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Crystal and Molecular Structure of the Silver(II) and Zinc(II) Derivatives of *meso*-Tetraphenylporphyrin. An Exploration of Crystal-Packing Effects on Bond Distance

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The crystal and molecular structures of four-coordinate silver(II) and zinc(II) tetraphenylporphyrinates have been determined. Both complexes crystallize in the triclinic system and are isomorphous with the triclinic modification of the parent macrocycle H_2TPP. Bond distances in the centrosymmetric coordination groups of both complexes are found to be statistically nonequivalent. Features of the crystal packing of the compounds suggest that this inequivalence arises from asymmetric lattice packing. The average Ag–N distance is 2.092 Å (individual values 2.082 (3) and 2.101 (3) Å), and that for Zn–N is 2.037 Å (individual values 2.045 (2) and 2.029 (2) Å). Crystal data for AgTPP: triclinic, $a = 10.503$ (2) Å, $b = 12.485$ (2) Å, $c = 6.351$ (2) Å, $\alpha = 97.72$ (1)°, $\beta = 100.68$ (1)°, $\gamma = 97.150$ (9)°, $Z = 1$, space group $P\bar{1}$, 5616 observed data, $R_1 = 0.059$. Crystal data for ZnTPP: triclinic, $a = 10.382$ (1) Å, $b = 12.421$ (2) Å, $c = 6.443$ (1) Å, $\alpha = 98.30$ (1)°, $\beta = 101.15$ (1)°, $\gamma = 96.47$ (1)°, $Z = 1$, space group $P\bar{1}$, 3729 observed data, $R_1 = 0.036$.

The determinations of structure for four-coordinate AgTPP and ZnTPP[4] were performed several years apart for a disparate variety of reasons. However, one important feature common to both is the probable modulation of porphinato nitrogen–metal bond distances by crystal-packing constraints. The statistically significant variation in the complexing M–N bond lengths in these d^9 and d^{10} complexes is unexpected on any electronic grounds. However, it is to be noted that crystallographic similarities in these two isomorphous complexes, along with that of triclinic H_2TPP,[5] suggest that the basis for the deviations lies in crystal-packing effects. This conclusion, although principally based on indirect evidence, is buttressed by the comparison of the zinc(II) and silver(II) derivatives, which represent metal ions of significantly different size and complexing requirements.

AgTPP was initially studied (at Cornell) as a member of a series[6] of metalloporphyrin derivatives with large central metal ions. These studies were designed to probe the limits of radial expansion that could be effected in the quasi-rigid porphyrin macrocycle. Complexation of the d^9 silver ion does indeed lead to substantial radial expansion of the macrocycle; the average Ag–N bond distance was found to be 2.092 Å. A wholly unanticipated structural feature is the large disparity in the two crystallographically unique complexing distances: 2.082 (3) and 2.101 (3) Å. This difference is unexpectedly large considering the close agreement between other chemically equivalent bond distances in the core. Indeed, the difference of 0.019 Å is 5 times the formal estimated standard deviation for the difference. Certain conformational features of triclinic H_2TPP, while wholly appropriate for relieving intraannular H···H contacts in crystalline H_2TPP, surprisingly remain in the crystal structure of AgTPP. It seemed plausible that the unequal Ag–N bond distances were the consequence of this unexpected retention of conformational features in crystalline AgTPP and that the conformation was itself a result of an asymmetric crystalline environment. It was uncertain which of the two Ag–N bond distances represents that most appropriate for an unconstrained core (D_{4h} geometry).

Table I. Summary of Crystal Data and Intensity Collection Parameters

	ZnTPP	AgTPP
T, K	296	296
formula	$ZnN_4C_{44}H_{28}$	$AgN_4C_{44}H_{28}$
fw	678.11	720.61
cryst dimens, mm	0.15 × 0.20 × 0.25	0.18 × 0.24 × 0.26
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.382 (1)	10.503 (2)
b, Å	12.421 (2)	12.485 (2)
c, Å	6.443 (1)	6.351 (2)
α, deg	98.30 (1)	97.72 (1)
β, deg	101.15 (1)	100.68 (2)
γ, deg	96.47 (1)	97.150 (9)
V, Å^3	798.1 (3)	801.4 (6)
radiation	graphite-monochromated MoKα (λ = 0.71073 Å)	Zr-filtered Mo Kα (λ = 0.709 26 Å)
diffractometer	Enraf-Nonius CAD4	Picker FACS-I
scan technique	θ–2θ	θ–2θ
scan range in 2θ, deg	$2(0.8 + 0.35 \tan \theta)$	$0.9 + 0.692(\tan \theta)$
scan rate, deg/min	2–8	1.0
bkgd	moving cryst, moving detector for additional 25% of scan at each extreme	stationary cryst, stationary detector, 40 s at each extreme
maximum 2θ, deg	63.7	66.76
criterion for observn	$F_o^2 > 3.0\sigma(F_o^2)$	$F_o \geq 1.35\sigma F_o$
unique obsd data	3729	5616
μ, mm^{-1}	0.82	0.64
R_1	0.036	0.059
R_2	0.050	0.079
goodness of fit	1.18	
data/parameter	16.65	20.44

Some years later (at Notre Dame), crystals of an unsolvated form of ZnTPP[7] were prepared in the course of other investigations. This crystalline form was found to be isomorphous with AgTPP and H_2TPP. Given the apparent high quality of the crystals, it was practical[8] to determine whether nonequal Zn–N bond distances would be found and if their origin was crystal-packing effects. In addition, there is intrinsic interest in the

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[4] Abbreviations used in this paper: TPP and OEP, dianions of *meso*-tetraphenylporphyrin and octaethylporphyrin, respectively; Ct, center of the porphyrin macrocycle; py, pyridine; pip, piperidine; THF, tetrahydrofuran.

[5] Silvers, S. J.; Tulinsky, A. *J. Am. Chem. Soc.* **1967**, *89*, 3331–3337.

[6] Collins, D. M.; Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 6689–6696.

[7] The molecular structure of a crystalline form of ZnTPP containing two toluene molecules of solvation has been reported: Scheidt, W. R.; Kastner, M. E.; Hatano, K. *Inorg. Chem.* **1978**, *17*, 706–710. The toluene molecules form a π complex with the metalloporphyrin.

[8] The question of practicality lies in the necessity of achieving a structure determination with high accuracy for the metal–nitrogen bond distances. One important feature is the ability to collect intensity data to high scattering angle.

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

atom type	10^4x	10^4y	10^4z
Ag	0	0	0
C_1	−376 (4)	−3306 (3)	1342 (6)
C_2	565 (4)	−2824 (3)	3116 (6)
C_3	2822 (4)	1066 (3)	6003 (6)
C_4	2837 (4)	2030 (3)	5259 (7)
C_5	−779 (3)	−2452 (2)	174 (5)
C_6	749 (3)	−1660 (2)	3044 (5)
C_7	1934 (3)	253 (3)	4384 (5)
C_8	1933 (3)	1843 (2)	3178 (6)
C_α	1690 (3)	−875 (3)	4516 (5)
C_β	1669 (3)	2634 (2)	1838 (5)
N_1	−83 (5)	−1473 (2)	1262 (5)
N_2	1408 (3)	756 (2)	2723 (5)
$C_{\alpha1}$	2542 (3)	−1259 (3)	6301 (5)
$C_{\alpha2}$	2026 (4)	−1776 (3)	7847 (7)
$C_{\alpha3}$	2845 (5)	−2129 (4)	9510 (7)
$C_{\alpha4}$	4192 (5)	−1965 (4)	9644 (8)
$C_{\alpha5}$	4717 (4)	−1453 (4)	8137 (9)
$C_{\alpha6}$	3896 (4)	−1114 (4)	6473 (7)
$C_{\beta1}$	2384 (3)	3770 (3)	2624 (6)
$C_{\beta2}$	2232 (5)	4375 (3)	4541 (8)
$C_{\beta3}$	2929 (7)	5431 (4)	5248 (10)
$C_{\beta4}$	3747 (7)	5897 (3)	4074 (4)
$C_{\beta5}$	3886 (6)	5310 (4)	2129 (13)
$C_{\beta6}$	3214 (5)	4245 (3)	1431 (9)

[a] In this and all other tables in this paper the number in parentheses following a datum is the estimated standard deviation.

structure of a completely unsolvated four-coordinate (porphinato)zinc(II) derivative.

Experimental Section

AgTPP. A powdered sample of the compound was provided by Dr. Alan Adler (for preparation, cf. ref 13). Single crystals were obtained by diffusing 1:1 chloroform–ethyl ether into a chloroform solution of AgTPP in a glass bottle. After 2 weeks, small, high-quality crystals were deposited on the bottom and sides of the 5-mL beaker. This procedure was repeated several times until crystals of ~¹/₄-mm size were obtained. One of the larger crystals was mounted on a glass fiber and subjected to a detailed photographic examination followed by intensity data collection on a Picker diffractometer. Details of the crystal data and intensity collection parameters are given in Table I. The axes for the triclinic lattice were chosen according to the Donnay[9] convention; this choice of cell parameters differs from that reported by Silvers and Tulinsky[5] for isomorphous, triclinic H_2TPP. Data reduction was performed as described previously.[10]

Refinement of structure for AgTPP was initiated in space group $P\bar{1}$ by placing the Ag atom at the origin and utilizing the coordinates of Tulinsky[5,11] for the porphinato core. At the end of the refinement, the structure was refined in two blocks: the Ag atom and the porphinato core in one cycle and refinement of the phenyl group parameters in the subsequent cycle. Since AgTPP is known to form a series of solid solutions[9] with H_2TPP, the occupancy factor of the Ag atom was varied at two separate stages of the refinements. The resulting effective occupations were 0.992 and 0.994, trivially different from the value for a pure substance. Near the end of the refinement, the data with $(\sin\theta)/\lambda < 0.434$ were excluded in order to minimize effects of the hydrogen atom contribution to the observed bond distances. A detailed comparison of this refinement technique to other refinement techniques has been described previously.[6] Even with the rejection of these low-angle data, the data/parameter ratio was 20.5. The final cycle of refinement with the 4579 reflections produced an R_1 of 0.062 and an R_2 of 0.072.[12] The structural parameters resulting from this refinement are reported herein. A structure factor calculation using these final parameters and including the complete set of 5616 data gives the discrepancy indices reported in Table I. A final difference Fourier synthesis showed regions of electron density for the 14 C–H bonds in the asymmetric unit of structure. These C–H bond densities accounted for the eight highest peaks in the map, followed by a residual peak near the Ag atom with a height of 0.73 e/Å³. Final atomic coordinates are listed in Table II, and the associated thermal parameters are given in Table IS of the supplementary material.

Table III. Fractional Coordinates of ZnTPP

atom	x	y	z
Zn	0.000 0	0.000 0	0.000 0
C_1	−0.039 62 (21)	−0.328 19 (16)	0.136 1 (3)
C_2	0.053 40 (21)	−0.279 08 (16)	0.311 3 (3)
C_3	0.280 52 (22)	0.108 05 (17)	0.594 1 (3)
C_4	0.281 66 (21)	0.204 43 (17)	0.521 4 (3)
C_5	−0.078 88 (18)	−0.243 75 (15)	0.017 1 (3)
C_6	0.073 40 (18)	−0.163 46 (15)	0.301 94 (29)
C_7	0.191 70 (18)	0.026 24 (15)	0.433 30 (29)
C_8	0.192 14 (18)	0.184 18 (15)	0.313 7 (3)
C_α	0.167 15 (18)	−0.085 22 (15)	0.448 99 (28)
C_β	0.167 02 (18)	0.263 28 (15)	0.183 0 (3)
N_1	−0.008 77 (15)	−0.143 63 (12)	0.120 49 (24)
N_2	0.137 77 (15)	0.074 66 (13)	0.264 86 (24)
$C_{\alpha1}$	0.253 08 (19)	−0.122 86 (15)	0.630 69 (29)
$C_{\alpha2}$	0.199 26 (20)	−0.172 13 (18)	0.780 4 (3)
$C_{\alpha3}$	0.280 04 (24)	−0.207 24 (20)	0.948 0 (3)
$C_{\alpha4}$	0.416 10 (25)	−0.193 49 (20)	0.966 7 (4)
$C_{\alpha5}$	0.470 27 (22)	−0.145 11 (21)	0.819 5 (4)
$C_{\alpha6}$	0.390 41 (20)	−0.110 83 (19)	0.651 1 (4)
$C_{\beta1}$	0.238 84 (19)	0.377 73 (15)	0.261 7 (3)
$C_{\beta2}$	0.221 42 (25)	0.439 25 (18)	0.448 3 (4)
$C_{\beta3}$	0.290 8 (3)	0.545 87 (21)	0.518 8 (5)
$C_{\beta4}$	0.373 9 (3)	0.590 60 (20)	0.404 9 (6)
$C_{\beta5}$	0.390 05 (28)	0.530 71 (21)	0.218 6 (6)
$C_{\beta6}$	0.323 94 (25)	0.424 15 (19)	0.147 5 (4)

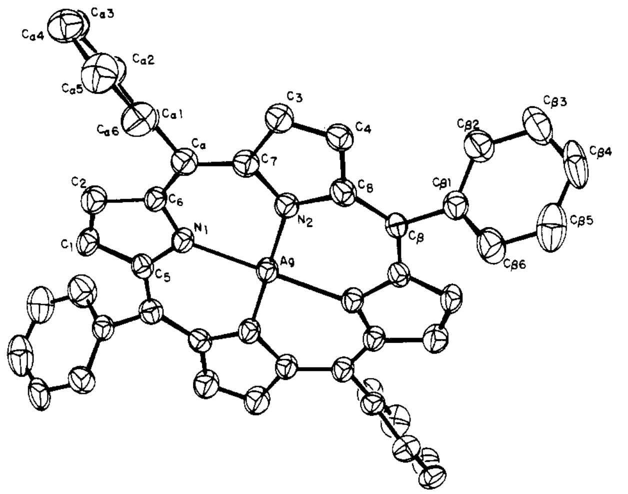

Figure 1. Computer-drawn model in perspective of the AgTPP molecule as it exists in the crystal. The atom-labeling scheme for the crystallographically unique atoms given. The notation system follows that given by Tulinsky.[5]

ZnTPP. Unsolvated crystals of ZnTPP were prepared by dissolving 0.07 g of ZnTPP[13] in 8 mL of chloroform. After filtration, 8 mL of (trifluoromethyl)benzene was carefully layered on top and the mixture set aside. After 3 days, crystals were deposited on the bottom of the vessel. After decantation and washing with methanol the crystalline material was subjected to preliminary examination on an Enraf-Nonius CAD4 diffractometer. The complex was found to be isomorphous with AgTPP and H_2TPP; the cell constants were chosen in agreement with those previously used in the AgTPP investigation. Final cell constants and intensity data collection parameters are reported in Table I. The structure ZnTPP was solved with use of the direct-methods program MULTAN.[14] Final refinement was carried out by full-matrix least-squares

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(9) Previous work by Donnay and Storm gave lattice constants of 10.52, 12.47, and 6.37 Å, and 97.62, 100.84, and 96.91°: Donnay, G.; Storm, C. B. *Mol. Cryst.* **1967**, *2*, 287–292.

(10) Collins, D. M.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2066–2072.

(11) The atomic coordinates were transformed to our choice of unit cell. The notation of Silvers and Tulinsky was retained for all atoms of the porphinato core.

(12) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

(13) ZnTPP was prepared by following the procedure in: Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.

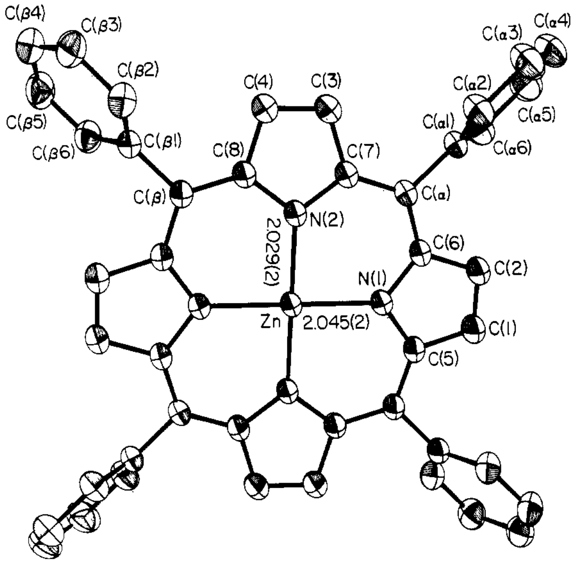

Figure 2. Computer-drawn model giving the same information as Figure 1 for the ZnTPP molecule.

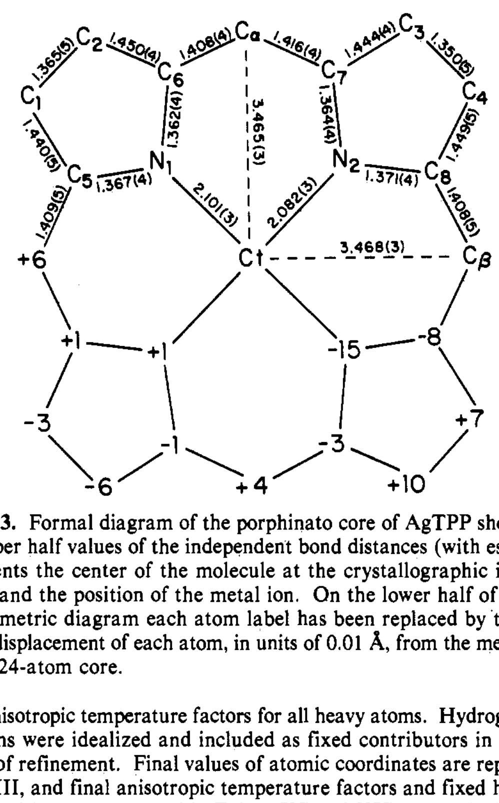

Figure 3. Formal diagram of the porphinato core of AgTPP showing on the upper half values of the independent bond distances (with esd's). Ct represents the center of the molecule at the crystallographic inversion center and the position of the metal ion. On the lower half of the centrosymmetric diagram each atom label has been replaced by the value of the displacement of each atom, in units of 0.01 Å, from the mean plane of the 24-atom core.

with anisotropic temperature factors for all heavy atoms. Hydrogen atom positions were idealized and included as fixed contributors in the final cycles of refinement. Final values of atomic coordinates are reported in Table III, and final anisotropic temperature factors and fixed hydrogen atom positions are reported in Tables IIS and IIIS, respectively. Final tables of observed and calculated structure factor amplitudes are available for both structures as supplementary material.

Results and Discussion

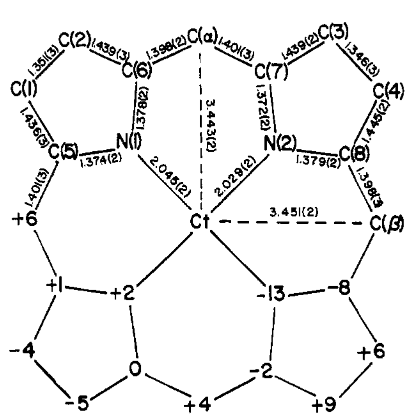

Figure 4. Formal diagram of the porphinato core of ZnTPP showing the same information as that in Figure 3.

Table IV. Bond Angles (deg) for AgTPP

N_1-Ag-N_2	89.9 (1)	$N_1-C_6-C_2$	108.6 (3)
$Ag-N_1-C_5$	124.7 (2)	$N_1-C_6-C_\alpha$	126.4 (3)
$Ag-N_1-C_6$	125.2 (2)	$N_2-C_7-C_3$	108.4 (3)
$C_5-N_1-C_6$	108.6 (3)	$N_2-C_7-C_\alpha$	126.7 (3)
$Ag-N_2-C_7$	125.4 (2)	$N_2-C_8-C_4$	107.9 (3)
$Ag-N_2-C_8$	125.9 (2)	$N_2-C_8-C_\beta$	126.2 (3)
$C_7-N_2-C_8$	108.7 (3)	$C_6-C_\alpha-C_7$	125.4 (3)
$C_2-C_1-C_5$	107.4 (3)	$C_6-C_\alpha-C_{\alpha1}$	117.8 (3)
$C_1-C_2-C_6$	106.8 (3)	$C_7-C_\alpha-C_{\alpha1}$	116.7 (3)
$C_4-C_3-C_7$	107.5 (3)	$C_8-C_\beta-C_5'$	125.8 (3)
$C_3-C_4-C_8$	107.6 (3)	$C_8C_\beta-C_{\beta1}$	117.3 (3)
$N_1-C_5-C_1$	108.5 (3)	$C_5'-C_\beta-C_{\beta1}$	116.9 (3)
$N_1-C_5-C_\beta'$	126.9 (3)		

Table V. Bond Angles for ZnTPP (deg)

N_1-Zn-N_2	90.16 (6)	$C_5-C_1-C_2$	107.29 (17)
N_1-Zn-N_2'	89.84 (6)	$C_1-C_2-C_6$	107.21 (17)
$Zn-N_1-C_5$	126.54 (12)	$C_7-C_3-C_4$	107.65 (17)
$Zn-N_1-C_6$	126.05 (12)	$C_3-C_4-C_8$	107.14 (17)
$C_5-N_1-C_6$	106.35 (15)	$N_1-C_5-C_1$	109.69 (16)
$Zn-N_2-C_7$	126.38 (12)	$N_1-C_5-C_\beta'$	125.73 (17)
$Zn-N_2-C_8$	126.81 (12)	$C_1-C_5-C_\beta'$	124.36 (17)
$C_7-N_2-C_8$	106.78 (14)	$N_1-C_6-C_2$	109.45 (16)
$N_2-C_8-C_4$	109.12 (16)	$N_1-C_6-C_\alpha$	125.75 (16)
$N_2-C_8-C_\beta$	125.88 (16)	$C_2-C_6-C_\alpha$	124.71 (17)
$C_4-C_8-C_\beta$	124.99 (17)	$N_2-C_7-C_3$	109.30 (16)
$C_6-C_\alpha-C_7$	124.71 (17)	$N_2-C_7-C_\alpha$	126.30 (16)
$C_6-C_\alpha-C_{\alpha1}$	118.38 (16)	$C_3-C_7-C_\alpha$	124.39 (17)
$C_7-C_\alpha-C_{\alpha1}$	116.83 (16)	$C_8-C_\beta-C_5'$	124.87 (17)
$C_{\alpha2}-C_{\alpha1}-C_{\alpha6}$	118.25 (18)	$C_8-C_\beta-C_{\beta1}$	118.00 (16)
$C_\alpha-C_{\alpha1}-C_{\alpha2}$	121.37 (17)	$C_5'-C_\beta-C_{\beta1}$	117.13 (17)
$C_\alpha-C_{\alpha1}-C_{\alpha6}$	120.37 (17)	$C_\beta-C_{\beta1}-C_{\beta2}$	121.05 (19)
$C_{\alpha1}-C_{\alpha2}-C_{\alpha3}$	120.86 (19)	$C_\beta-C_{\beta1}-C_{\beta6}$	120.26 (19)
$C_{\alpha2}-C_{\alpha3}-C_{\alpha4}$	120.00 (20)	$C_{\beta2}-C_{\beta1}-C_{\beta6}$	118.69 (20)
$C_{\alpha3}-C_{\alpha4}-C_{\alpha5}$	119.62 (20)	$C_{\beta1}-C_{\beta2}-C_{\beta3}$	119.76 (24)
$C_{\alpha4}-C_{\alpha5}-C_{\alpha6}$	120.73 (21)	$C_{\beta2}-C_{\beta3}-C_{\beta4}$	120.98 (25)
$C_{\alpha5}-C_{\alpha6}-C_{\alpha1}$	120.53 (20)	$C_{\beta3}-C_{\beta4}-C_{\beta5}$	119.52 (22)
$C_{\beta4}-C_{\beta5}-C_{\beta6}$	120.47 (27)	$C_{\beta5}-C_{\beta6}-C_{\beta1}$	120.57 (25)

Figures 1 and 2 present overall perspective views of the two four-coordinate molecules. Individual values of bond distances in the coordination groups and porphinato cores are presented in Figures 3 and 4. Values of individual bond angles are given in Tables IV and V. We briefly consider the stereochemistry of these four-coordinate species individually.

The two independent Ag–N bond distances are 2.101 (3) and 2.082 (3) Å; the two bonds are different at the 5σ level. The average Ag–N bond distance is 2.092 Å. This distance is at the very short end of the range of Ag(II)–N distances reported.[15] This compression of the Ag–N complexing bonds is typically observed[16]

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(14) Programs used in this study included local modifications of Main, Hull, Lessinger, Germain, Declerq, and Woolfsons's MULTAN78, Jacobson's ALLS, Zalkin's FORDAP, Busing and Levy's ORFFE and ORFLS, and Johnson's ORTEP2. Atomic form factors were from: Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321–323. Real and imaginary corrections for anomalous dispersion in the form factor of the silver atom were from: Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17–23. That for zinc was from: Cromer, D. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1. Scattering factors for hydrogen were from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(15) The range of values in square-planar and tetragonal six-coordinate species involving pyridine or macrocyclic ligands is ~2.12–2.20 Å. Mertes, K. B. *Inorg. Chem.* **1978**, *17*, 49–52. Ito, T.; Ito, H.; Toriumi, K. *Chem. Lett.* **1981**, 1101–1104. Bushnell, G. W.; Khan, M. A. *Can. J. Chem.* **1972**, *50*, 315–323. Drew, M. G. B.; Matthews, R. W.; Walton, R. A. *J. Chem. Soc. A* **1970**, 1405–1410; **1971**, 2959–2962. Po, H. N. *Coord. Chem. Rev.* **1976**, *20*, 171–195.

Table VI. Dihedral Angles (deg) between Selected Least-Squares Planes

planes[a]	ZnTPP	AgTPP	H_2TPP
PYR1-PYR2	6.5	7.5	7.4
PYR1-PHEN1	63.2	63.3	66.3
PYR1-PHEN2	68.2	68.7	68.4
PYR1-CORE	5.5	6.3	6.5
PYR2-PHEN1	61.6	60.8	63.4
PYR2-PHEN2	62.0	61.7	61.7
PYR2-CORE	1.7	1.7	1.5
PHEN1-PHEN2	78.0	79.3	81.6
PHEN1-CORE	60.6	60.1	62.6
PHEN2-CORE	63.4	63.8	63.8

[a] PYR1 is pyrrole 1 (N1), PYR2 is pyrrole 2 (N2), PHEN1 is bonded to C_α, PHEN2 is bonded to C_β, and CORE is the 24-atom core.

in porphinato derivatives with large metal ions and is the consequence of the limited radial expansion possible in the macrocycle. A second expected stereochemical feature appropriate for accommodating a large metal ion is realized only in part. As noted previously,[6,16] the core conformation most appropriate for a radially expanded core is one of D_{4h} symmetry. As can be seen in Figure 3, the AgTPP core has a significant deviation from planarity that is not observed in, for example, the cores of $[Sn(TPP)Cl_2]$[6] or $[Sn(OEP)Cl_2]$,[17] which are equally expanded in the radial direction. The fact that the longer Ag–N bond extends to a pyrrole ring that was substantially tilted from the mean plane gave rise to the notion that the bond distances were affected by asymmetric crystal-packing constraints. However, it should be noted that tilting of the pyrrole ring itself can only lead to a ~0.006-Å increase in the Ag–N distance. Finally it remained uncertain whether the crystal-packing effects led to modulation in both bonds or only one. The subsequent determination of structure for ZnTPP gives some insight into this last question as well as provides further confirmation of the effects of crystal packing.

The two independent Zn–N distances are 2.0454 (15) and 2.0292 (15) Å. The average value of the two unique Zn–N bond distances is 2.037 Å. Although this distance is relatively short[18] for Zn–N bond distances, it is virtually identical with the values found in two solvated four-coordinate zinc(II) porphyrinates: 2.036 Å in $ZnTPP{\cdot}2C_7H_8$[7] and 2.039 Å in Zn(α-NO_2-OEP).[19] Thus despite the significant difference (7.6σ) in the two distances in triclinic ZnTPP, the average value is not materially distinguishable from those of other zinc porphyrinates. We conclude that for ZnTPP (and probaly AgTPP as well) the average M–N distance represents the best value for the unconstrained molecule.

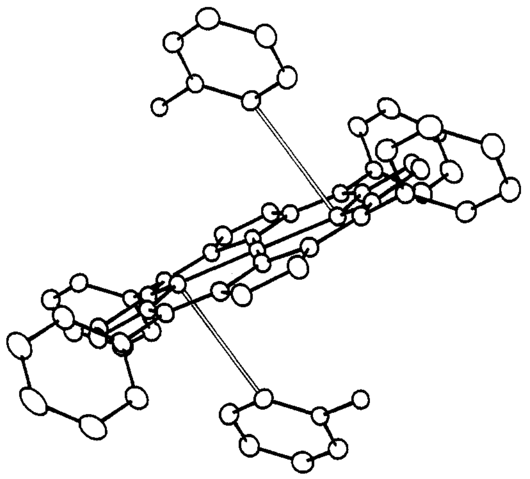

Figure 5. Illustration showing the nonbonded interaction between N_1 and the adjacent phenyl group.

The unusual conformational features found for AgTPP are also retained in crystalline ZnTPP as can be seen from an examination of Figure 4. Again the longer Zn–N bond is found to the pyrrole ring that is more tilted from the mean plane of the core. Most remarkably, these tilted rings are the same as the tilted ring in triclinic H_2TPP; i.e., all rings have the same orientation with respect to a common crystallographic axis set. The conformational similarity of the three molecules is shown quantitatively in Table VI, where the dihedral angles between a number of different least-squares planes are reported. In trinclinic H_2TPP, the tilted pyrrole rings are the pyrroles bearing the N–H substituent. In this case, the tilt of the pyrrole rings serves to increase the transannular H···H distance. Hence, in triclinic H_2TPP the conformation of the macrocycle has a stereochemical basis not pertintent in the remaining two crystalline species. As discussed below, the tilted pyrrole ring appears to result from a particularly tight intermolecular contact. The most plausible explanation for the occurrence of this series of isomorphous crystalline compounds is that it is the result of a particularly efficient and stable packing arrangement for four-coordinate tetraphenylporphyrin derivatives with expanded cores. This arrangement leads to an asymmetric crystalline environment, which yields the dissimilar Ct···N distances and pyrrole ring tilts that ideally fit the requirements of H_2TPP. The other species, although not so ideally fit as H_2TPP for the packing arrangement, still find it a thermodynamically favorable lattice.

Evidence for this hypothesis is somewhat indirect but nonetheless credible. First is the existence of a complete series of solid solutions of H_2TPP and AgTPP.[9] Second is the observation of a number of isomorphous series of porphyrin compounds. The existences of these series all appear to be related to efficient packing of molecules with similar external shapes. We briefly note six series with the largest number of members. One is the well-known tetragonal series of four-coordinate M(TPP)'s,[20] a second series is a group of M(OEP)X complexes,[21] and a third is a series of Fe(TPP)X species.[22] Three additional isomorphous series are the most interesting in this regard since they are able to accommodate a variety of different axial ligands, solvent molecules, and unusual stoichiometries as a consequence, at least in part, of solid-state lattice effects. The first is the tetragonal set of complexes $[M(TPP)X_n]$,[23] where $4/m$ symmetry is required and where $[Sn(TPP)Cl_2]$ is the prototypical ordered example. Most of these species have $n = 1$ and consequently have disordered structures in the solid. The second series has general form $[M(TPP)L_2]$.[24] Two members of this series ($[FeTPP(THF)_2]$ and

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(17) Cullen, D. L.; Meyers, E. F., Jr. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 2507–2515.

(18) A discussion of observed Zn–N bond distances is given in ref 7.

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(20) Members of the series are as follows. (a) CuTPP and PdTPP: Fleischer, E. B.; Miller, C. K.; Webb, L. E. *J. Am. Chem. Soc.* **1964**, *86*, 2342–2347. (b) FeTPP: Collman, J. P.; Hoard, J. L.; Kin, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676–2681. (c) CoTPP: Madura, P.; Scheidt, W. R. *Inorg. Chem.* **1976**, *15*, 3182–3184. (d) NiTPP: Hoard, J. L.; Sayler, A. A., to be submitted for publication.

(21) [V(OEP)O]: Molinaro, F. S.; Ibers, J. A. *Inorg. Chem.* **1976**, *15*, 2278–2283. [Ti(OEP)O] and $[Ti(OEP)O_2]$: Guilard, R.; Latour, J.-M.; Lecomte, C.; Marchon, J.-C.; Protas, J.; Ripoll, D. *Inorg. Chem.* **1978**, *17*, 1228–1237.

(22) (a) [Fe(TPP)Br]: Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 2655–2660. (b) [Fe(TPP)I]: Hatano, K.; Scheidt, W. R. *Inorg. Chem.* **1979**, *18*, 877–879. (c) $[Fe(TPP)NO_3]$: Phillippi, M. A.; Baenziger, N.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3904–3911.

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Table VII. Averaged Parameters in H_2TPP and Two Related Metalloporphyrins[a]

parameter	H_2TPP	AgTPP	ZnTPP
A. Pyrrole Rings Carrying N–H Bonds in the Porphyrin			
Ct···N	2.099	2.101	2.045
$N-C_a$	1.374	1.365	1.376
C_a-C_b	1.428	1.445	1.438
C_b-C_b	1.355	1.365	1.351
C_a-N-C_a	109.2	108.6	106.4
$N-C_a-C_b$	107.3	108.6	109.6
$C_a-C_b-C_b$	108.1	107.1	107.3
$N-C_a-C_m$	126.0	126.4	125.7
B. Pyrrole Rings Lacking N–H Bonds in the Porphyrin			
Ct···N	2.026	2.082	2.029
$N-C_a$	1.364	1.368	1.376
C_a-C_b	1.455	1.447	1.442
C_b-C_b	1.347	1.350	1.346
C_a-N-C_a	106.2	108.7	106.8
$N-C_a-C_b$	110.3	108.2	109.2
$C_a-C_b-C_b$	106.8	107.5	107.4
$N-C_a-C_m$	126.3	126.5	126.1

[a] Distances in angstroms, angles in degrees.

$[ZnTPP(THF)_2]$) have little or no stability outside the crystal lattice; their existence is directly attributable to solid-state effects. The final series has general formula $[M(TPP)(py)X]\cdot$solvent;[25] the isolation of these difficult to prepare, mixed-ligand iron(III) species of the series is directly attributable to lattice stabilization factors.

A careful examination of nonbonded packing interactions reveals one especially interesting contact between the tilted pyrrole ring and a phenyl ring of an adjacent molecule (related by ±*c* translations). The observed N1···Cα2 separation is 3.37 Å in ZnTPP, 3.39 Å in AgTPP, and 3.39 Å in H_2TPP; the separation would be ~0.15 Å less if the pyrrole ring had not tilted. Finally, the direction of the nonbonded contact is such that it is reasonable to imagine that it also leads to a "pushing" of the pyrrole ring away from the center of the molecule. The directional nature of this nonbonded contact is illustrated in Figure 5, and a complete cell-packing diagram is available as Figure 1S of the supplementary material. This localized repulsive portion of the lattice interactions is necessarily counterbalanced elsewhere in the solid-state structure. A complete examination of intermolecular contacts shows no others as imporatant as these.

An additional comparison can be made with the aid of Table VII, which displays averaged parameters for the two crystallographically unique rings in H_2TPP, AgTPP, and ZnTPP. The parameters for the two types of rings, A and B, in the free base are comparable to those observed in a number of other examples.[26] The two pyrrole rings in either AgTPP or ZnTPP are seen to be internally equivalent; however, the rings in AgTPP are most like ring A of H_2TPP and the rings in ZnTPP are most like ring B. These differences in the internal geometry of the rings are compatible with the differences in the radial expansion of the two cores, and their expectation has been discussed previously.[6,16]

Summary

The determinations of structure for AgTPP and ZnTPP have demonstrated that crystal-packing effects can have modest (~ 0.01–0.02 Å) effects on bond distances in the coordination group while not substantially modifying bond parameters of the macrocycle itself. On the basis of comparisons with other zinc(II) porphyrinates, the average M–N bond length represents the value most appropriate for the *unconstrained* molecule. Hence, we suggest that the average value of the M–N bond lengths in metalloporphyrin complexes best represents the objective significance of the experimental data.

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Registry No. AgTPP, 14641-64-6; ZnTPP, 14074-80-7.

Supplementary Material Available: Table IS, anisotropic temperature factors for AgTPP; Table IIS, anisotropic temperature factors for ZnTPP; Table IIIS, fixed hydrogen atom coordinates for ZnTPP; Figure 1S, a cell-packing diagram for ZnTPP; listings (×10) of observed and calculated structure amplitudes for ZnTPP and AgTPP (44 pages). Ordering information is given on any current masthead page.

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