will be dominated by the 6-membered ring pair awaits confirmation.

There still remain some assignments in the literature that require modification. The absolute configuration of the Co(en)(cyclam)$^{3+}$ enantiomer presented by Lai and Poon[4] (Figure 2) should be (*SSSS*), and the chirality defined by the 5-membered chelate rings in isomer I (Figure 3 of ref 6) should be Λ.

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Registry No. [Cr(ox)(cyclam)]ClO$_4$, 93110-52-2; *cis*-[CrCl$_2$(cyclam)]ClO$_4$, 27435-97-8; (−)-[Cr(ox)(cyclam)]ClO$_4$, 93219-75-1; (−)-*cis*-[CrCl$_2$(cyclam)]ClO$_4$, 93219-77-3; (+)-*cis*-CrCl(cyclam)(OH$_2$)$^{2+}$, 93220-77-0; (+)-*cis*-Cr(cyclam)(OH$_2$)$_2^{3+}$, 93219-78-4; (−)-*cis*-Cr(OH)$_2$(cyclam)$^+$, 93110-53-3.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic temperature factors, coordinates of hydrogen atoms, and calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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X-ray Crystal and Molecular Structures of Related Octahedral Magnesium Tetraphenylporphyrin Complexes

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The crystal and molecular structures are reported for the magnesium tetraphenylporphyrin complexes, MgTPP(1-methylimidazole)$_2$ MgTPP(4-picoline)$_2$, and MgTPP(piperidine)$_2$. MgTPP(1-methylimidazole)$_2$ crystallizes in the tetragonal space group $P4_2/n$ with 4 molecules per unit cell of dimensions $a = 20.764$ (5) Å, $c = 9.659$ (3) Å. MgTPP(4-picoline)$_2$ and MgTPP(piperidine)$_2$ are isostructural. These two compounds crystallize in the triclinic space group $P\bar{1}$ with 1 molecule in unit cells of dimensions $a = 10.146$ (2), 9.944 (3) Å, $b = 11.210$ (2), 11.436 (3) Å, $c = 11.643$ (3), 11.914 (3) Å, $\alpha = 65.63$ (2), 101.78 (2)°, $\beta = 76.32$, 104.59 (2)°, and $\gamma = 67.42$ (1), 115.60 (2)°, respectively. As observed for related complexes the binding in the axial, octahedral positions is weak. The Mg–N axial bond distances are long, varying from 2.297 (8) Å (1-methylimidazole) to 2.386 (2) and 2.419 (3) Å (4-picoline and piperidine, respectively). Corresponding values for isostructural low-spin Fe(II) 1-methylimidazole and piperidine complexes are significantly shorter, indicating that an absence of t_{2g} electrons for Mg(II) limits the binding of axial ligands to porphyrin systems to a significant extent. The stronger binding of 1-methylimidazole, compared with piperidine, for both Mg(II) and Fe(II) complexes indicates that an electronic effect as well as a smaller steric interaction favors the axial coordination of this ligand.

Introduction

The crystal and molecular structures of metalloporphyrins have been of considerable interest because of their relevance to the structure and function of biological compounds.[1] The majority of these metalloporphyrin structures consist of elements in the first-row transition series, particularly iron.[2] However, the structures of magnesium porphyrins are also of interest because of their relationship to chlorophyll, as highlighted in a recent report.[3]

Most X-ray structural studies of magnesium macrocyclic tetrapyrrole complexes are those of five-coordinated entities. In these cases the magnesium atom is displaced out of the mean plane of the four chelating nitrogen atoms toward the axial ligands, by values ranging from 0.27 to 0.496 Å.[3-9] Equilibrium studies of Mg porphyrins with nitrogenous bases also indicate that five-coordination is the preferred coordination state of Mg. However, under suitable conditions, six-coordination can be realized[10-13] as shown in particular by X-ray structural results.

Although the first attempt to determine the crystal structure of a six-coordinated complex, (Mg etioporphyrin)(py)$_2$ (py = pyridine), was limited by a high degree of disorder, it did reveal the existence of long Mg–N axial ligand bonds.[14-16] More recently, a complete structure determination of six-coordinated MgOEP(py)$_2$ (OEP = octaethylporphyrin) confirmed this result.[17] In this paper, we report details of the crystal and molecular structures of three related six-coordinated MgTPP (TPP = tetraphenylporphyrin) complexes, MgTPP(1-MeIm)$_2$

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Table I. Crystal Data

	MgTPP-(1-MeIm)$_2$	MgTPP-(4-pic)$_2$	MgTPP-(pip)$_2$
empirical formula	$C_{52}H_{40}N_8Mg$	$C_{56}H_{42}N_6Mg$	$C_{54}H_{50}N_6Mg$
mol wt	801.3	823.3	806.9
cryst syst	tetragonal	triclinic	triclinic
space group	$P4_2/n$	$P\bar{1}$	$P\bar{1}$
cell dimens			
a, Å	20.764 (4)	10.146 (2)	9.944 (3)
b, Å		11.210 (2)	11.463 (3)
c, Å	9.659 (3)	11.643 (3)	11.914 (3)
α, deg		65.63 (2)	101.78 (2)
β, deg		76.32 (2)	104.59 (2)
γ, deg		67.42 (1)	115.60 (2)
V, Å^3	4164.3	1108.9	1103.7
D_{measd}, g cm^{-3}	1.28	1.25	1.23
D_{calcd}, g cm^{-3}	1.28	1.23	1.21
Z	4	1	1
$F(000)$	1679.6	431.91	425.91
μ, cm^{-1}	0.85	0.81	0.79
cryst dimens, mm	0.22 × 0.2 × 0.2	0.43 × 0.19 × 0.21	0.56 × 0.75 × 0.28
mosaicity	0.31	0.25	0.22
radiation	Mo Kα	Mo Kα	Mo Kα
2θ range	3–45	3–50	3–50
total no. of indep reflcns	2741	3927	3907
no. of reflcns with $I_O \geqslant 3\sigma(I_O)$	1132	2059	2144
R	0.074	0.0449	0.0591
R_W	0.057	0.045	0.0579
g	−0.00	−0.000 109	−0.000 262

(1-MeIm = 1-methylimidazole), MgTPP(4-pic)$_2$ (pic = picoline), and MgTPP(pip)$_2$ (pip = piperidine). Two of these structures, MgTPP(1-MeIm)$_2$ and MgTPP (pip)$_2$, are isomorphorous with those reported for the low-spin iron(II) analogues,[18,19] while MgTPP(4-pic)$_2$ and MgTPP(pip)$_2$ are isostructural with each other.

From these results a number of useful comparisons can be made, in particular the bonding characteristics of a transition-metal ion (Fe^{2+}) with those of a non-transition-metal one (Mg^{2+}). In addition, the effect of the aromatic character of an axial ligand can be assessed by comparing the structure of the 1-methylimidazole and 4-picoline complexes with that of the piperidine complex.

Experimental Section

(TPP)H_2 was prepared by the condensation of pyrrole and benzaldehyde[20] and purified by a procedure adapted from Barnett et al.[21] Mg(II) was inserted into (TPP)H_2 by using the dimethylformamide method.[22] Shiny, red-purple hexagonal-shaped crystals of MgTPP(1-MeIm)$_2$ were obtained by heating the MgTPP complex in pure 1-methylimidazole and then crystallizing in an acetone–1-methylimidazole solution. The crystals were assigned to the tetragonal system after examination by precession photography, using Mo Kα radiation. A similar technique was used to obtain MgTPP(pip)$_2$ and MgTPP(4-pic)$_2$. Long needlelike crystals were obtained from a solution of chloroform and the nitrogenous ligand.

The crystals chosen for data collection were mounted on a computer-controlled Nicolet R3m diffractometer. The cell constants and orientation matrices were determined from a least-squares fit of at least 20 reflections. Important crystal data are summarized in Table I.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2) of MgTPP(1-MeIm)$_2$

atom	x	y	z	10^3U^a
Mg	5000	0	0	31 (1)*
N(1)	4609 (3)	908 (3)	359 (7)	34 (3)*
N(2)	4100 (3)	−332 (3)	−603 (6)	28 (3)*
N(3)	5246 (4)	299 (4)	−2228 (8)	47 (3)*
N(4)	5642 (5)	396 (5)	−4333 (9)	79 (5)*
C(1)	4958 (4)	1449 (4)	628 (8)	33 (2)
C(2)	4528 (4)	2001 (4)	576 (8)	38 (2)
C(3)	3937 (4)	1770 (4)	263 (8)	39 (2)
C(4)	3989 (3)	1085 (3)	114 (9)	25 (2)
C(5)	3485 (4)	674 (4)	−308 (8)	32 (2)
C(6)	3545 (4)	20 (4)	−690 (8)	29 (2)
C(7)	3043 (4)	−392 (4)	−1178 (7)	33 (2)
C(8)	3281 (4)	−990 (4)	−1383 (7)	31 (2)
C(9)	6043 (4)	951 (4)	982 (8)	30 (2)
C(10)	5615 (4)	1478 (4)	957 (8)	28 (2)
C(30)	5912 (4)	2128 (4)	1235 (8)	30 (2)
C(31)	5740 (4)	2494 (4)	2374 (8)	37 (2)
C(32)	6038 (4)	3086 (4)	2635 (10)	50 (3)
C(33)	6510 (4)	3297 (4)	1763 (9)	49 (3)
C(34)	6690 (4)	2954 (4)	618 (9)	56 (3)
C(35)	6379 (3)	2364 (4)	347 (9)	41 (2)
C(41)	5630 (5)	22 (5)	−3129 (11)	67 (5)*
C(42)	5273 (5)	886 (5)	−4180 (11)	68 (5)*
C(43)	5036 (5)	840 (5)	−2911 (11)	63 (5)*
C(44)	6024 (6)	266 (6)	−5507 (13)	60 (5)
C(44′)	5300 (13)	1202 (12)	−5306 (28)	50 (10)
C(50)	2820 (4)	951 (3)	−298 (8)	29 (2)
C(51)	2532 (4)	1116 (4)	951 (9)	56 (3)
C(52)	1918 (4)	1400 (4)	970 (10)	67 (3)
C(53)	1600 (4)	1497 (4)	−239 (10)	59 (3)
C(54)	1861 (4)	1317 (4)	−1455 (9)	56 (3)
C(55)	2481 (4)	1046 (4)	−1498 (9)	45 (3)

[a] Asterisks denote equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Data were collected at room temperature with use of graphite-monochromated Mo Kα radiation and the θ–2θ scan technique (3° < 2θ < 45° (MgTPP(1-MeIm)$_2$), 50° (MgTPP(4-pic)$_2$), 50° (MgTPP(pip)$_2$)). Crystal stabilities were monitored by recording three standard reflections every 100 reflections, and no significant variations were observed. Intensities were corrected for Lorentz–polarization effects, and empirical absorption corrections were applied based on ψ-scan data. Only those reflections for which $I_o \geqslant 3\sigma(I_o)$ were used in the subsequent structural analyses.

The structure of MgTPP(1-MeIm)$_2$ was solved by direct methods, using the program SOLV, which revealed the positions of all the non-hydrogen atoms. For both MgTPP(4-pic)$_2$ and MgTPP(pip)$_2$, crystal symmetry defined the position of the Mg atom (0, 0, 0 in each case) and the remaining non-hydrogen atoms were located from difference Fourier maps. The structures were refined by blocked-cascade least-squares refinement, and hydrogen atoms were included at calculated positions (C–H = 0.96 Å) with thermal parameters equal to 1.2U of their carrier atoms. All the programs used for data reduction and structure solution are included in the SHELXTL (version 3.0) package.[23] Mg scattering factors were obtained from Cromer and Mann[24] and the anomalous dispersion corrections from Cromer and Liberman.[25]

MgTPP(1-MeIm)$_2$ was refined to $R = 0.074$ and $R_w = 0.057$ with all atoms isotropic except the Mg, the coordinated nitrogen atoms, and the 1-MeIm group. A final difference map showed no features greater than ±0.3 e Å^{-3}. The 1-MeIm group shows twofold disorder about the Mg–N(3) axis; thus, the 1-Me group was found to have site occupancy of 0.68 (C(44)) and 0.32 (C(44′) in the two related orientations.

MgTPP(4-pic)$_2$ was refined with all the non-hydrogen atoms anisotropic and converged with $R = 0.0499$ and $R_w = 0.045$, and the final difference map showed no features greater than ±0.26 e Å^{-3}.

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Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2$) of MgTPP(4-pic)$_2$

atom	x	y	z	10^3U^a
Mg	0	0	0	46 (1)*
N(1)	1253 (3)	1026 (3)	116 (2)	44 (1)*
N(2)	−1175 (3)	119 (2)	1686 (2)	43 (1)*
N(5)	−1633 (3)	2233 (3)	−1000 (2)	55 (2)*
C(1)	−2329 (3)	−1413 (3)	760 (3)	44 (2)*
C(2)	−2763 (4)	−2306 (3)	416 (3)	53 (2)*
C(3)	1935 (3)	2465 (3)	631 (3)	53 (2)*
C(4)	976 (3)	1673 (3)	973 (3)	44 (2)*
C(5)	−85 (3)	1588 (3)	1999 (3)	43 (2)*
C(6)	−1084 (3)	880 (3)	2324 (3)	41 (2)*
C(7)	−2226 (3)	893 (3)	3343 (3)	47 (2)*
C(8)	−2989 (3)	166 (3)	3305 (3)	49 (2)*
C(9)	−2342 (3)	−319 (3)	2262 (3)	41 (2)*
C(10)	−2860 (3)	−1062 (3)	1850 (3)	43 (2)*
C(21)	−4067 (3)	−1556 (3)	2663 (3)	45 (2)*
C(22)	−3859 (4)	−2576 (3)	3852 (3)	56 (2)*
C(23)	−4945 (4)	−3111 (4)	4570 (4)	77 (2)*
C(24)	−6259 (4)	−2595 (4)	4133 (4)	89 (3)*
C(25)	−6507 (4)	−1561 (4)	2986 (4)	85 (3)*
C(26)	−5417 (3)	−1044 (4)	2243 (3)	66 (2)*
C(31)	−250 (3)	2410 (3)	2802 (3)	43 (2)*
C(32)	352 (4)	1803 (4)	3937 (3)	59 (2)*
C(33)	117 (4)	2562 (4)	4699 (3)	67 (2)*
C(34)	−697 (4)	3925 (4)	4323 (3)	62 (2)*
C(35)	−1287 (4)	4546 (4)	3192 (4)	70 (2)*
C(36)	−1062 (4)	3790 (3)	2435 (3)	64 (2)*
C(51)	−3038 (4)	2575 (4)	−669 (4)	69 (2)*
C(52)	−3969 (4)	3910 (4)	−1065 (4)	78 (2)*
C(53)	−3473 (4)	4997 (4)	−1830 (3)	66 (2)*
C(54)	−2045 (5)	4649 (4)	−2181 (4)	85 (2)*
C(55)	−1181 (4)	3293 (4)	−1765 (4)	79 (2)*
C(56)	−4444 (5)	6475 (4)	−2246 (4)	103 (3)*

[a] Asterisks denote equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2$) of MgTPP(pip)$_2$

atom	x	y	z	10^3U^a
Mg	0	0	0	49 (1)*
N(1)	−1044 (3)	159 (3)	−1661 (2)	42 (2)*
N(2)	2251 (3)	1010 (3)	−88 (2)	42 (2)*
N(5)	426 (4)	2226 (3)	1126 (3)	58 (2)*
C(1)	2646 (4)	249 (3)	2226 (3)	43 (1)
C(2)	−2824 (4)	287 (4)	−3220 (3)	51 (1)
C(3)	−1356 (4)	999 (4)	−3238 (3)	48 (1)
C(4)	−225 (4)	929 (3)	−2263 (3)	42 (1)
C(5)	1464 (4)	1596 (3)	−1942 (3)	42 (1)
C(6)	2606 (4)	1645 (3)	−927 (3)	40 (1)
C(7)	4337 (4)	2410 (4)	−573 (3)	48 (1)
C(8)	5003 (4)	2240 (3)	472 (3)	48 (1)
C(9)	3696 (4)	1371 (3)	783 (3)	41 (1)
C(10)	3897 (4)	1009 (3)	1855 (3)	40 (1)
C(21)	5582 (4)	1501 (4)	2695 (3)	43 (2)*
C(22)	6503 (4)	989 (4)	2330 (4)	57 (2)*
C(23)	8075 (5)	1490 (4)	3124 (4)	66 (3)*
C(24)	8762 (5)	2523 (4)	4257 (4)	67 (3)*
C(25)	7857 (5)	3029 (4)	4625 (4)	67 (3)*
C(26)	6278 (4)	2507 (4)	3865 (3)	56 (2)*
C(31)	2102 (4)	2380 (4)	−2737 (3)	45 (2)*
C(32)	2077 (5)	1727 (4)	−3855 (3)	59 (2)*
C(33)	2658 (5)	2467 (4)	−4582 (4)	67 (3)*
C(34)	3248 (4)	3856 (4)	−4212 (4)	63 (2)*
C(35)	3284 (5)	4522 (4)	−3101 (4)	78 (3)*
C(36)	2722 (5)	3801 (4)	−2370 (4)	69 (3)*
C(51)	−613 (5)	2688 (4)	490 (4)	74 (3)*
C(52)	−427 (5)	4004 (4)	1297 (4)	77 (3)*
C(53)	1290 (6)	5168 (5)	1848 (4)	86 (3)*
C(54)	2353 (6)	4714 (5)	2561 (5)	102 (3)*
C(55)	2108 (5)	3378 (4)	1737 (5)	89 (3)*

[a] Asterisk denote equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Lengths (Å) of MgTPP(1-MeIm)$_2$

Mg–N(1)	2.082 (6)	C(2)–C(3)	1.352 (11)
Mg–N(2)	2.074 (6)	C(3)–C(4)	1.433 (10)
Mg–N(3)	2.297 (8)	C(4)–C(5)	1.496 (10)
N(1)–C(1)	1.361 (10)	C(5)–C(6)	1.412 (11)
N(1)–C(4)	1.360 (9)	C(5)–C(50)	1.496 (10)
N(2)–N(6)	1.368 (10)	C(6)–C(7)	1.429 (11)
N(2)–C(9a)	1.370 (10)	C(7)–C(8)	1.352 (10)
N(3)–C(43)	1.373 (14)	C(8)–C(9a)	1.460 (10)
N(3)–C(41)	1.314 (13)	C(9a)–C(10a)	1.409 (11)
N(4)–C(41)	1.399 (14)	C(10)–C(11)	1.403 (10)
N(4)–C(42)	1.282 (15)	C(42)–C(43)	1.324 (15)
N(4)–C(44)	1.410 (16)	C(42)–C(44′)	1.272 (28)
C(1)–C(2)	1.454 (11)		

Table VI. Selected Angles (deg) of MgTPP(1-MeIm)$_2$

N(1)-Mg-N(2)	89.8 (2)	C(6)–C(7)–C(8)	109.4 (7)
N(1)-Mg-N(3)	89.9 (3)	C(7)–C(8)–C(9a)	105.1 (7)
N(2)-Mg-N(3)	91.5 (3)	C(1)-N(1)-C(4)	108.2 (6)
Mg-N(1)–C(1)	124.9 (5)	C(6)-N(2)-C(9a)	107.6 (6)
Mg-N(1)-C(4)	125.8 (5)	C(2)–C(1)–C(10)	124.8 (7)
Mg-N(2)–C(6)	126.8 (5)	C(3)–C(4)–C(5)	125.0 (7)
Mg-N(2)–C(9a)	125.6 (5)	C(5)–C(6)–C(7)	126.7 (7)
N(1)-C(1)-C(2)	108.5 (6)	C(8)–C(9a)–C(10a)	124.6 (7)
N(1)–C(4)–C(3)	108.8 (6)	Mg-N(3)-C(41)	129.6 (7)
N(2)–C(6)–C(7)	108.4 (6)	Mg-N(3)–C(43)	126.9 (7)
N(2)-C(9a)–C(8)	109.4 (6)	N(3)–C(41)–N(4)	108.5 (9)
N(1)-C(1)–C(10)	126.6 (7)	N(3)–C(43)–C(42)	112.8 (9)
N(1)–C(4)–C(5)	126.1 (6)	N(4)–C(42)–C(43)	105.7 (10)
N(2)–C(6)–C(5)	124.9 (7)	N(4)–C(42)–C(44′)	106.5 (15)
N(2)–C(9a)–C(10a)	126.0 (7)	C(41)-N(4)–C(42)	109.6 (9)
C(4)–C(5)–C(6)	126.3 (7)	C(41)-N(3)–C(43)	103.4 (8)
C(1)–C(10)–C(9)	125.7 (7)	C(41)-N(4)–C(44)	124.8 (10)
C(1)–C(2)–C(3)	106.5 (7)	C(42)–N(4)–C(44)	125.6 (10)
C(2)–C(3)–C(4)	107.8 (7)	C(43)–C(42)–C(44′)	147.8 (16)

Table VII. Selected Bond Lengths (Å) of MgTPP(4-pic)$_2$

Mg–N(1)	2.072 (3)	C(5)–C(6)	1.409 (5)
Mg–N(2)	2.069 (2)	C(5)–C(31)	1.508 (6)
Mg–N(5)	2.386 (2)	C(6)–C(7)	1.450 (4)
N(1)–C(1a)	1.376 (4)	C(7)–C(8)	1.340 (6)
N(1)–C(4)	1.380 (5)	C(8)–C(9)	1.448 (5)
N(2)–C(6)	1.380 (5)	C(9)–C(10)	1.408 (6)
N(2)–C(9)	1.375 (4)	C(10)–C(1)	1.408 (5)
N(5)–C(51)	1.330 (5)	C(10)–C(21)	1.498 (4)
N(5)–C(55)	1.329 (5)	C(51)–C(52)	1.377 (5)
C(1a)–C(2a)	1.452 (6)	C(52)–C(53)	1.377 (6)
C(2a)–C(3)	1.342 (5)	C(53)–C(54)	1.355 (6)
C(3)–C(4)	1.444 (6)	C(53)–C(56)	1.503 (5)
C(4)–C(5)	1.404 (4)	C(54)–C(55)	1.373 (5)

Table VIII. Selected Angles (deg) of MgTPP(4-pic)$_2$

N(1)-Mg-N(2)	90.9 (1)	C(1a)-N(1)–C(4)	107.0 (3)
N(1)-Mg-N(5)	86.6 (1)	C(6)-N(2)-C(9)	106.6 (3)
N(2)-Mg-N(5)	86.3 (1)	C(2a)–C(1a)–C(10a)	125.8 (3)
Mg-N(1)-C(1a)	126.9 (3)	C(3)–C(4)–C(5)	125.7 (4)
Mg-N(1)-C(4)	125.1 (2)	C(5)–C(6)–C(7)	125.8 (3)
Mg-N(2)-C(6)	125.1 (2)	C(8)–C(9)–C(10)	125.8 (3)
Mg-N(2)-C(9)	127.4 (3)	C(1)-C(10)-C(21)	116.6 (4)
N(1)–C(1a)–C(2a)	108.9 (3)	C(9)-C(10)–C(21)	117.1 (3)
N(1)–C(4)–C(3)	109.1 (3)	C(4)–C(5)-C(31)	117.2 (3)
N(2)-C(6)-C(7)	109.0 (3)	C(6)–C(5)–C(31)	115.6 (3)
N(2)–C(9)–C(8)	109.4 (3)	Mg-N(5)-C(51)	122.7 (2)
N(1)–C(1a)–C(10a)	125.5 (2)	Mg-N(5)-C(55)	121.7 (2)
N(1)–C(4)–C(5)	125.3 (4)	N(5)–C(51)-C(52)	123.7 (4)
N(2)-C(9)-C(10)	124.8 (3)	N(5)-C(55)-C(54)	124.7 (4)
N(2)-C(6)–C(5)	125.5 (3)	C(51)-N(5)–C(55)	114.6 (3)
C(2a)-C(3)–C(4)	107.6 (4)	C(51)-C(52)–C(53)	120.8 (4)
C(1a)-C(2a)–C(3)	107.5 (3)	C(52)–C(53)-C(54)	115.5 (3)
C(6)–C(7)–C(8)	107.6 (4)	C(52)–C(53)–C(56)	122.5 (4)
C(7)–C(8)–C(9)	107.3 (3)	C(53)–C(54)–C(55)	120.7 (4)
C(4)–C(5)–C(6)	127.7 (2)	C(54)–C(53)–C(56)	122.0 (4)
C(9)-C(10)–C(1)	126.2 (3)		

For MgTPP(pip)$_2$ the Mg, coordinated nitrogen atoms, phenyl groups, and axial ligand were refined anisotropically to give $R = 0.0591$ and $R_w = 0.0579$ with no features greater than ±0.24 e $Å^{-3}$ in the final difference map.

In all three cases the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. Atomic coordinates and associated thermal

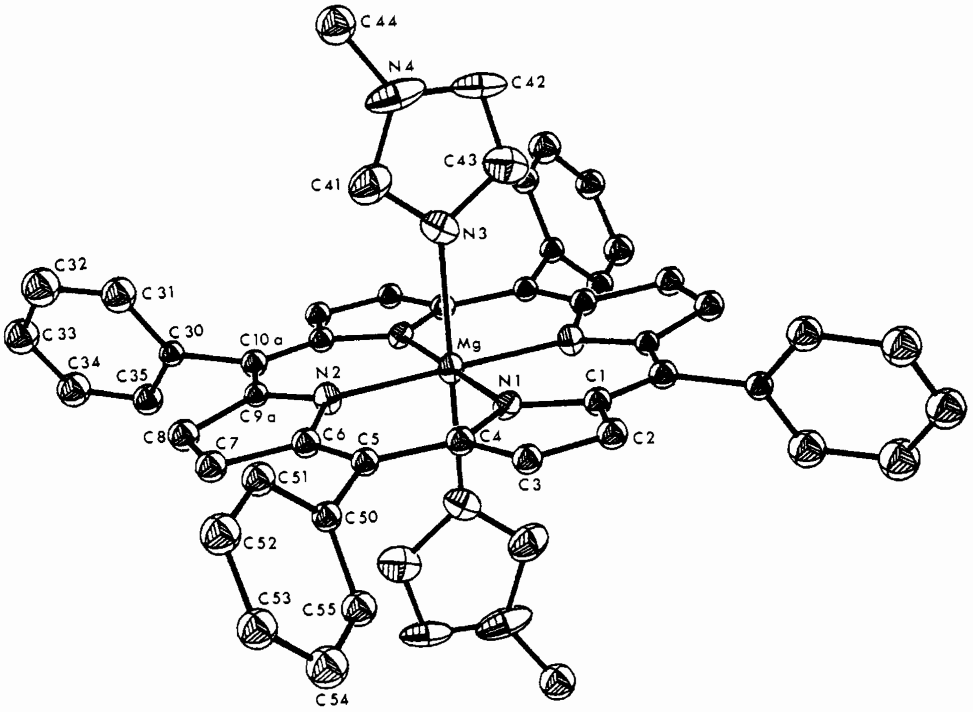

Figure 1. Computer-drawn structure of MgTPP(1-MeIm)$_2$ showing the numbering scheme (30% probability ellipsoids).

Table IX. Selected Bond Lengths (Å) of MgTPP(pip)$_2$

Mg-N(1)	2.074 (3)	C(5)-C(6)	1.408 (5)
Mg-N(2)	2.071 (3)	C(5)-C(31)	1.503 (6)
Mg-N(5)	2.419 (4)	C(6)-C(7)	1.445 (5)
N(1)-C(1a)	1.378 (5)	C(7)-C(8)	1.349 (6)
N(1)-C(4)	1.374 (5)	C(8)-C(9)	1.446 (5)
N(2)-C(6)	1.379 (5)	C(9)-C(10)	1.414 (6)
N(2)-C(9)	1.369 (4)	C(10)-C(1)	1.413 (5)
N(5)-C(51)	1.470 (7)	C(10)-C(21)	1.496 (5)
N(5)-C(55)	1.467 (4)	C(51)-C(52)	1.517 (7)
C(1a)-C(2)	1.447 (6)	C(52)-C(53)	1.494 (5)
C(2)-C(3)	1.338 (5)	C(53)-C(54)	1.521 (9)
C(3)-C(4)	1.441 (6)	C(54)-C(55)	1.581 (8)
C(4)-C(5)	1.414 (5)		

Table X. Selected Angles (deg) of MgTPP(pip)$_2$

N(1)-Mg-N(2)	90.1 (1)	C(9)-C(10)-C(1)	125.8 (3)
N(1)-Mg-N(5)	89.8 (1)	C(1a)-N(1)-C(4)	107.0 (3)
N(2)-Mg-N(5)	89.3 (1)	C(6)-N(2)-C(9)	106.8 (3)
Mg-N(1)-C(1a)	126.1 (3)	C(2)-C(1a)-C(10a)	125.6 (4)
Mg-N(1)-C(4)	125.8 (2)	C(3)-C(4)-C(5)	125.6 (4)
Mg-N(2)-C(6)	126.0 (2)	C(5)-C(6)-C(7)	125.3 (4)
Mg-N(2)-C(9)	126.4 (3)	C(8)-C(9)-C(10)	124.8 (3)
N(1)-C(1a)-C(2)	108.9 (3)	C(1)-C(10)-C(21)	116.6 (3)
N(1)-C(4)-C(3)	109.0 (3)	C(9)-C(10)-C(21)	117.6 (3)
N(2)-C(6)-C(7)	109.3 (3)	C(4)-C(5)-C(31)	116.4 (3)
N(2)-C(9)-C(8)	109.4 (3)	C(6)-C(5)-C(31)	117.1 (3)
N(1)-C(1a)-C(10a)	125.5 (4)	Mg-N(5)-C(51)	116.9 (2)
N(1)-C(4)-C(5)	125.4 (3)	Mg-N(5)-C(55)	116.9 (3)
N(2)-C(6)-C(5)	125.3 (3)	N(5)-C(51)-C(52)	114.3 (3)
N(2)-C(9)-C(10)	125.7 (3)	N(5)-C(55)-C(54)	115.0 (5)
C(1a)-C(2)-C(3)	107.3 (4)	C(51)-N(5)-C(55)	110.2 (4)
C(2)-C(3)-C(4)	107.9 (4)	C(51)-C(52)-C(53)	111.4 (5)
C(6)-C(7)-C(8)	107.1 (3)	C(52)-C(53)-C(54)	109.1 (4)
C(7)-C(8)-C(9)	107.4 (3)	C(53)-C(54)-C(55)	110.8 (4)
C(4)-C(5)-C(6)	126.5 (4)		

parameters are listed in Tables II–IV. Selected interatomic distances and angles are given in Tables V–X.

Description of the Structures

A perspective view of MgTPP(1-MeIm)$_2$ is shown in Figure 1, which also defines the numbering system used throughout this paper. The Mg atom lies at the centroid of the porphyrin core, which is slightly deviated from planarity. The perpendicular displacements of the atoms from this core are illustrated in the lower half of Figure 2. The pyrrole rings are planar to ±0.012 Å. They are inclined at 8.9 and 2.4° to the plane of the four chelating nitrogen atoms and mutually at 7.7°. Important averaged bond distances of the core are given in the upper half of the centrosymmetric molecule in Figure 2. The nonbonded distances between N(1) and N(3) and between N(3) and N(2) are 3.097 and 3.136 Å, respectively, which are slightly longer than the 3-Å van der Waals radii for nitrogen.[26] The averaged values for the bond angles are NMgN = 90.0 (2), MgNC$_a$ = 125.8 (8), C$_a$NC$_a$ = 107.9 (4), C$_a$C$_m$C$_a$ = 126.2 (5), NC$_a$C$_b$ = 108.8 (5), NC$_a$C$_m$ = 125.9 (7), and C$_a$C$_b$C$_b$ = 107.2 (18)°. The averaged values for the internal angles and bond lengths of the phenyl rings are 120 (1)° and 1.382 (20) Å, respectively. The dihedral angles between the mean plane of the porphyrin core and the mean planes of the phenyl groups are 62.3 and 69.3°. The dihedral angle between the mean planes of the imidazole ring and the

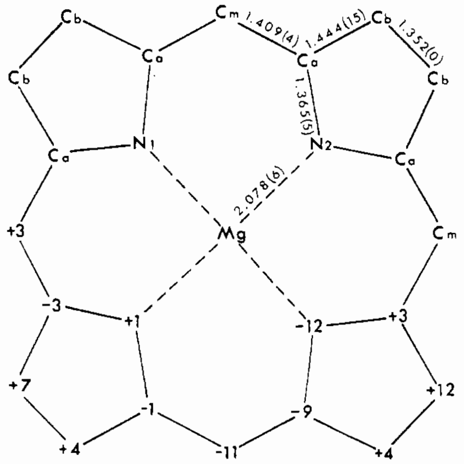

Figure 2. Diagram of the porphyrin core of MgTPP(1-MeIm)$_2$ displaying, on the upper half, the averaged bond lengths. On the lower half of the centrosymmetric diagram, atomic displacements in units of 0.01 Å from the mean porphyrin plane are given.

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(26) Weast, R. C.; Astle, M. J. "CRC Handbook of Chemistry and Physics", 60th ed.; Chemical Rubber Co.: Cleveland, OH, 1979–1980.

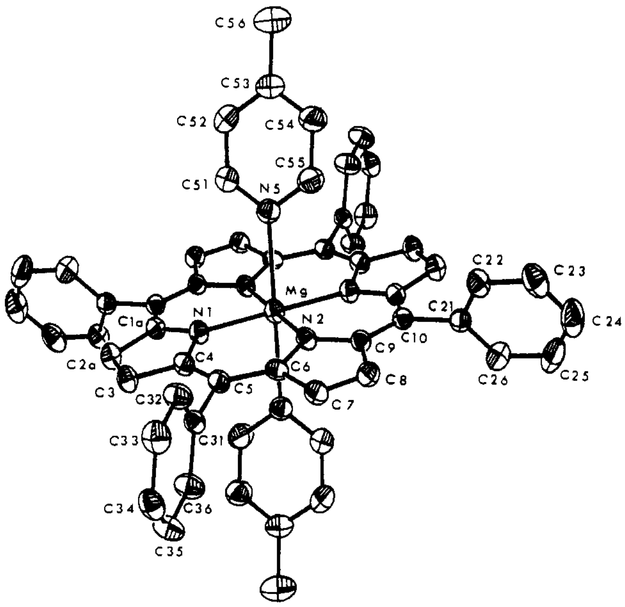

Figure 3. Computer-drawn structure of MgTPP(4-pic)$_2$ showing the numbering system (30% probability ellipsoids).

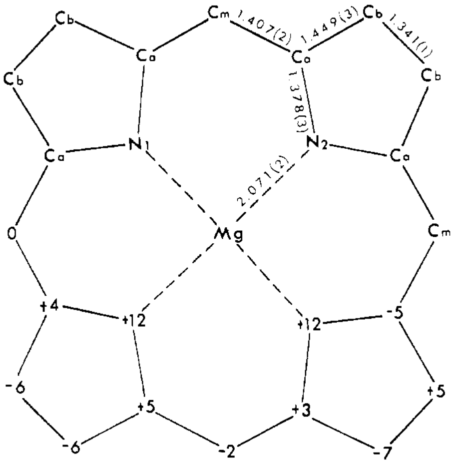

Figure 4. Formal diagram of the porphyrin core of MgTPP(4-pic)$_2$ displaying, on the upper half, the averaged bond lengths. On the lower half of the centrosymmetric diagram, the numbered symbol for each atom is replaced by its perpendicular displacement, in units of 0.01 Å, from the mean plane of the porphyrin core.

four chelating nitrogen atoms is 87° while the dihedral angle between the mean planes of the core and the four chelating nitrogen atoms is only 3.2°. The angle between the lines joining C(41) to C(43) and N(2) to N(2a) is 13.2°. The bond angles and distances of the imidazole ring agree well with the previously reported values.[27]

Figure 3 is a perspective diagram of MgTPP(4-pic)$_2$ with Mg at the center of the four chelating nitrogen atoms and an octahedral configuration. The porphyrin core as a whole is slightly nonplanar, and the deviations of atoms from the mean plane of this core are given in the lower half of Figure 4. Individually, the pyrrole rings are planar to ±0.008 Å with angles of 8.3 and 8.7° to the plane of the four chelating nitrogen atoms and mutually at 6.1°. The upper half of Figure 4 shows important averaged bond distances of the porphyrin core. The bond distances between the nitrogen atoms of the pyrrole and pyridine rings are 3.066 and 3.056 Å.

The averaged bond angles are NMgN = 90 (1), $MgNC_a$ = 126.1 (12), C_aNC_a = 106.8 (3), $C_aC_mC_a$ = 126.7 (7), NC_aC_b = 109.1 (2), NC_aC_m = 125.2 (3), and $C_aC_bC_b$ = 107.5 (1)°. The averaged values of the internal angles and bond lengths of the phenyl rings are 120 (1)° and 1.378 (12) Å, respectively. The two unique phenyl groups form dihedral angles of 84.9 and 70.3° with the mean plane of the core, while the dihedral angle between the mean planes of the pyridine ring and the four coordinating nitrogen atoms is 74.5°. The angle between the lines C(51)–C55 and N(1)–N(1a) is 41.2°. The averaged bond lengths of the pyridine ring are N–C = 1.330 (1) and C–C = 1.371 (10) Å, while the averaged bond angles are MgNC = 122.2 (7), CCC = 119 (3), and CCN = 124.2 (7)°.

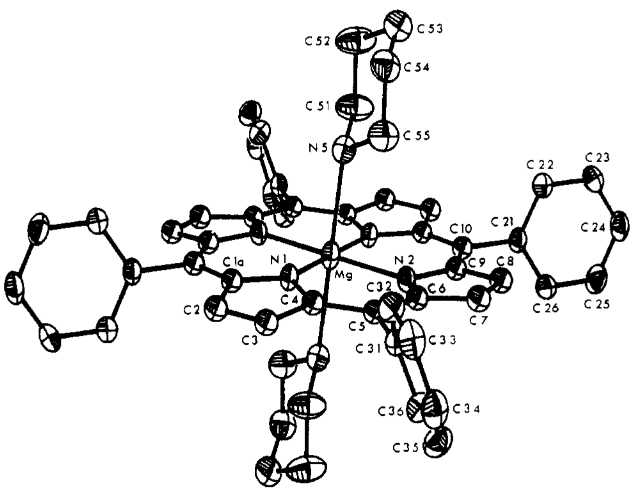

Figure 5. Computer-drawn structure of MgTPP(pip)$_2$ showing the numbering scheme (30% probability ellipsoids).

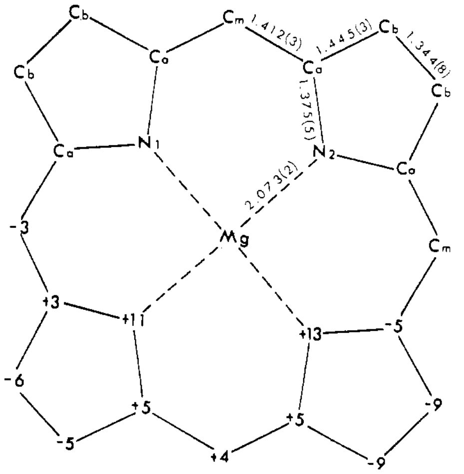

Figure 6. Diagram of the porphyrin core of MgTPP(pip)$_2$ displaying on the upper half, the averaged bond lengths. On the lower half of the centrosymmetric diagram, atomic displacements in units of 0.01 Å from the mean plane of the porphyrin core are given.

An illustration of a single molecule of MgTPP(pip)$_2$ with labeling of the atoms is given in Figure 5. This complex shows a basically similar octahedral structure to that of MgTPP(4-pic)$_2$. On the whole, the porphyrin core shows small but significant departures from planarity that are given in the lower half of Figure 6. The pyrrole rings are planar to ±0.006 Å with angles of 9.7 and 7.7° to the plane of the four chelating nitrogen atoms and mutually at 7.5°. The upper half of Figure 6 gives some important averaged bond distances of the porphyrin core. The nonbonded distances between the nitrogen atoms of the pyrrole rings and piperidine are 3.180 and 3.163 Å.

The averaged values for the bond angles are NMgN = 90.0 (1). $MgNC_a$ = 126.1 (3), C_aNC_a = 106.9 (1), $C_aC_mC_a$ = 126.2 (5), NC_aC_b = 109.2 (2), NC_aC_m = 125.5 (2), and $C_aC_bC_b$ = 107.4 (3)°. The averaged internal angles and bond

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[27] Lauher, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4447.

Table XI. Comparison of the Nitrogenous Base Complexes of Mg-, Fe^{II}-, and Co^{III}TPP

compd	oxidn no.	cryst syst	space group	cell dimens	Z	av bond length M-N (eq)	av bond length M-N (ax)	ref
MgTPP(1-MeIm)$_2$	2	tetragonal	$P4_2/n$	$a = 20.764$ (5) Å $c = 9.659$ (3) Å	4	2.071	2.297	this work
FeTPP(1-MeIm)$_2$	2	tetragonal	$P4_2/n$	$a = 20.651$ (4) Å $c = 9.526$ (1) Å	4	1.997	2.014	19
MgTPP(pip)$_2$	2	triclinic	$P\bar{1}$	$a = 9.944$ (3) Å $b = 11.436$ (3) Å $c = 11.914$ (3) Å $\alpha = 101.78°$ $\beta = 104.59°$ $\gamma = 115.60°$	1	2.071	2.419	this work
FeTPP(pip)$_2$	2	triclinic	$P\bar{1}$	$a = 11.113$ (3) Å $b = 12.071$ (3) Å $c = 9.797$ (3) Å $\alpha = 105.67°$ $\beta = 113.70°$ $\gamma = 101.02°$	1	2.004	2.127	18
CoTPP(pip)$_2{}^+$	3	triclinic	$P\bar{1}$	$a = 12.049$ (3) Å $b = 12.911$ (3) Å $c = 10.405$ (5) Å $\alpha = 102.73°$ $\beta = 92.04°$ $\gamma = 65.24°$	1	1.978	2.060	33
MgTPP(4-pic)$_2$	2	triclinic	$P\bar{1}$	$a = 10.146$ (2) Å $b = 11.210$ (2) Å $c = 11.643$ (3) Å $\alpha = 65.63°$ $\beta = 76.32°$ $\gamma = 67.42°$	1	2.071	2.386	this work
MgOEP(py)$_2$	2	triclinic	$P\bar{1}$	$a = 10.607$ (3) Å $b = 10.423$ (4) Å $c = 9.957$ (4) Å $\alpha = 114.69°$ $\beta = 90.56°$ $\gamma = 99.27°$	1	2.068	2.389	19

lengths of the phenyl rings are 120 (1)° and 1.377 (10) Å, respectively. The phenyl groups form dihedral angles of 81.7 and 70.2° with the mean plane of the core, while the dihedral angle between the mean plane of the piperidine and the four coordinating nitrogen atoms is 79°. The angle between the lines C(51)–C(55) and N(1)–N(1a) is 43.9°. The piperidine ring is in the chair form with averaged angles of CNMg = 116.6 (4), CCC = 110.4 (12), and NCC = 114.7 (5)°.

Discussion

The structural results presented here enable the following comparisons to be made: (1) comparison of the relative binding of different axial ligands in MgTPP(L)$_2$ complexes; (2) comparison of the coordinating properties of Mg(II) and Fe(II) in octahedral porphyrin complexes; (3) comparisons of MgTPP(L)$_2$ complexes with other octahedral and also five-coordinate Mg porphyrin complexes.

(1) Comparison of Axial Ligand Binding for Mg Complexes. The results show that MgTPP(pip)$_2$ and MgTPP(4-pic)$_2$ crystallize in the same space group, while MgTPP(1-MeIm)$_2$ adopts a different packing arrangement. The axial Mg–N bonds of MgTPP(pip)$_2$ are extremely weak, being even longer than bonds in seven-coordinated Mg complexes.[28,29] The bond lengths for these Mg–N bonds are pip > 4-pic > 1-MeIm. This apparently bears no relation to the basicity of the ligands where the order as given by pK_a values is pip > 1-MeIm > 4-pic.[30] Steric effects between the porphyrin and the hydrogen atoms of the ligands may be important in determining these bond lengths. Although both piperidine and pyridine are six-membered rings, the steric effects would be less for pyridine than for piperidine. It is observed that the axial Mg–N bonds for the picoline complex are slightly shorter than those for piperidine. The imidazole ring, being five-membered, exhibits even smaller steric effects than picoline and the axial Mg–N bond lengths are even shorter. This type of result has also been observed for low-spin Fe^{II}TPP complexes.[31] However, the Mg–N axial bond lengths for all of the MgTPP(L)$_2$ complexes are significantly longer than the Fe–N porphyrin ones, and differences in steric interaction would be expected to be reduced at such longer distances. Consequently, some kind of additional electronic effect may be responsible for the significantly shorter Mg–N axial bond observed for MgTPP(1-MeIm)$_2$ compared with those for the pip and 4-pic Mg complexes.

The overall orientation of the imidazole ring to the plane of the four chelating nitrogen atoms is different from those of 4-pic and pip. A possible factor in this difference is the existence of an intermolecular packing effect within the unit cell of the 1-MeIm complex. A stereodiagram of the unit cell shows that a phenyl group of TPP makes a relatively close contact with the coordinated imidazole group (nonbonding interatomic distances for these two groups are as close as 3.37 Å).

(2) Comparison of Fe^{II}TPP and MgTPP Complexes. The availability of X-ray data for isostructural pairs of Fe(II) (low spin) and MgTPP(L)$_2$ complexes for both L = pip and 1-MeIm enables a direct comparison of the binding properties of these two metal ions to be made. The ionic radius of low-spin Fe(II) is somewhat smaller than that for Mg(II) (0.61 and 0.72 Å, respectively[32]). Nonetheless, bond angle/bond

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[32] Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

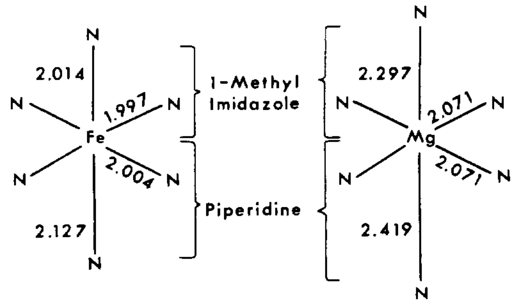

Figure 7. Comparison of bond lengths for Fe^{II}- and $Mg^{II}TPP(L)_2$.

length values (Table II) show that there are no significant differences within the porphyrin cores of the Mg and Fe(II) complexes. However there are significant differences in the metal–nitrogen bond lengths. The equatorial values are consistently shorter (by about 0.07 Å) for the corresponding Fe(II) complexes but very much more so for the axial binding (almost 0.3 Å) (Table XI; Figure 7). Shorter metal–nitrogen bond lengths have also been observed for the TPP complex of Co(III), which is isoelectronic with Fe(II) and has an ionic radius of 0.63 Å[33] (Table XI). Apparently the presence of d electrons for Fe(II) and Co(III) considerably enhances the binding of nitrogen donors, especially in the axial positions (the increase in formal charge for Co(III) further enhances axial binding (Table XI)).[34] For Mg, having no d electrons, there is a low affinity for axial ligands in porphyrin systems.

(3) Comparison of Mg Porphyrin Complexes. A comparison of the bond lengths and angles of $MgOEP(py)_2$[17] and $MgTPP(4\text{-pic})_2$ shows that the two structures are very similar (Table XI) to each other. Corresponding axial and equatorial Mg–N bond lengths have about the same values. Thus, ring substitutions at the C_b atoms and at C_m atoms do not appear to affect Mg–N distances in Mg porphyrin complexes. In addition, substitution of a methyl group for hydrogen at the 4-position of pyridine has no significant steric effect on the metal–nitrogen bond lengths. This result contrasts with that for 2-pic where a different, five-coordinated hydrated MgTPP complex, $MgTPP(H_2O)(2\text{-pic})_2$, is formed.[35] The coordinated water molecule is stabilized by hydrogen bonding to nitrogen atoms of two 2-picoline solvate molecules. In this complex and another nonsolvated five-coordinated $MgTPP(H_2O)$[5] complex the Mg^{2+} is displaced by 0.416 and 0.273 Å out of the plane of the four chelating nitrogen atoms, respectively. The radius of the central core is ~2.05 Å in both complexes. The longer ~2.07-Å equatorial value for the six-coordinated structures shows that there is a radial expansion of the Mg–N bonds to accommodate the Mg^{2+} ion into the center of the core for these complexes. This radial expansion is also found for high-spin six-coordinated FeTPP complexes.[36] However, the other bond distances around the core remain the same, and this holds also for the radical cation $MgTPP^{+}$.[3]

For all three Mg structures reported here the phenyl porphyrin substituents make angles greater than 60° with the core. This is considered to be an indication that there are insignificant steric interactions between the pyrrole hydrogens and phenyl hydrogen atoms within the porphyrin rings.[37]

Tables of observed and calculated structure factors and other crystallographic data are deposited as supplementary material and can be obtained from the authors on request.

Registry No. $MgTPP(1\text{-MeIm})_2$, 80186-54-5; $MgTPP(4\text{-pic})_2$, 80186-52-3; $MgTPP(pip)_2$, 80186-55-6.

Supplementary Material Available: Tables of observed and calculated structure factors and additional temperature factor, hydrogen coordinate, and phenyl group bond length/angle data (Tables XII–XX) and additional stereoscopic diagrams (Figures 8–11) (46 pages). Ordering information is given on any current masthead page.

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