to James Loo of this department for performing the NMR measurements.

Registry No. 2-py$CH_2NHCH_2CH_2SH$, 65149-73-7; [Co(2-py$CH_2NHCH_2CH_2S)_2](ClO_4)_2$, 65150-30-3; [Co(2-py$CH_2NHCH_2CH_2SO_2)_2](ClO_4)\cdot 2H_2O$, 65150-37-0.

Supplementary Material Available: A listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Stereochemistry of the Toluene Solvate of $\alpha,\beta,\gamma,\delta$-Tetraphenylporphinatozinc(II)

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The crystal and molecular structure of the toluene solvate of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatozinc(II) has been determined by x-ray diffraction techniques. The compound crystallizes in the triclinic system, space group $P\bar{1}$. The unit cell has a = 11.349 (2) Å, b = 11.404 (2) Å, c = 10.502 (2) Å, α = 110.48 (2)°, β = 103.87 (2)°, γ = 107.65 (2)°, and Z = 1. Measurement of diffracted intensities employed ω scans with graphite-monochromated Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer. All independent reflections for $(\sin\theta)/\lambda \leq 0.725$ Å^{-1} (5436 unique observed data) were examined. These data were used for the determination of structure and full-matrix least-squares refinement. The final conventional and weighted discrepancy factors were 0.047 and 0.057. The molecule has required C_i-$\bar{1}$ symmetry. The average Zn–N bond distance is 2.036 (6) Å with the zinc atom precisely centered in the porphinato plane. The interplanar spacing between the porphyrin mean plane and a toluene plane is 3.34 Å.

Earlier studies[2–6] have established the structures of the $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatometal(II) derivatives of the first-row transition elements manganese(II) through copper(II). These studies have provided a quantitative picture of the structural changes, in a closely related series of complexes, resulting from the stepwise addition of d electrons. We report herein the molecular stereochemistry of the final member of this series, $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatozinc(II), and in the following paper[7] that of the earliest known member[8] in the sequence, $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatochromium(II).

All of the previously studied derivatives, except MnTPP,[2] have the metal ion centered in the plane of the porphinato ligand. However in MnTPP, despite a substantial radial expansion of the porphinato core, the high-spin manganese(II) ion appears to be too large to fit into the central hole of the porphinato ligand and the metal ion takes an out-of-plane position. A similar configuration for the metal ion in four-coordinate zinc porphyrins was suggested by Collins and Hoard.[9] Our structure determination for ZnTPP shows, however, that the zinc(II) ion is centered in the central hole of the core with somewhat compressed Zn–N bonds.

We obtained crystals of ZnTPP as the bis(toluene) solvate as was also the case for crystals of MnTPP. This provided us with the opportunity to further examine the specific interaction of the toluene molecules with the metalloporphyrin molecule.

Experimental Section

ZnTPP was prepared by the method of Adler et al.[10] Crystals appropriate for diffraction studies were obtained by recrystallization of ZnTPP from dry chloroform–toluene solutions. In order to prevent loss of solvent and reaction with atmospheric moisture, crystals were mounted in thin-walled glass capillaries. Preliminary x-ray examination established a one-molecule triclinic unit cell. The choice of centrosymmetric $P\bar{1}$ as the space group was confirmed by the successful refinement. Least-squares refinement of the setting angles of 30 reflections, each collected at $\pm 2\theta$, led to the cell constants (λ 0.710 69 Å) $a = 11.349$ (2) Å, $b = 11.404$ (2) Å, $c = 10.502$ (2) Å, $\alpha = 110.48$ (2)°, $\beta = 103.87$ (2)°, and $\gamma = 107.65$ (2)°. For a cell content of $ZnN_4C_{44}H_{28}\cdot 2C_7H_8$, the calculated density is 1.280 g/cm^3; the experimental density was 1.275 g/cm^3.

X-ray intensity data were collected using graphite-monochromated Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer. Initial intensity data collection was attempted using θ–2θ scans; however, instability of the crystals in the x-ray beam made this unfeasible. Therefore, in order to minimize the required data collection time, all intensity data were measured using ω scans with data collection techniques and reduction similar to that described previously.[11] Data were collected to a 2θ limit of 62.1° ($(\sin\theta)/\lambda = 0.725$ Å^{-1}) using a crystal of approximate dimensions of 0.23 × 0.32 × 0.42 mm. Four standard reflections were remeasured every 50 reflections during the data collection. Three of these standards showed a small monotonic decrease in intensity (9% total); the fourth displayed only random variations (±3%) from its average value. With the cited dimensions of the crystal and a linear absorption coefficient of 0.604 mm^{-1}, the error in any structure factor amplitude is less than 3%; this was confirmed by ψ scans and no correction applied. Data were retained as objectively observed if $F_o > 3\sigma(F_o)$, leading to 5436 unique observed data (76% of the theoretical number possible).

The close similarity of the cell constants of MnTPP[2] and ZnTPP suggested similar atomic arrangements. Accordingly, the atomic coordinates of the porphyrin moiety in MnTPP were used as a trial set of coordinates for ZnTPP. A difference Fourier synthesis[12] yielded positions of the unique toluene molecule. Full-matrix least-squares refinement[13] converged smoothly using isotropic temperature factors for all atoms and standard values[14,15] for atomic form factors. A difference Fourier synthesis gave electron density concentrations appropriately located for all hydrogen atom positions; these positions were idealized (C–H = 0.95 Å) with temperature factors fixed one unit higher than that of the associated carbon atom. Subsequent refinement used anisotropic temperature factors for all heavy atoms and fixed hydrogen contributions and was carried to convergence. An isotropic extinction correction[16] was included in the refinement. The final parameter shifts were less than 10% of the estimated standard deviations during the last cycle. The final value of the discrepancy index for $R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|$ was 0.047 and for $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o^2)]^{1/2}$ was 0.057. The estimated standard deviation of an observation of unit weight was 1.59, with a final data/parameter ratio of 19.0. An examination of $\sum w(|F_o| - |F_c|)^2$ for various classes of Miller indices, $|F_o|$, and setting angles showed no unusual trends.

The effect of the crystal decomposition was considered. Data were corrected for the decrease in the intensity of the three standards by fitting, via least squares, the average decrease of the standards vs. the exposure time of a given reflection. This data set was refined to convergence. Other than the scale factor, all parameters changed by less than 1 esd from the original refinement. Identical discrepancy indices were obtained. In view of the uncertainty of the correction, all data reported herein are derived from the refinement utilizing the original uncorrected data set.

Table I. Atomic Coordinates in the Unit Cell[a]

Atom type	Coordinates		
	10^4x	10^4y	10^4z
Zn	0	0	0
N_1	1473 (2)	369 (2)	1839 (2)
N_2	18 (1)	1874 (2)	1091 (2)
C_{a1}	2079 (2)	−476 (2)	1977 (2)
C_{a2}	2079 (2)	1540 (2)	3175 (2)
C_{a3}	759 (2)	2792 (2)	2564 (2)
C_{a4}	−832 (2)	2388 (2)	573 (2)
C_{b1}	3090 (2)	180 (2)	3450 (2)
C_{b2}	3099 (2)	1420 (2)	4177 (2)
C_{b3}	347 (2)	3899 (2)	2976 (2)
C_{b4}	−633 (2)	3654 (2)	1757 (2)
C_{m1}	1751 (2)	2668 (2)	3526 (2)
C_{m2}	−1788 (2)	1764 (2)	−870 (2)
C_1	2524 (2)	3842 (2)	5054 (2)
C_2	2323 (2)	3703 (2)	6256 (2)
C_3	3035 (2)	4799 (3)	7666 (2)
C_4	3948 (2)	6025 (3)	7883 (2)
C_5	4164 (3)	6176 (3)	6713 (3)
C_6	3443 (2)	5083 (2)	5295 (2)
C_7	−2564 (2)	2538 (2)	−1237 (2)
C_8	−1935 (2)	3759 (2)	−1291 (3)
C_9	−2645 (3)	4481 (3)	−1609 (3)
C_{10}	−3999 (3)	3989 (3)	−1889 (3)
C_{11}	−4635 (2)	2781 (3)	−1849 (3)
C_{12}	−3926 (2)	2059 (2)	−1523 (2)
C_{13}	7935 (4)	744 (4)	3150 (4)
C_{14}	7109 (3)	491 (4)	1794 (5)
C_{15}	6909 (3)	−570 (4)	550 (4)
C_{16}	7500 (4)	−1436 (4)	563 (5)
C_{17}	8349 (4)	−1216 (4)	1876 (6)
C_{18}	8551 (4)	−109 (4)	3190 (4)
C_{19}	8165 (6)	1963 (5)	4576 (6)

[a] The number in parentheses following each datum is the estimated standard deviation in the least significant figure.

A final difference Fourier synthesis was judged to have no significant features. A final listing of the observed and calculated structure factors (×10) is available.[17] Atomic coordinates and the associated anisotropic thermal parameters in the asymmetric unit of structure are listed in Tables I and II. Primed and unprimed symbols, C_i' and C_i, represent atoms related by the center of symmetry at the origin (and the metal atom).

Results and Discussion

Figure 1 is a computer-drawn model[18] in perspective of the centrosymmetric ZnTPP molecule as it exists in the crystal. On the upper right-hand side of the figure are displayed the labels assigned to the crystallographically unique atoms of the molecule. On the lower left-hand side of the figure, the atom symbols have been replaced by the value of the displacement of the atom from the mean plane of the porphinato core in units of 0.01 Å. The magnitude of the displacements from the mean plane is unremarkable. Individual units (pyrrole and phenyl rings) are planar to within less than 0.01 Å. The dihedral angles between the two unique phenyl rings and the mean porphinato core are 71.7 and 68.0°.

Individual bond lengths and angles for the ZnTPP molecule are given in Tables III and IV, respectively. Using C_a and C_b to denote the respective α- and β-carbon atoms of a pyrrole ring and C_m for methine carbon atoms, averaged values (assuming fourfold geometry) for the unique chemical types of bonds in the core are Zn–N = 2.036 (6) Å, N–C_a = 1.375 (4) Å, C_a–C_b = 1.443 (4) Å, C_b–C_b = 1.351 (5) Å, and C_a–C_m = 1.399 (4) Å. Averaged bond angles are C_aNC_a = 106.5 (1) Å, NC_aC_m = 125.7 (1)°, NC_aC_b = 109.6 (2)°, $C_aC_bC_b$ = 107.2 (1)°, $C_aC_mC_a$ = 125.0 (2)°, and $C_mC_aC_b$ = 124.7 (1)°. The number in parentheses following each averaged value is the estimated standard deviation calculated on the

Table II. Thermal Parameters[a]

Atom type	Anisotropic parameters						B,[b] Å^2
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
Zn	3.33 (1)	3.10 (1)	2.79 (1)	1.45 (1)	0.36 (1)	0.96 (1)	3.22
N_1	3.51 (6)	3.33 (6)	2.93 (6)	1.62 (5)	0.69 (5)	1.12 (5)	3.35
N_2	3.12 (6)	3.29 (6)	2.86 (6)	1.37 (5)	0.45 (5)	1.12 (5)	3.24
C_{a1}	3.54 (7)	3.65 (7)	2.99 (7)	1.71 (6)	0.57 (6)	1.43 (6)	3.41
C_{a2}	3.75 (8)	3.52 (7)	2.72 (7)	1.49 (6)	0.43 (6)	1.08 (6)	3.50
C_{a3}	3.37 (7)	3.19 (7)	2.89 (7)	1.32 (6)	0.68 (5)	1.04 (6)	3.34
C_{a4}	3.18 (7)	3.26 (7)	3.27 (7)	1.47 (6)	0.79 (6)	1.33 (6)	3.32
C_{b1}	4.48 (9)	4.37 (9)	3.25 (8)	2.27 (8)	0.21 (7)	1.39 (7)	4.01
C_{b2}	4.50 (9)	4.58 (9)	2.91 (7)	2.28 (8)	0.05 (6)	1.07 (7)	4.03
C_{b3}	4.02 (8)	3.50 (8)	3.34 (7)	1.78 (7)	0.75 (6)	0.92 (6)	3.80
C_{b4}	3.79 (8)	3.50 (8)	3.69 (8)	1.86 (7)	0.93 (6)	1.14 (6)	3.75
C_{m1}	3.51 (7)	3.40 (7)	2.72 (6)	1.44 (6)	0.57 (5)	1.04 (6)	3.38
C_{m2}	3.13 (7)	3.59 (7)	3.30 (7)	1.57 (6)	0.81 (6)	1.55 (6)	3.35
C_1	3.7 (1)	3.8 (1)	2.8 (1)	1.8 (1)	0.5 (1)	0.9 (1)	3.59
C_2	4.4 (1)	5.0 (1)	3.4 (1)	2.0 (1)	1.0 (1)	1.4 (1)	4.43
C_3	5.1 (1)	6.7 (1)	3.1 (1)	3.2 (1)	1.3 (1)	1.4 (1)	4.70
C_4	5.0 (1)	5.3 (1)	3.4 (1)	2.5 (1)	0.3 (1)	0.4 (1)	4.83
C_5	5.5 (1)	4.2 (1)	4.5 (1)	1.0 (1)	0.4 (1)	0.6 (1)	5.40
C_6	5.2 (1)	4.3 (1)	3.5 (1)	1.3 (1)	0.8 (1)	1.1 (1)	4.69
C_7	3.4 (1)	3.7 (1)	3.1 (1)	1.7 (1)	0.8 (1)	1.5 (1)	3.41
C_8	3.6 (1)	4.3 (1)	5.1 (1)	1.8 (1)	1.3 (1)	2.5 (1)	4.18
C_9	5.5 (1)	4.8 (1)	5.8 (1)	2.8 (1)	2.1 (1)	3.2 (1)	4.78
C_{10}	5.4 (1)	6.3 (1)	4.8 (1)	3.8 (1)	1.8 (1)	3.1 (1)	4.68
C_{11}	3.7 (1)	6.2 (1)	4.6 (1)	2.7 (1)	1.3 (1)	2.6 (1)	4.46
C_{12}	3.5 (1)	4.5 (1)	4.1 (1)	1.7 (1)	1.2 (1)	2.1 (1)	4.00
C_{13}	6.7 (2)	6.9 (2)	8.7 (2)	1.4 (1)	3.3 (2)	3.7 (2)	7.48
C_{14}	5.8 (2)	7.1 (2)	9.7 (2)	2.0 (1)	3.2 (2)	4.8 (2)	7.05
C_{15}	6.3 (2)	7.2 (2)	7.7 (2)	0.9 (1)	2.2 (1)	3.6 (2)	7.33
C_{16}	7.7 (2)	6.5 (2)	9.5 (2)	1.3 (2)	4.7 (2)	3.6 (2)	7,53
C_{17}	7.0 (2)	8.5 (2)	15.1 (4)	3.7 (2)	5.6 (2)	7.3 (3)	8.37
C_{18}	6.6 (2)	8.8 (2)	8.5 (2)	1.5 (2)	1.4 (2)	4.9 (2)	8.07
C_{19}	15.8 (4)	8.4 (3)	10.8 (3)	2.9 (3)	6.8 (3)	1.6 (2)	11.69

[a] The number in parentheses following each datum is the estimated standard deviation in the least significant figure. B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a^*{}_j$. [b] Isotropic thermal parameter calculated from $B = 4[V^2\det(\beta_{ij})]^{1/3}$.

Table III. Bond Lengths in the Coordination Group and Porphinato Skeleton[a]

Type	Length, Å	Type	Length, Å	Type	Length, Å
Zn–N_1	2.040 (2)	C_{a1}–C_{b1}	1.445 (3)	C_{a4}–C_{b4}	1.447 (3)
Zn–N_2	2.032 (2)	C_{a1}–C_{m2}'	1.394 (3)	C_{a4}–C_{m2}	1.403 (3)
N_1–C_{a1}	1.370 (2)	C_{a2}–C_{b2}	1.442 (3)	C_{b1}–C_{b2}	1.347 (3)
N_1–C_{a2}	1.376 (2)	C_{a2}–C_{m1}	1.397 (3)	C_{b3}–C_{b4}	1.354 (3)
N_2–C_{a3}	1.373 (2)	C_{a3}–C_{b3}	1.439 (3)	C_{m1}–C_1	1.499 (3)
N_2–C_{a4}	1.380 (2)	C_{a3}–C_{m1}	1.400 (2)	C_{m2}–C_7	1.500 (3)

[a] The numbers in parentheses are the estimated standard deviations.

assumption the values are drawn from the same population.

A major aim of this work was to determine whether the zinc atom is in the center of the porphinato plane or whether it is displaced to give a pyramidal geometry for the molecule. The crystallographically required C_i-$\bar{1}$ symmetry of the ZnTPP molecule demands precise centering of the zinc atom in the center of the core if the structure is ordered. Unlike the case for the isomorphous crystals of MnTPP,[2] all features of the structural analysis of ZnTPP suggest a completely ordered structure and hence that the zinc atom is located at the center of the four porphinato nitrogen atoms.

This centering leads to a Zn–N bond length of 2.036 (6) Å. This distance is a relatively short bond distance for zinc complexes. A survey[19] of known Zn–N bond distances in complexes with a variety of coordination numbers and geometries reveals that for all cases, except tetrahedral, the observed Zn–N bond distances are equal to or greater than 2.06 Å (and frequently much greater). One important exception is phthalocyanatozinc(II) (ZnPc),[20] wherein the Zn–N bond distance is 1.980 Å. In both ZnPc and ZnTPP, the constraints of the macrocyclic ligand lead to substantially shortened zinc ligand bonds. However, an examination of Table V, which lists the average values of the metal–porphinato nitrogen bond distances for the entire known sequence of first-row derivatives, shows that the Zn–N distance is the longest of all the derivatives in the sequence except for MnTPP.[21]

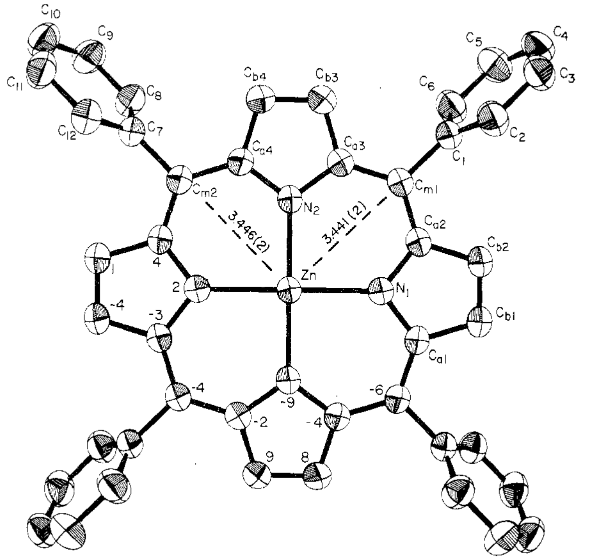

Figure 1. An ORTEP plot of the ZnTPP molecule. Atoms are represented by their vibrational ellipsoids contoured to enclose 50% of the electron density. The labeling scheme for the atoms is shown in the upper right-hand side of the diagram. The perpendicular displacement of each unique atom in the core, in units of 0.01 Å, is displayed on the lower left-hand side of the figure. The values of the two unique Zn···C_m distances are also shown in the figure.

Table IV. Bond Angles in the Coordination Group and Porphinato Skeleton[a]

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N_1ZnN_2	90.3 (1)	$N_2C_{a3}C_{b3}$	109.7 (2)	$C_{a2}C_{m1}C_1$	117.5 (2)
$C_{a1}N_1C_{a2}$	106.6 (1)	$C_{m1}C_{a3}C_{b3}$	124.7 (2)	$C_{a3}C_{m1}C_1$	117.2 (2)
$C_{a3}N_2C_{a4}$	106.4 (1)	$N_2C_{a4}C_{m2}$	125.7 (2)	$C_{a4}C_{m2}C_{a1}'$	124.9 (2)
$N_1C_{a1}C_{m2}'$	125.8 (2)	$N_2C_{a4}C_{b4}$	109.7 (2)	$C_{a4}C_{m2}C_7$	117.3 (2)
$N_1C_{a1}C_{b1}$	109.4 (2)	$C_{m2}C_{a4}C_{b4}$	124.6 (2)	$C_{a1}'C_{m2}C_7$	117.8 (2)
$C_{m2}'C_{a1}C_{b1}$	124.8 (2)	$C_{a1}C_{b1}C_{b2}$	107.3 (2)	ZnN_1C_{a1}	126.9 (1)
$N_1C_{a2}C_{m1}$	125.7 (2)	$C_{a2}C_{b2}C_{b1}$	107.2 (2)	ZnN_1C_{a2}	126.4 (1)
$N_1C_{a2}C_{b2}$	109.4 (2)	$C_{a3}C_{b3}C_{b4}$	107.3 (2)	ZnN_2C_{a3}	126.3 (1)
$C_{m1}C_{a2}C_{b2}$	124.8 (2)	$C_{a4}C_{b4}C_{b3}$	107.0 (2)	ZnN_2C_{a4}	126.8 (1)
$N_2C_{a3}C_{m1}$	125.6 (2)	$C_{a2}C_{m1}C_{a3}$	125.2 (2)		

[a] The numbers in parentheses are the estimated standard deviations.

Table V. The M-N Bond Lengths in a Sequence of Four-Coordinate Metallotetraphenylporphyrins[a]

	Metal ion						
	d^4Cr	d^5Mn	d^6Fe	d^7Co	d^8Ni	d^9Cu	d^{10}Zn
M-N, Å	2.033 (1)	>2.084	1.972 (4)	1.949 (3)	1.928 (3)	1.981 (7)	2.036 (6)
Spin state, S	2	$^5/_2$	1	$^1/_2$	0	$^1/_2$	0
Symmetry[b]	C_i	C_i	S_4	S_4	S_4	S_4	C_i
Ref	7	2	3	4	5	6	c

[a] The number in parentheses is the estimated standard deviation for the bond distance. [b] Symmetry required of the molecule in the crystal. [c] This work.

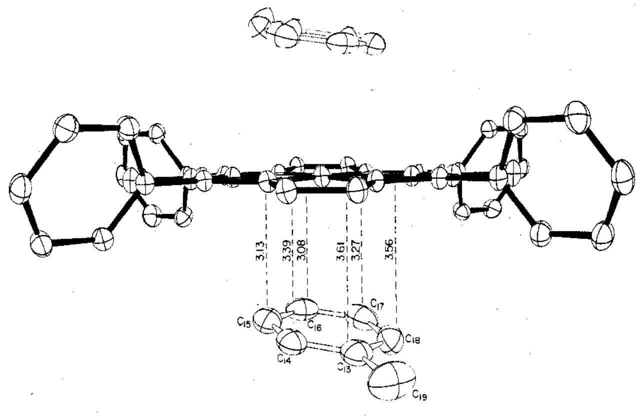

Figure 2. A view of the ZnTPP molecule illustrating the relationship between the toluene molecules and the metalloporphyrin. The porphinato plane is approximately perpendicular to the plane of the paper. Perpendicular distances between the toluene atoms and the mean porphinato plane are shown. Vibrational ellipsoids are at the 20% probability level.

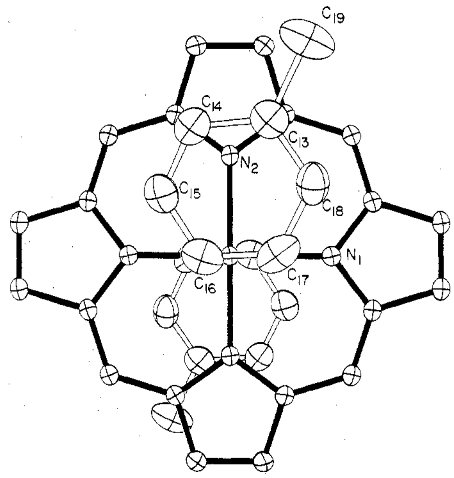

Figure 3. A second view of the ZnTPP molecule showing the relationship between the toluene molecules and the metalloporphyrin. Phenyl rings have been omitted for clarity. Vibrational ellipsoids are shown at the 20% probability level.

The zinc–porphyrin nitrogen bond distances in several five-coordinate derivatives are substantially longer than the 2.036 Å value in four-coordinate ZnTPP. In ZnTPyP(Py),[22] Zn–N = 2.073 (8) Å; in ZnOEP(Py),[23] Zn–N = 2.067 (6) Å; in ZnTPP(ClO$_4$),[24] Zn–N = 2.076 (9) Å; and in ZnTPC(Py),[25] Zn–N = 2.065 (6) Å; the average Zn–N distance for the four derivatives is 2.070 (5) Å. The 0.034 Å increase in bond length is not unreasonable for the increase in the coordination number. It is interesting to note how this increase in the Zn–N bond distance arises. A substantial component results from an out-of-plane displacement of the zinc atom of 0.33 Å. The remainder of the increase, however, is possibly derived from a radial expansion of the porphinato core; the average Ct···N distance in the five-coordinate complexes is 2.045 Å, compared to 2.036 Å in four-coordinate ZnTPP.[26] Given the generally accepted conclusion that the porphinato core resists undue radial expansion in the mean plane,[27] this possible second component is somewhat unexpected and commands further notice.

Four-coordinate ZnTPP forms adducts with various Lewis bases. Nitrogen donors have been most commonly studied,[28-30] but S, O, and P donors have also been examined.[31-32] In all cases 1:1 stoichiometry is observed. Thus, the zinc porphyrins, unlike the magnesium porphyrins, show no tendency to add a sixth axial ligand. The lack of formation of six-coordinate derivatives has been interpreted in terms of the stereochemical constraints of the porphinato core,[22] wherein it was suggested that the zinc atom was too large, in the four-, five-, and six-coordinate derivatives, to be "squeezed" into the porphinato hole. The results reported herein, however, do show that the zinc atom can be "squeezed" into the central hole of the porphinato core in a four-coordinate derivative and, indeed, that the radius of the central hole is possibly smaller or equal to that in the five-coordinate derivatives. It is particularly this possible difference in the radius of the central hole which suggests that the formation of an axial ligand–zinc bond leads to a substantially decreased interaction of the zinc atom with the porphinato ligand. This decreased interaction of the zinc atom with the porphinato ligand would only be accentuated by the addition of two axial ligands. Hence, "squeezing" the six-coordinate zinc atom into the plane of the porphinato ligand does appear unlikely.

Figures 2 and 3 show the centrosymmetric relationship of the two toluene molecules of crystallization and the ZnTPP molecule. The dihedral angle (cf. Figure 2) between the plane of a toluene molecule and the mean plane of the porphinato plane is 12.0°. Figure 2 also displays the perpendicular distances between individual atoms of the toluene molecule and the mean plane of the core; the average distance is 3.34 Å. Figure 3 shows the specific orientation of the toluene solvate with respect to the metalloporphyrin; the C_{16} and C_{17} carbon atoms of the toluene make rather close contacts of 3.121 and 3.379 Å, respectively, with the zinc atom. The geometry and interplanar spacings observed in this crystal structure are quite similar to those observed in the isomorphous crystals of MnTPP and also to those observed in the toluene solvate of CrTPP.[7] The arrangement suggests the possibility of π-complex formation between the toluene and the metalloporphyrin; this matter is considered in the following paper.[7] Other than the close intermolecular contacts between toluene and ZnTPP, there are no significantly short intermolecular contacts.

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Registry No. ZnTPP·2(toluene), 65150-26-7.

Supplementary Material Available: A listing of structure factor amplitudes (×10) (25 pages). Ordering information is given on any current masthead page.

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Stereochemistry of the Toluene Solvate of $\alpha,\beta,\gamma,\delta$-Tetraphenylporphinatochromium(II)

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The crystal and molecular structure of the toluene solvate of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatochromium(II) has been determined by x-ray diffraction techniques. The compound crystallizes in the monoclinic system, space group $P2_1/c$. The unit cell constants are $a = 10.518$ (3) Å, $b = 15.778$ (4) Å, $c = 13.425$ (3) Å, $\beta = 101.02$ (3)°, and $Z = 2$. Measurements of diffracted intensities employed θ–2θ scans with graphite-monochromated Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer. All independent reflections for $(\sin\theta)/\lambda \leq 0.648$ Å^{-1} (2707 unique observed data) were examined. These data were employed for the determination of structure and least-squares refinement. The final values of the conventional and weighted discrepancy factors were 0.070 and 0.067. The CrTPP molecule has required C_i—$\bar{1}$ molecular symmetry. The average Cr–N bond distance is 2.033 (1) Å. The interplanar spacing between the porphyrin mean plane and a plane of the toluene solvate is 3.37 Å and the interplanar angle is 4.5°. The similarity in structure of the toluene solvates of CrTPP, ZnTPP, and MnTPP is discussed.

The preceding paper[3] has noted that the structural study of the first-row, divalent transition metal derivatives of $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin provides a quantitative description of the structural changes resulting from the stepwise addition of d electrons. We report herein the molecular stereochemistry of the recently reported[4] $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatochromium(II), the earliest of the presently known derivatives. Derivatives of this chromium(II) porphyrin have been reported[4] to form, irreversibly, dioxygen complexes.

Crystals of two members of this series of first-row complexes, MnTPP[5] and ZnTPP,[3] were obtained as bis(toluene) solvates. Crystal structure determination showed an apparently specific interaction of the toluene molecules with both the central metal atom and the porphyrin moiety. The similar interaction of toluene and the metalloporphyrin in the manganese(II) and zinc(II) complexes is virtually demanded

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