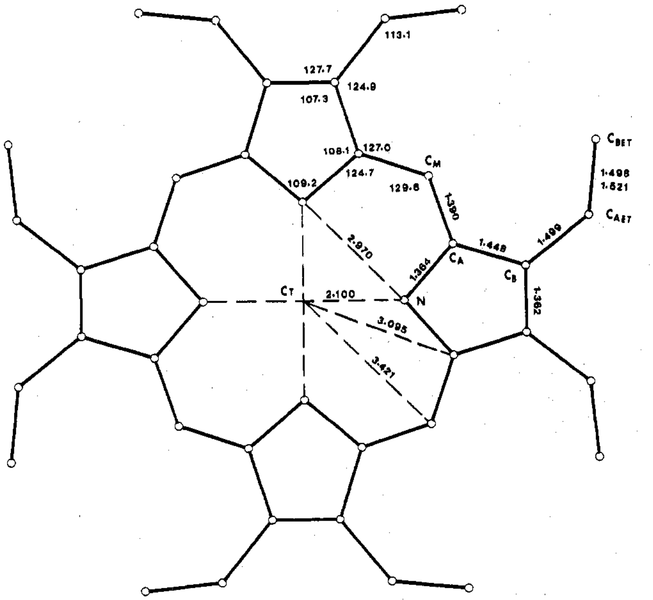

Figure 4. Schematic drawing of the macrocycle in ClTl(OEP) showing average bond lengths in angstroms and angles in degrees. The two values for the C_{aet}–C_{bet} bonds are the uncorrected distances (upper value) and the distance corrected for thermal motion. Also shown is the notation for different types of carbon atoms. C_t refers to the center of the plane of four pyrrole nitrogen atoms.

0.16–0.21 Å out of the P_n plane in the opposite direction from the metal ion. On the other hand ring II is nearly coplanar with the P_n plane (interplanar angle 1.0°, maximum deviation of C_b atoms 0.021 Å). Ring IV is intermediate (interplanar angle 3.0°, deviation of C_b atoms 0.10–0.11 Å). A similar description has been made for the doming in (py)Zn(OEP), in which this feature is more pronounced.[30]

Figure 4 is a schematic drawing of the macrocycle showing the average bond lengths and angles. It also shows the nomenclature used in the subsequent discussion. Some other interatomic distances of interest are also shown. The presence of a very heavy atom like thallium, which contributes to a large percentage of the x-ray scattering power, means the accuracy of the positions of the lighter atoms is decreased. This can be seen from the estimated standard deviations of individual bond lengths and angles as well as the root-mean-square deviations from the average of chemically equivalent bond parameters. This makes it somewhat difficult to assess the significance of these values. A tabulation[30] of bond lengths in various octaethylporphyrin complexes shows that certain bond parameters, in particular some of the bond angles (e.g., C_a–N–C_a, C_a–C_m–C_a), are sensitive to changes in the radius of the core. The averaged values in ClTl(OEP) agree very

Table VIII. Least-Squares Planes

A. Deviations (Å) from Planes

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
Tl	−0.753	−0.693	−0.544	−0.632	−0.537	−0.575
Cl(1)	−3.206	−3.145	−2.985	−3.080	−2.983	−3.030
N(1)	−0.042	0.018	0.005	0.067	0.339	0.128
N(2)	−0.057	−0.018	0.186	0.011	0.092	0.210
N(3)	−0.042	0.018	0.326	0.094	0.005	0.142
N(4)	−0.100	−0.018	0.072	0.076	0.178	−0.012
C(1)	0.027	0.099	−0.006	0.158	0.504	0.149
C(2)	0.136	0.203	0.004	0.248	0.710	0.271
C(3)	0.108	0.162	−0.001	0.184	0.642	0.301
C(4)	−0.006	0.043	−0.002	0.068	0.404	0.209
C(5)	−0.028	0.007	0.035	0.016	0.305	0.244
C(6)	−0.056	−0.025	0.116	−0.015	0.158	0.241
C(7)	0.006	0.022	0.231	0.013	0.145	0.362
C(8)	−0.024	−0.008	0.306	−0.007	0.007	0.337
C(9)	−0.058	−0.028	0.284	−0.003	−0.021	0.245
C(10)	−0.010	0.025	0.423	0.065	−0.063	0.276
C(11)	0.040	0.089	0.487	0.153	−0.009	0.273
C(12)	0.156	0.209	0.701	0.288	0.010	0.376
C(13)	0.099	0.165	0.621	0.266	−0.007	0.261
C(14)	−0.017	0.054	0.393	0.153	0.001	0.123
C(15)	−0.034	0.051	0.318	0.165	0.061	0.049
C(16)	−0.045	0.044	0.200	0.158	0.166	0.013
C(17)	−0.008	0.096	0.178	0.228	0.284	−0.010
C(18)	0.009	0.113	0.092	0.236	0.408	0.003
C(19)	−0.045	0.045	0.028	0.143	0.346	0.006
C(20)	−0.009	0.076	−0.031	0.159	0.474	0.058

B. Angles (deg) between Least-Squares Planes

	Plane 2	Plane 3	Plane 4	Plane 5	Plane 6
Plane 1	0.59	4.51	1.51	4.91	2.44
Plane 2		4.68	0.96	4.72	3.03
Plane 3			4.71	9.39	4.46
Plane 4				4.96	3.90
Plane 5					6.34

C. Equations of Planes[a]

Plane 1	Macrocycle P_c; N(1)-N(4), C(1)-C(20) $-8.743x + 0.046y + 8.594z = 1.6603$
Plane 2	P_n; N(1)-N(4) $-8.846x + 0.031y + 8.542z = 1.572$
Plane 3	Pyrrole I; N(1), C(1)-C(4) $-8.190x + 1.214y + 8.490z = 1.701$
Plane 4	Pyrrole II; N(2), C(6)-C(9) $-8.966x + 0.107y + 8.448z = 1.485$
Plane 5	Pyrrole III; N(3), C(11)-C(14) $-9.387x - 1.187y + 8.578z = 1.142$
Plane 6	Pyrrole IV; N(4), C(16)-C(19) $-8.297x + 0.153y + 8.793z = 1.606$

[a] All Planes are unweighted. x, y, z are in triclinic fractional coordinates.

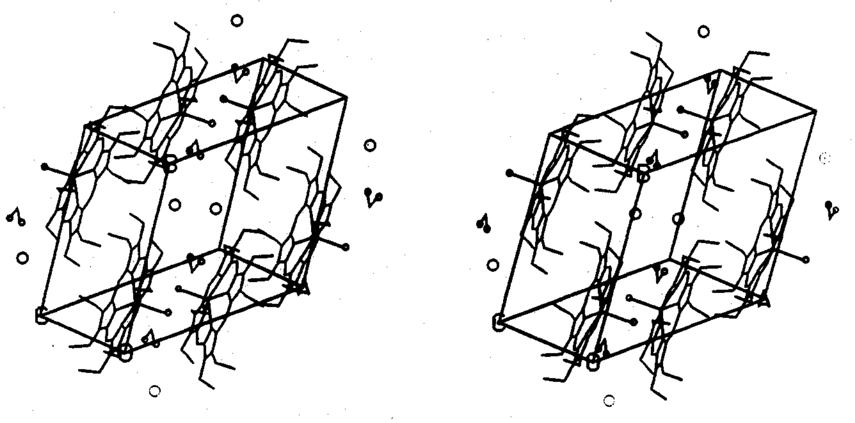

Figure 5. Stereoview of the packing in the unit cell. Hydrogen atoms have been omitted. Also shown are the dichloromethane and water solvent molecules. The oxygen positions (represented by the larger, isolated circles) inside the unit cell correspond to the position of O(1). Those outside correspond to positions of O(2). Smaller circles represent chlorine atoms.

well with those found for $Cl_2Sn(OEP)$,[11] in which the radius of the core is approximately the same, more so that they agree with those of any of the complexes having a less expanded core.

In several comparisons of β-pyrrole-carbon-substituted porphyrins and analogous meso-carbon-substituted porphyrins,[11,30,35,36] it has often been noted that the C_t–C_m distance is longer in the latter. There has been a question raised as to whether this is a real difference or an artifact from using too high a percentage of data from within the Cr Kα sphere ($(\sin\theta)/\lambda = 0.44$ Å^{-1}).[31] In the present study approximately 61% of the reflections used in the analysis came from beyond this sphere of data. The C_t–C_m distance of 3.421 (18) Å agrees at least qualitatively with the value of 3.424 (10) Å found for $Cl_2Sn(OEP)$[5] rather than the value of 3.469 (2) Å in $Cl_2Sn(TPP)$.[6] The difference in the ClTl(OEP) and $Cl_2Sn(TPP)$ values is about 3 times the root-mean-square standard deviation of the ClTl(OEP) value which indicates it may be significant. The difference may also be significant in the case of the C_a–C_m–C_a angles, where the value of 129.6 (13)° agrees with that of 129.5 (4)° for $Cl_2Sn(OEP)$ rather than the 126.3 (2)° in $Cl_2Sn(TPP)$.

The bond lengths for the terminal C–C bonds as originally calculated are unusually short. When these bond distances were corrected for thermal motion, assuming a "riding" model, more reasonable values were obtained. Both sets of values are given in Table VI. Thermal shortening may account for the C–Cl bond lengths in the dichloromethane solvent molecule being somewhat shorter than normally reported.

As mentioned earlier the disordered water molecule lies near a center of inversion. The closest approach (O(2)–O(2)′) would be 2.13 Å, the furthest (O(1)–O(1)′) would be 3.27 Å, with an intermediate O(1)–O(2)′ approach of 2.60 Å. Considering the extreme disorder and the observation that the O(1) position is probably the major site, these distances are not unreasonable.

The pattern of all eight terminal ethyl carbon atoms being pointed in one direction with respect to the porphyrin ring is unusual for octaethylporphyrin complexes. Such a pattern has been observed in two $H_3(OEP)^+$ salts[37,38] but not for any other metalloporphyrin complexes.

A stereoview of the packing in the unit cell is shown in Figure 5. There is one intermolecular contact shorter than 3.5 Å. That is the C(20)–C(20)′ distance of 3.40 Å. (Primed atom is related to the unprimed by the relationship $x' = -x$, $y' = -y$, $z' = -z$.) This contact is not considered to cause any significant structural change in the molecular conformation.

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Registry No. $(C_{36}H_{44}N_4)TlCl\cdot CH_2Cl_2\cdot H_2O$, 61506-23-8.

Supplementary Material Available: Tables III–V, containing calculated hydrogen atom positions, root-mean-square components of the thermal ellipsoids, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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