Structure and Chemistry of the Porphyrins. The Crystal and Molecular Structure of the Monohydrated Dipyridinated Magnesium Phthalocyanin Complex[1]

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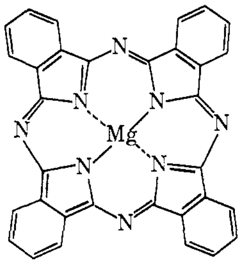
Abstract: The crystal and molecular structure of the monohydrated, dipyridinated magnesium phthalocyanin, $MgC_{32}H_{16}N_8 \cdot H_2O \cdot 2C_5H_5N$, has been determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/n$, with cell parameters $a = 17.098 \pm 0.003$, $b = 16.951 \pm 0.003$, $c = 12.449 \pm 0.003$ Å, and $\beta = 105.88 \pm 0.003°$. The structure was solved by a combination of statistical and Fourier methods. All hydrogen atoms were located, and least-squares refinement has reduced the conventional unweighted R value to 0.050 for the 3323 independent, nonzero reflections. The asymmetric unit contains one magnesium phthalocyanin molecule in which the magnesium atom is also coordinated to the oxygen atom of a water molecule. The hydrogens of the water molecule are hydrogen bonded to two pyridine molecules of crystallization. The phthalocyanin ring deviates significantly from a plane, and the magnesium atom is 0.496 ± 0.004 Å out of the plane of the inner nitrogen atoms toward the water molecule. The phthalocyanin molecules are close together in pairs and their minimum intermolecular atomic separation is 3.239 ± 0.004 Å. The biosynthesis and possible nonplanarity of chlorophyll are discussed.

Phthalocyanin and metallophthalocyanins have often been used as models of the porphyrins and chlorins, and we have been seeking to extend our knowledge of their structures. Several phthalocyanin (Pc) structures have been determined previously by Robertson and his coworkers,[2-6] by Brown,[7,8] and by Vogt, Zalkin, and Templeton.[9] The phthalocyanin ring was found to be roughly planar, with the central metal atom in the plane of the molecule. One of the metallophthalocyanin structures studied by Robertson[4] was the magnesium derivative, MgPc (1). Through a comparison of cell parameters and qualitative intensity data, Linstead and Robertson showed that MgPc, when crystallized in an anhydrous environment, was isomorphous with the other β-Pc's. In the course of an investigation of several porphyrin crystals, we observed that MgPc, when crystallized from an uncovered pyridine solution, *i.e.*, a nonanhydrous environment, had different cell dimensions than the other Pc's studied. We were interested in obtaining a Pc structure of high accuracy since this would be an important ingredient in the calculation of molecular orbitals and the related chemical ground- and excited-state properties. A detailed structure of a magnesium complex,[10] particularly if solvated, may help one understand the chemistry of magnesium porphyrin complexes[11,12] and of chlorophyll.[13]



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Experimental Procedure

The MgPc used in this structural analysis was obtained from E. I. du Pont Co., du Pont Code No. DD 1383. Although the bottle was labeled magnesium phthalocyanin, the analysis of nitrogen written on the bottle ($N_{calcd} = 20.88\%$, $N_{obsd} = 19.5\%$) and an independent assay of the hydrogen present ($H_{calcd} = 2.98\%$, $H_{obsd} = 3.53\%$) implies that two water molecules of hydration are present per MgPc molecule. The violet-colored powder was recrystallized from an air-exposed solution in pyridine by slow evaporation to dryness. The deep violet crystals which remained were well formed. The most prominent faces of the crystals are the forms (011), (110), (101), (10$\bar{1}$), and (210).

Weissenberg photographs of the $0kl$, $1kl$, $2kl$, $3kl$, and $4kl$ levels indicated Laue symmetry $2/m$. The observed systematic absences ($0k0$, for $k \neq 2n$; $h0l$, for $h + l \neq 2n$) correspond to the monoclinic space group $P2_1/n$, with the four general equivalent positions: $x, y, z;\ -x, -y, -z;\ {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z;\ {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$. A General Electric XRD-5 X-ray diffractometer equipped with a copper X-ray tube, a manual quarter-circle Eulerian-cradle goniostat, and a 0.0005-in. thick Ni filter at the receiving slit were used to measure both the cell dimensions and the intensity data. The unit cell dimensions were determined from the d spacings of the $h00$, $00l$, $0k0$, $h0h$, and $h0\bar{h}$ reflections. The α doublet (λ 1.5405 Å for Cu $K\alpha_1$) was resolved for those reflections of highest order.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission. Presented in part at the National Meeting of the American Crystallographic Association, Seattle, Wash., March 1969.

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[8] C. J. Brown, *ibid.*, *A*, 2494 (1968).

[9] L. H. Vogt, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).

[10] Recently, R. Timkovich and A. Tulinsky, *J. Amer. Chem. Soc.*, **91**, 4430 (1969), reported the determination of the structure of a disordered aquomagnesium–tetraphenylporphyrin complex. As in our result, the magnesium atom is out of the plane of the nitrogen atoms (but by 0.27 Å) and is coordinated to one water molecule (at 2.10 Å). However, because of the disorder, there is some ambiguity concerning the precise molecular dimensions.

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The cell dimensions are $a = 17.098 \pm 0.003$, $b = 16.951 \pm 0.003$, $c = 12.449 \pm 0.003$ Å, and $\beta = 105.88 \pm 0.03°$. The observed density of 1.368 ± 0.015 g cm^{-3}, which was determined by flotation in an aqueous $ZnBr_2$ solution, agrees well with the calculated density of 1.364 for a formula weight of 713.1 of one MgPc, one water, and two pyridine molecules, for $Z = 4$, and for a unit cell volume of 3470 Å^3. The calculated densities for 1 MgPc, 1.5 MgPc, and 1 MgPc and 2 pyridine molecules are 1.025, 1.539, and 1.329 g cm^{-3}, respectively.

The data were taken on a crystal of approximate dimensions 0.1 × 0.1 × 0.15 mm so aligned that the reciprocal a axis coincided with the instrument φ axis. The distances from the source and from the receiving slit to the crystal were 14.5 and 17.8 cm, respectively. All of the independent reflections (excluding space group absences) lying within one quadrant of a sphere in reciprocal space corresponding to spacings $\geqq 1.006$ Å ($2\theta \leqq 100°$) were counted for 10 sec with both crystal and counter stationary and at a takeoff angle of 4°. Individual backgrounds were measured for those reflections seriously affected by streaking from lower orders; for the rest, backgrounds were taken from a plot of the background counts as a function of the Bragg scattering angle for various values of φ and χ. Of the 3558 reflections measured, the intensities of 3323 were above background. Periodic checks of four standard reflections showed only small ($\pm 2\%$) random variations in intensity. Variations of only 5% in the intensities of the $h00$ reflections were observed as a function of the crystal orientation, and no absorption correction ($\mu = 9.1$ cm^{-1}) was applied.

Atomic scattering factors of Cromer and Mann[14] for the nonhydrogen atoms and those of Stewart, Davidson, and Simpson[15] for the hydrogen atoms were used. The anomalous dispersion corrections given by Cromer[16] ($\Delta f' = 0.15$, $\Delta f'' = 0.19$) were used for magnesium. The function minimized by least squares was $R_2{}^2 = \Sigma w(\Delta F)^2/\Sigma w(F_o)^2$. In the early stages of refinement $w = 1.0$, but later $w = 0$ if $I = 0$ and $w = 1/\sigma^2(F)$ otherwise; $\sigma(F)$ was calculated from $\sigma^2(I) = I + 2I_b + (cI)^2$: $\sigma(F^2) = (LP)^{-1}\sigma(I)$, $\sigma(F) = [\sigma(F^2)]^{1/2}$ if $I \leqq \sigma(I)$, and $\sigma(F) = F - [F^2 - \sigma(F^2)]^{1/2}$ if $I > \sigma(I)$. In these expressions I is the net count, I_b is the background count, LP is the Lorentz-polarization factor, and c is a parameter which was originally fixed at 0.07, later at 0.05.

The following programs for the CDC 6600 computer were used in this structure analysis and interpretation: GONIO, a goniometric settings program; INCOR, a general data reduction program; FORDAP, a Fourier analysis program; DISTAN, a crystallographic bond distance and bond angle program; LIST, a data presentation program; WILSON, an unpublished Wilson-plot program by Maddox and Maddox; R. E. Long's phase determination program;[17] LS200, our unpublished modified version the of Ganzel-Sparks-Trueblood least-squares program; DATLOK, D. J. St. Clair's unpublished weighting scheme analysis program; and ORTEP, Johnson's molecular crystallographic plotting program.[18]

Solution and Refinement of the Structure

Normalized structure factors, E_h, were calculated using Wilson's method.[19] The phases of the highest 181 E values $\geqq 2.0$ were determined from Long's sign determination program[17] which iteratively applies the equation: $\text{sign}(E_h) = \text{sign}(\Sigma_k E_k E_{h-k})$. The fixed positive phases of the $13\bar{5}$, 014, and $13\bar{2}$ reflections defined the origin, and the phases of an additional four reflections 024, $38\bar{1}$, $19\bar{2}$, and $11\bar{5}$ were held fixed for each of the 16 computer runs in which they were allowed to have all combinations of positive and negative phases. A consistency index defined as $C = \Sigma_h\Sigma_k E_h E_k E_{h-k}/\Sigma_h\Sigma_k|E_h E_k E_{h-k}|$ was calculated for each combination. Of the 16 possibilities, 2 had $C = 0.68$, whereas $C = 0.47$–0.55 for the other 14.

Fourier maps were calculated from the E values phased from the two most consistent sets. One map showed a half molecule adjacent to a center of symmetry while the other showed a full molecule with the same orientation but translated to a general position with the magnesium atom at the fractional coordinates (0.30, 0.00, 0.55). We checked the orientation obtained from the statistical approach in two ways. First, we found that the plane through the highest peaks of each E map agreed well with the plane of highest density calculated from a three-dimensional Patterson map. Second, an optical transform of a single molecule was made by shining a laser beam through a photoreduced image of the molecule. The orientation of the molecule on the plane was determined by rotating the image of the molecule and comparing resultant rotated optical transforms with the E values (*i.e.*, the normalized transform of the electron density) for the $h0l$ data. This technique suggested that the orientation of the molecule in the plane agreed with the E-map orientation to within 5°.

Conventional least-squares and Fourier calculations were used to distinguish between the two possibilities. The positions of the 22 highest peaks on the E map with the molecule in the special position were refined to a discrepancy index of $R_1 = \Sigma||kF_o| - |F_c||/\Sigma|kF_o| = 0.62$. A Fourier synthesis using F_o with the phases of F_c revealed no additional atoms in reasonable locations, and the use of this trial structure was terminated. Thirty-six of the highest peaks on the other E map with the high consistency index refined to $R_1 = 0.45$. The remaining six atoms in the MgPc ring were among the highest peaks of a difference Fourier synthesis, and R_1 with the 42 atoms refined to 0.37. Another difference Fourier was calculated using all of the data. The 12 highest peaks, in the form of 2 pyridine rings, were added to the previous 42 to bring the number of atoms up to 54 and the R_1 value down to 0.18. Subsequently it was determined that 52 of the 56 highest peaks in the correct E map corresponded to atoms in the asymmetric unit. The remaining two atoms appeared only as shoulders on two other peaks.

After several mispunched data were corrected, R_1 dropped to 0.13. Anisotropic temperature factors of the form $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2kl\beta_{23} - 2hl\beta_{13})$ were used for the 54 atoms. A diagonal least-squares refinement of the 487 parameters including the scale factor k reduced R_1 to 0.101. The positions of the hydrogen atoms were found in a difference Fourier map calculated from all nonzero reflections. They were given isotropic temperature factors which were allowed to vary, and the discrepancy index dropped to 0.070. To economize on computing time the 82 atoms were split into three groups, the water and two pyridine molecules as one group and the two halves of the MgPc molecule as the other two groups. Full-matrix least-squares refinements were run on one group at a time, keeping the atomic coordinates of the other two groups fixed. Each group was refined for only one cycle before refining the coordinates of another group. Three cycles for each group reduced R_1 to 0.054. At this point it was noticed that the values of $|F_o/F_c|$ for the reflections of highest intensity were all less than 1.0. Remeasurement of the intensities of these strong reflections at lower X-ray flux proved that nonlinearity of the

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(18) C. K. Johnson, Oak Ridge National Report-3794, Revised, Oak Ridge, Tenn., June 1965.

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Table I. Final Atomic Fractional Coordinates and Thermal Parameters[a] of All Nonhydrogen Atoms in the Asymmetric Unit[b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mg	0.33142 (6)	0.01498 (5)	0.53984 (7)	3.98 (5)	3.13 (5)	3.05 (5)	−0.17 (4)	0.84 (4)	−0.20 (4)
O(1)	0.2195 (1)	0.0569 (1)	0.4624 (2)	4.44 (12)	4.81 (12)	3.45 (11)	0.33 (9)	1.05 (11)	0.21 (9)
N(1)	0.4600 (1)	0.1644 (1)	0.5118 (2)	4.01 (12)	3.54 (13)	4.14 (13)	−0.16 (10)	0.84 (10)	−0.02 (11)
C(2)	0.4447 (2)	0.1069 (2)	0.4351 (2)	3.57 (15)	3.66 (16)	3.94 (16)	0.13 (13)	0.74 (12)	0.28 (14)
N(3)	0.4029 (1)	0.0386 (1)	0.4368 (2)	3.91 (12)	3.57 (13)	3.54 (12)	−0.23 (10)	1.07 (9)	−0.07 (10)
C(4)	0.4045 (2)	−0.0051 (2)	0.3447 (2)	3.22 (14)	3.87 (16)	3.69 (15)	0.19 (12)	0.76 (12)	0.12 (14)
C(5)	0.4481 (2)	0.0384 (2)	0.2785 (2)	3.43 (14)	4.16 (17)	3.53 (15)	0.43 (13)	0.89 (12)	0.31 (13)
C(6)	0.4637 (2)	0.0228 (2)	0.1769 (3)	4.28 (17)	4.65 (19)	4.20 (18)	0.38 (15)	1.07 (14)	0.11 (16)
C(7)	0.5024 (2)	0.0800 (2)	0.1320 (3)	4.57 (18)	6.33 (23)	4.16 (18)	0.44 (16)	1.71 (15)	0.64 (18)
C(8)	0.5282 (2)	0.1505 (2)	0.1888 (3)	4.53 (18)	5.40 (21)	5.15 (21)	−0.28 (16)	1.82 (15)	1.07 (18)
C(9)	0.5159 (2)	0.1651 (2)	0.2920 (3)	4.20 (17)	4.38 (19)	4.52 (19)	−0.10 (14)	0.87 (14)	0.16 (16)
C(10)	0.4735 (2)	0.1092 (2)	0.3352 (2)	3.34 (14)	4.13 (17)	4.08 (15)	0.18 (13)	0.97 (12)	0.55 (14)
N(11)	0.3724 (1)	−0.0761 (1)	0.3163 (2)	4.08 (12)	3.69 (13)	3.52 (12)	0.00 (11)	0.92 (10)	−0.00 (10)
C(12)	0.3361 (2)	−0.1186 (2)	0.3789 (2)	3.72 (15)	3.62 (16)	3.22 (15)	0.01 (12)	0.73 (12)	−0.07 (13)
N(13)	0.3237 (1)	−0.0975 (1)	0.4789 (2)	4.13 (12)	3.33 (12)	3.26 (12)	−0.48 (10)	0.86 (10)	0.00 (10)
C(14)	0.2872 (2)	−0.1587 (2)	0.5165 (2)	4.09 (15)	3.33 (15)	3.24 (15)	0.18 (12)	0.54 (12)	0.04 (13)
C(15)	0.2729 (2)	−0.2229 (2)	0.4362 (2)	4.01 (15)	3.40 (16)	3.44 (15)	0.15 (12)	0.37 (12)	−0.19 (13)
C(16)	0.2356 (2)	−0.2965 (2)	0.4328 (3)	4.72 (17)	3.78 (17)	4.26 (18)	−0.43 (14)	0.66 (14)	−0.26 (15)
C(17)	0.2292 (2)	−0.3426 (2)	0.3390 (3)	5.95 (19)	3.92 (18)	5.12 (20)	−0.81 (15)	1.01 (15)	−1.02 (17)
C(18)	0.2600 (2)	−0.3163 (2)	0.2520 (3)	6.16 (20)	4.28 (19)	4.34 (18)	−0.20 (16)	0.91 (15)	−1.44 (16)
C(19)	0.2973 (2)	−0.2445 (2)	0.2552 (3)	4.76 (17)	4.16 (19)	4.15 (18)	0.30 (14)	1.26 (14)	−0.33 (15)
C(20)	0.3035 (2)	−0.1975 (2)	0.3493 (2)	3.89 (15)	3.38 (15)	3.51 (15)	0.44 (12)	0.80 (12)	−0.16 (13)
N(21)	0.2658 (1)	−0.1628 (1)	0.6125 (2)	4.34 (13)	4.06 (13)	3.12 (12)	−0.34 (10)	0.86 (10)	−0.37 (11)
C(22)	0.2798 (2)	−0.1049 (2)	0.6888 (2)	3.63 (14)	3.90 (17)	3.41 (15)	−0.05 (13)	0.71 (11)	0.13 (13)
N(23)	0.3129 (1)	−0.0324 (1)	0.6814 (2)	4.25 (12)	3.32 (12)	3.34 (12)	−0.18 (10)	0.75 (9)	−0.03 (10)
C(24)	0.3223 (2)	0.0057 (2)	0.7812 (2)	3.81 (15)	3.77 (16)	3.08 (15)	0.51 (13)	0.42 (12)	−0.26 (13)
C(25)	0.2929 (2)	−0.0447 (2)	0.8562 (2)	3.46 (14)	4.13 (16)	3.19 (15)	0.15 (12)	0.82 (12)	0.05 (13)
C(26)	0.2908 (2)	−0.0350 (2)	0.9660 (3)	4.28 (17)	4.53 (18)	3.69 (17)	−0.37 (14)	0.87 (13)	−0.22 (15)
C(27)	0.2598 (2)	−0.0961 (2)	1.0147 (3)	5.70 (19)	6.57 (24)	3.90 (18)	−0.68 (17)	1.64 (15)	−0.22 (18)
C(28)	0.2307 (2)	−0.1645 (2)	0.9560 (3)	6.33 (20)	5.98 (23)	4.41 (20)	−1.40 (17)	2.20 (16)	0.40 (18)
C(29)	0.2323 (2)	−0.1750 (2)	0.8466 (3)	4.68 (17)	4.91 (19)	3.84 (18)	−0.58 (15)	1.16 (13)	−0.22 (15)
C(30)	0.2653 (2)	−0.1138 (2)	0.7976 (2)	3.56 (15)	4.09 (16)	3.40 (15)	−0.13 (12)	0.89 (12)	0.07 (14)
N(31)	0.3563 (1)	0.0763 (1)	0.8103 (2)	4.34 (13)	3.38 (13)	3.55 (12)	0.07 (11)	0.80 (10)	−0.30 (10)
C(32)	0.3895 (2)	0.1197 (2)	0.7458 (2)	3.88 (15)	3.36 (15)	3.64 (16)	0.32 (12)	0.44 (12)	−0.11 (13)
N(33)	0.3927 (1)	0.1035 (1)	0.6386 (2)	4.10 (12)	3.53 (12)	3.59 (12)	−0.27 (10)	0.87 (10)	−0.10 (10)
C(34)	0.4381 (2)	0.1605 (2)	0.6071 (2)	3.87 (15)	3.22 (15)	3.91 (16)	0.08 (12)	0.81 (13)	0.05 (13)
C(35)	0.4626 (2)	0.2191 (2)	0.6961 (2)	4.04 (15)	2.99 (15)	4.36 (16)	0.03 (13)	0.54 (13)	0.11 (13)
C(36)	0.5073 (2)	0.2885 (2)	0.7066 (3)	5.21 (19)	4.02 (19)	5.41 (21)	−0.44 (15)	1.10 (16)	−0.08 (17)
C(37)	0.5217 (2)	0.3295 (2)	0.8050 (3)	6.02 (20)	3.97 (19)	6.33 (23)	−1.01 (16)	0.81 (17)	−0.85 (18)
C(38)	0.4916 (2)	0.3028 (2)	0.8917 (3)	6.67 (22)	4.51 (21)	5.64 (22)	−0.62 (17)	0.44 (18)	−1.04 (18)
C(39)	0.4472 (2)	0.2341 (2)	0.8830 (3)	5.32 (19)	4.17 (19)	4.76 (20)	−0.25 (15)	0.65 (15)	−0.76 (16)
C(40)	0.4329 (2)	0.1930 (2)	0.7834 (3)	3.98 (15)	3.06 (15)	4.00 (16)	0.40 (12)	0.15 (13)	−0.35 (14)
N(41)	0.1310 (2)	0.0761 (2)	0.6137 (2)	6.61 (16)	5.85 (17)	5.69 (16)	0.23 (14)	2.05 (13)	−0.37 (15)
C(42)	0.1031 (2)	0.0185 (3)	0.6650 (4)	6.30 (21)	5.47 (23)	6.92 (26)	−0.36 (17)	1.69 (18)	−0.86 (21)
C(43)	0.0955 (2)	0.0237 (3)	0.7703 (4)	6.63 (23)	8.29 (31)	6.77 (28)	−0.14 (21)	2.67 (20)	0.94 (26)
C(44)	0.1177 (3)	0.0911 (4)	0.8279 (4)	6.87 (24)	11.00 (39)	5.03 (25)	2.46 (24)	1.91 (20)	−0.51 (28)
C(45)	0.1465 (3)	0.1524 (3)	0.7776 (4)	6.70 (23)	6.34 (26)	7.67 (30)	1.52 (20)	0.41 (20)	−1.65 (25)
C(46)	0.1513 (2)	0.1420 (3)	0.6704 (4)	6.93 (22)	5.59 (23)	7.06 (26)	−0.05 (18)	1.91 (19)	0.38 (21)
N(47)	0.1301 (2)	−0.0224 (2)	0.2762 (3)	5.50 (15)	5.37 (18)	6.38 (19)	−0.09 (12)	0.47 (13)	−0.99 (14)
C(48)	0.1117 (2)	−0.0118 (3)	0.1670 (4)	7.65 (24)	6.57 (26)	7.11 (27)	−0.94 (20)	2.80 (20)	−0.97 (24)
C(49)	0.0834 (3)	−0.0709 (4)	0.0897 (4)	7.93 (26)	10.01 (36)	7.38 (30)	−1.52 (24)	3.13 (22)	−2.71 (30)
C(50)	0.0757 (3)	−0.1452 (3)	0.1281 (5)	5.90 (22)	8.09 (33)	9.81 (36)	0.09 (22)	1.41 (23)	−4.11 (32)
C(51)	0.0940 (3)	−0.1571 (3)	0.2386 (6)	5.98 (22)	5.18 (26)	12.05 (41)	−0.07 (19)	−1.40 (24)	−0.54 (31)
C(52)	0.1199 (2)	−0.0948 (3)	0.3098 (4)	5.71 (21)	6.70 (27)	8.07 (29)	0.13 (19)	−1.10 (19)	0.17 (25)

[a] The form of the anisotropic thermal ellipsoid (expressed in units of A^2) is: $\exp(-0.25\Sigma_{i=1}{}^3\Sigma_{j=1}{}^3B_{ij}b_ib_jh_ih_j)$, where b_i is the ith reciprocal axis length and h_i is the ith Miller index. [b] The numbers in parentheses here and in succeeding tables are the estimated standard deviations of the least significant digit(s).

scintillation counter was not responsible. Therefore an extinction correction of the form $F_o' = F_o(1 + (\mathrm{EF})(I))$, where the extinction factor EF is a constant = 5×10^{-7}, was applied to give a maximum correction of 14% for the strongest reflection. The most intense reflections were now given a higher weight by changing c in the weighting equation from 0.07 to 0.05. R_1 was reduced to 0.052. The atoms were now divided into two groups, the 57 atoms in the MgPc ring and the remaining 25 atoms. Three full-matrix least-squares cycles run on one group at a time reduced the maximum shift of any parameter to less than one-tenth of its standard deviation.

The final discrepancy values are $R_1 = 0.050$ for 3323 nonzero data, $R_1 = 0.056$ for all 3558 data, and the weighted $R_2 = 0.050$. The standard deviation of an observation of unit weight is 1.02. There is no systematic trend in either $|F_o/F_c|$ or $w^{1/2}|\Delta F|$ as a function of intensity or Bragg angle. In a Fourier synthesis of ΔF based on the final structure no peak was higher than 0.18 electron Å^{-3}.

Results and Discussion

The asymmetric unit contains one MgPc, one water, and two pyridine molecules. Figure 1 shows the atoms in the asymmetric unit projected on the bc plane and indicates the numbering system. The final atomic parameters for the nonhydrogen atoms are listed in Table I,

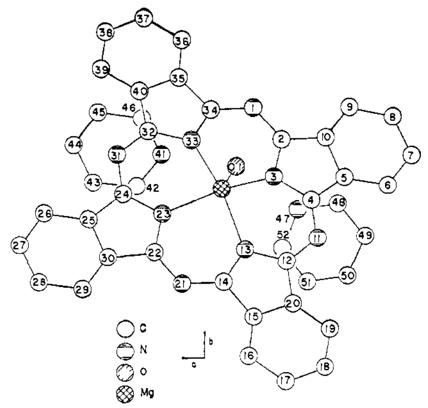

Figure 1. The molecular structure projected on the *bc* plane.

while those for the hydrogen atoms are presented in Table II. Hydrogen atoms are numbered by the atom to which they are attached. The observed and calculated structure factor amplitudes $|F_o|$ and $|F_c|$ are listed elsewhere.[20]

Table II. Final Fractional Atomic Positional and Isotropic Thermal Parameters for All Hydrogen Atoms in the Asymmetric Unit

Atom	x	y	z	B, Å^2
H(01-1)	0.1932 (19)	0.0644 (20)	0.4984 (27)	5.4 (11)
H(01-2)	0.1921 (23)	0.0354 (22)	0.3934 (33)	9.5 (13)
H(6)	0.4466 (15)	−0.0286 (16)	0.1380 (21)	3.84 (68)
H(7)	0.5107 (17)	0.0713 (17)	0.0612 (25)	4.99 (79)
H(8)	0.5569 (16)	0.1896 (16)	0.1579 (22)	4.22 (71)
H(9)	0.5336 (16)	0.2126 (17)	0.3314 (23)	4.17 (74)
H(16)	0.2172 (15)	−0.3157 (16)	0.4956 (22)	4.00 (71)
H(17)	0.2052 (17)	−0.3967 (18)	0.3370 (23)	4.91 (75)
H(18)	0.2502 (15)	−0.3461 (16)	0.1843 (22)	4.00 (68)
H(19)	0.3209 (16)	−0.2256 (16)	0.1971 (22)	4.30 (72)
H(26)	0.3110 (14)	0.0135 (15)	1.0058 (19)	2.59 (59)
H(27)	0.2605 (18)	−0.0924 (18)	1.0928 (28)	6.51 (89)
H(28)	0.2104 (17)	−0.2066 (18)	0.9920 (24)	5.19 (80)
H(29)	0.2112 (15)	−0.2228 (16)	0.8035 (22)	3.87 (68)
H(36)	0.5302 (15)	0.3060 (15)	0.6496 (21)	2.97 (65)
H(37)	0.5534 (20)	0.3819 (22)	0.8118 (27)	7.8 (10)
H(38)	0.5014 (18)	0.3326 (19)	0.9602 (25)	6.18 (91)
H(39)	0.4257 (17)	0.2154 (17)	0.9468 (24)	5.15 (79)
H(42)	0.0905 (19)	−0.0261 (20)	0.6223 (27)	7.0 (10)
H(43)	0.0763 (24)	−0.0185 (24)	0.8020 (33)	10.0 (14)
H(44)	0.1176 (22)	0.0972 (23)	0.8993 (33)	9.5 (13)
H(45)	0.1667 (21)	0.2036 (23)	0.8082 (30)	8.9 (12)
H(46)	0.1759 (20)	0.1839 (21)	0.6336 (28)	8.1 (10)
H(48)	0.1203 (18)	0.0418 (18)	0.1438 (25)	5.83 (86)
H(49)	0.0762 (27)	−0.0581 (27)	0.0121 (38)	12.5 (17)
H(50)	0.0680 (23)	−0.1907 (25)	0.0713 (33)	11.1 (13)
H(51)	0.0827 (26)	−0.2016 (26)	0.2727 (35)	10.8 (16)
H(52)	0.1311 (22)	−0.0981 (21)	0.3931 (31)	8.8 (12)

The MgPc molecule itself is nonplanar, and the magnesium atom is 0.496 Å out of the plane of the central nitrogen atoms directed toward the water molecule. The two hydrogen atoms of the water molecule are hydrogen bonded to the two pyridine molecules of crystallization, and the planes through the pyridine molecules make angles of 8.6 and 30.8° with the plane through the four central nitrogen atoms of MgPc. The intramolecular bond distances and bond angles, which are presented in Tables III and IV, respectively, are the same as those in other Pc's$^{2-9}$ to within the respective standard deviations. The precision, however, is greater by at least a factor of 2 for the MgPc in this work than for the other Pc's.

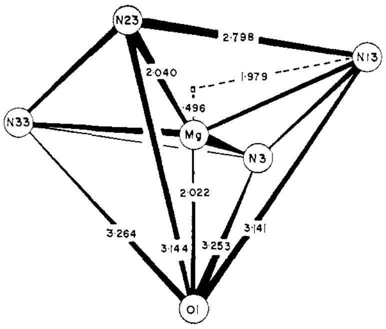

Figure 2. Geometry of the center of the MgPc molecule. Average values are given for the Mg–N and N–N distances.

Table III. Intramolecular Bond Distances (Å)[a]

Atoms	Distance	Atoms	Distance	Atoms	Distance
Mg–O(1)	2.022	C(22)–N(23)	1.366	C(49)–C(50)	1.366
Mg–N(3)	2.039	C(22)–C(30)	1.451	C(50)–C(51)	1.340
Mg–N(13)	2.043	N(23)–C(24)	1.370	C(51)–C(52)	1.372
Mg–N(23)	2.038	C(24)–C(25)	1.453	H(01)1–O(1)	0.73
Mg–N(33)	2.039	C(24)–N(31)	1.335	H(01)2–O(1)	0.93
N(1)–C(2)	1.339	C(25)–C(26)	1.387	H(6)–C(6)	1.00
N(1)–C(34)	1.340	C(25)–C(30)	1.392	H(7)–C(7)	0.94
C(2)–N(3)	1.364	C(26)–C(27)	1.376	H(8)–C(8)	0.97
C(2)–C(10)	1.459	C(27)–C(28)	1.388	H(9)–C(9)	0.95
N(3)–C(4)	1.371	C(28)–C(29)	1.382	H(16)–C(16)	0.98
C(4)–C(5)	1.454	C(29)–C(30)	1.398	H(17)–C(17)	1.00
C(4)–N(11)	1.330	N(31)–C(32)	1.326	H(18)–C(18)	0.96
C(5)–C(6)	1.388	C(32)–N(33)	1.379	H(19)–C(19)	0.97
C(5)–C(10)	1.400	C(32)–C(40)	1.457	H(26)–C(26)	0.97
C(6)–C(7)	1.376	N(33)–C(34)	1.362	H(27)–C(27)	0.97
C(7)–C(8)	1.397	C(34)–C(35)	1.461	H(28)–C(28)	0.96
C(8)–C(9)	1.378	C(35)–C(36)	1.389	H(29)–C(29)	0.99
C(9)–C(10)	1.388	C(35)–C(40)	1.392	H(36)–C(36)	0.95
N(11)–C(12)	1.333	C(36)–C(37)	1.371	H(37)–C(37)	1.03
C(12)–N(13)	1.368	C(37)–C(38)	1.392	H(38)–C(38)	0.97
C(12)–C(20)	1.457	C(38)–C(39)	1.379	H(39)–C(39)	1.01
N(13)–C(14)	1.358	C(39)–C(40)	1.384	H(42)-C(42)	0.92
C(14)–C(15)	1.452	N(41)–C(42)	1.324	H(43)–C(43)	0.92
C(14)–N(21)	1.343	N(41)–C(46)	1.316	H(44)–C(44)	0.90
C(15)–C(16)	1.396	C(42)–C(43)	1.355	H(45)–C(45)	0.97
C(15)–C(20)	1.392	C(43)–C(44)	1.348	H(46)–C(46)	1.00
C(16)–C(17)	1.384	C(44)–C(45)	1.372	H(48)–C(48)	0.98
C(17)–C(18)	1.400	C(45)–C(46)	1.371	H(49)–C(49)	0.97
C(18)–C(19)	1.371	N(47)–C(48)	1.321	H(50)–C(50)	1.03
C(19)–C(20)	1.396	N(47)–C(52)	1.323	H(51)–C(51)	0.91
N(21)–C(22)	1.341	C(48)–C(49)	1.383	H(52)–C(52)	1.00

[a] Standard deviations (Å), estimated by the method of least squares, are 0.002 for Mg–N, 0.003 for Mg–O, 0.003–0.004 for C–N, and 0.004–0.005 for C–C in Pc, 0.006 for C–N and 0.007–0.010 for C–C in pyridine, 0.02–0.03 for C–H in Pc, 0.03–0.04 for O–H, and 0.03–0.05 for C–H in pyridine. As is well known, the X-ray method detects a center of electron density for hydrogen which is displaced in the direction of the bond by about 0.1 Å from the proton, and the stated standard deviations do not include this effect.

The environment around the central magnesium atom is depicted in Figure 2. The 2.022 ± 0.003 Å Mg–O(1) distance is increased to 2.028 if corrected for thermal

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(20) The table of observed and calculated structure factors has been deposited as Document No. NAPS-01162 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be obtained by citing the document number and remitting $5.00 for photocopies or $2.00 for microfiche. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

Table IV. Intramolecular Bond Angles (deg) of $MgPc \cdot H_2O \cdot 2C_5H_5N$[a]

Atoms	Angle	Atoms	Angle
O(1)–Mg–N(3)	106.5	N(11)–C(12)–N(13)	127.2
O(1)–Mg–N(13)	101.2	N(11)–C(12)–C(20)	123.8
O(1)–Mg–N(23)	101.5	N(13)–C(12)–C(20)	109.0
O(1)–Mg–N(33)	107.0	Mg–N(13)–C(12)	124.9
N(3)–Mg–N(13)	86.5	Mg–N(13)–C(14)	125.1
N(3)–Mg–N(23)	152.0	C(12)–N(13)–C(14)	108.3
N(3)–Mg–N(33)	86.4	N(13)–C(14)–C(15)	110.0
N(13)–Mg–N(23)	86.8	N(13)–C(14)–N(21)	127.4
N(13)–Mg–N(33)	151.8	C(15)–C(14)–N(21)	122.6
N(23)–Mg–N(33)	86.8	C(14)–C(15)–C(16)	132.8
C(2)–N(1)–C(34)	123.3	C(14)–C(15)–C(20)	106.0
N(1)–C(2)–C(3)	127.5	C(16)–C(15)–C(20)	121.2
N(1)–C(2)–C(10)	122.9	C(15)–C(16)–C(17)	117.4
N(3)–C(2)–C(10)	109.6	C(16)–C(17)–C(18)	120.8
Mg–N(3)–C(2)	125.6	C(17)–C(18)–C(19)	122.1
Mg–N(3)–C(4)	124.9	C(18)–C(19)–C(20)	117.3
C(2)–N(3)–C(4)	108.4	C(12)–C(20)–C(15)	106.7
N(3)–C(4)–C(5)	109.3	C(12)–C(20)–C(19)	132.2
N(3)–C(4)–N(11)	127.6	C(15)–C(20)–C(19)	121.2
C(5)–C(4)–N(11)	123.1	C(14)–N(21)–C(22)	123.6
C(4)–C(5)–C(6)	132.6	N(21)–C(22)–N(23)	127.4
C(4)–C(5)–C(10)	106.6	N(21)–C(22)–C(30)	122.9
C(6)–C(5)–C(10)	120.8	N(23)–C(22)–C(30)	109.6
C(5)–C(6)–C(7)	118.0	Mg–N(23)–C(22)	125.3
C(6)–C(7)–C(8)	121.2	Mg–N(23)–C(24)	126.2
C(7)–C(8)–C(9)	121.2	C(22)–N(23)–C(24)	108.1
C(8)–C(9)–C(10)	117.8	N(23)–C(24)–C(25)	109.3
C(2)–C(10)–C(5)	106.0	N(23)–C(24)–N(31)	127.1
C(2)–C(10)–C(9)	133.1	C(25)–C(24)–N(31)	123.6
C(5)–C(10)–C(9)	120.9	C(24)–C(25)–C(26)	132.1
C(4)–N(11)–C(12)	123.9	C(24)–C(25)–C(30)	106.6
C(26)–C(25)–C(30)	121.3	C(36)–C(35)–C(40)	120.3
C(25)–C(26)–C(27)	117.6	C(35)–C(36)–C(37)	118.2
C(26)–C(27)–C(28)	121.4	C(36)–C(37)–C(38)	121.0
C(27)–C(28)–C(29)	121.7	C(37)–C(38)–C(39)	121.7
C(28)–C(29)–C(30)	117.0	C(38)–C(39)–C(40)	117.0
C(22)–C(30)–C(25)	106.4	C(32)–C(40)–C(35)	106.5
C(22)–C(30)–C(29)	132.6	C(32)–C(40)–C(39)	131.7
C(25)–C(30)–C(29)	121.0	C(35)–C(40)–C(39)	121.8
C(24)–N(31)–C(32)	124.0	C(42)–N(41)–C(46)	116.4
N(31)–C(32)–N(33)	127.8	N(41)–C(42)–C(43)	124.1
N(31)–C(32)–C(40)	123.0	C(42)–C(43)–C(44)	118.9
N(33)–C(32)–C(40)	109.2	C(43)–C(44)–C(45)	118.9
Mg–N(33)–C(32)	125.5	C(44)–C(45)–C(46)	118.1
Mg–N(33)–C(34)	126.1	N(41)–C(46)–C(45)	123.7
C(32)–N(33)–C(34)	108.3	C(48)–N(47)–C(52)	116.0
N(1)–C(34)–N(33)	127.5	N(47)–C(48)–C(49)	123.8
N(1)–C(34)–C(35)	123.1	C(48)–C(49)–C(50)	118.3
N(33)–C(34)–C(35)	109.4	C(49)–C(50)–C(51)	118.7
C(34)–C(35)–C(36)	133.1	C(50)–C(51)–C(52)	119.4
C(34)–C(35)–C(40)	106.6	N(47)–C(52)–C(51)	123.8

[a] Standard deviations are 0.1° for all angles involving Mg, 0.2–0.3° for all angles in the Pc ring, and 0.4–0.6° for all angles in the pyridine rings.

motion according to the model with the water molecule riding on the Mg atom. This distance is only slightly shorter than the average $Mg–OH_2$ distances for the six-coordinate magnesium atom in the crystals $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ (2.06 ± 0.01 Å),[21] $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (2.07 ± 0.01 Å),[22] and $MgSO_4 \cdot 6H_2O$ (2.06 ± 0.02 Å).[23]

Other five-coordinate metalloporphyrins whose crystal structures have been determined include methoxyiron(III) mesoporphyrin IX dimethyl ester (MeOFeMeso),[24] chlorohemin,[25] and vanadyldeoxophylloerythroetioporphyrin.[26] The nonplanarities of the metal atoms are 0.455 Å for the first, 0.475 Å for the second, and 0.48 Å for the third case. A major difference is that the metal chloride or oxide vector in each of the other three studied is colinear with the Ct–M vector to within 0.06°, where Ct is the center of the square formed by the four central nitrogen atoms. For the MgPc there is a distortion of 3.66 ± 0.15° for the Ct–O(1) vector. The distortion in MgPc, which results in the four different N···O distances in Figure 2, is most likely due to the strong interaction between the water and pyridine molecules.

In MgPc the O···N distances of 2.739 ± 0.004 Å to N(41) and 2.753 ± 0.004 Å to N(47) are somewhat shorter than the average hydrogen-bonded O···N distance of 2.80 Å.[27] The O–H–N angles to the N(41) and N(47) atoms are 172 ± 4 and 167 ± 4°, respectively. The closest approaches between the Pc and pyridine molecules are shown in Table V. The relatively short O···N distances and the stability of the air-exposed crystals indicate that the hydrogen bonds are relatively strong.

Table V. Intermolecular Distances Less Than 3.5 Å for C–C and C–N and Less Than 3.0 Å for C–H and N–H[a]

Position of adjacent molecule 2	Atom of 1	Atom of 2	Distance, Å
$1 - x, -y, 1 - z$[b]	C(7)	C(24)	3.239
	C(8)	C(22)	3.310
	C(19)	C(36)	3.327
	C(8)	N(23)	3.406
	N(1)	N(11)	3.417
	C(6)	C(32)	3.426
	N(11)	C(34)	3.430
	C(7)	N(23)	3.466
	N(1)	C(12)	3.466
	C(6)	N(31)	3.470
x, y, z[c]	C(15)	C(52)	3.433
	C(25)	C(43)	3.451
	C(14)	C(52)	3.456
	C(14)	H(52)	2.88
$x, y, 1 + z$	C(27)	C(49)	3.419
	C(26)	H(6)	2.93
$x, y, -1 + z$	C(6)	H(26)	2.89
	N(11)	H(27)	2.93
$^1/_2 - x, ^1/_2 + y, ^1/_2 - z$	N(1)	H(50)	2.66
	C(9)	H(51)	2.80
	C(5)	H(17)	2.84
$^1/_2 - x, ^1/_2 + y, ^3/_2 - z$	C(40)	H(29)	2.80
$^1/_2 - x, -^1/_2 + y, ^3/_2 - z$	N(21)	H(45)	2.61
	C(29)	H(46)	2.84

[a] Standard deviations are less than 0.004–0.006 Å for distances not involving hydrogen. [b] Position of the other molecule in the "dimer." [c] Only the closest pyridine–MgPc distances are listed.

Chemically equivalent bond lengths and angles for the Pc averaged in accordance with $C_{4v}(4mm)$ symmetry are shown in Figure 3. The departures from the mean bond lengths larger than 0.006 Å are (Å): +0.012 for C(32)–N(33), −0.011 for N(13)–C(14), −0.009 for N(31)–C(32), and +0.007 for C(14)–N(21). None is more than 3σ of the respective bond length. The largest

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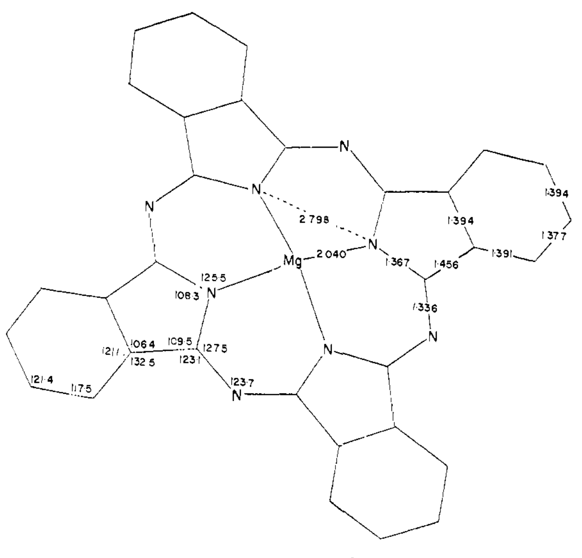

Figure 3. Average bond distances (Å) and bond angles (deg). Standard deviations are 0.006 Å and 0.4°, respectively.

differences from the mean angles are 3.5σ for Mg–C(23)–C(24), 3.0σ for Mg–C(33)–C(34), and 3.0σ for Mg–C(13)–C(12). These are deviations of 0.6–0.7°.

Because of the deviations from planarity, shown in Figure 4, the atomic positions in MgPc do not conform to C_{4v} symmetry, and they differ from even mirror symmetry by more than 30 times the standard deviations for some atoms. However, each pyrrole and benzene ring is planar within 0.02 Å. Most of the deviations from planarity for the MgPc molecule can be described by three sets of operations indicated in Figure 5: (a) the tilt of the pyrrole groups around the line through atoms C(2) and C(4), (b) the rotation of both pyrrole and benzene groups around the line between N(3) and the midpoint between atoms C(7) and C(8), and (c) the tilt of the benzene rings around bond C(5)–C(10). The first of these can be as large as 30° for the porphyrin diacids.[28] The third, which is the angle between the planes through a pyrrole and its fused benzene ring, is an indicator of the amount of conjugation between the pyrrole and benzene rings. The amounts of the rotations for each of the three operations and for each of the four corners of the MgPc molecule are listed in Table VI.

Table VI. Rotation Angles (deg) for Nonplanarity of MgPc

Atoms	"a"	"b"	"c"
C(2)–C(10)	3.5	0.8	3.5
C(12)–C(20)	1.2	−0.8	−2.3
C(22)–C(30)	6.8	−2.7	−1.6
C(32)–C(40)	7.4	1.3	−0.7

The packing arrangement of the unit cell is shown in Figure 6. The MgPc molecules are close together in pairs about the centers of symmetry at ($^1/_2$, 0, $^1/_2$) and (0, $^1/_2$, 0). A view of the "dimer" as seen perpendicular to the plane of the central nitrogens is shown in Figure 7. The planes through the pyrrole nitrogens are separated by only 3.506 Å, a distance only slightly greater than the 3.354-Å interplanar spacing of graphite[29] and the 3.34-Å spacing of β-CuPc.[7] The closest atomic approach between molecules not involving hydrogen atoms is 3.239 Å, which is the distance between atoms C(7) of one molecule and C(24) of the other. All C···C and C···N intermolecular distances less than 3.5 Å and all C···H and N···H intermolecular distances less than 3.0 Å are listed in Table V. In comparison, the shortest non-H-atom intermolecular contacts in some other porphyrin structures are 3.43 Å in porphine,[30] 3.38 Å in H_2Pc[3] and NiPc,[5] and 3.39 Å in MeOFeMeso,[24] which are all longer than the shortest distance in MgPc.

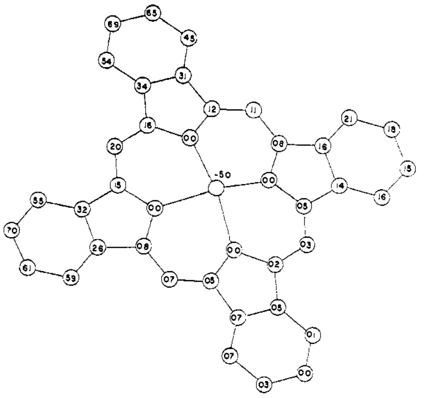

Figure 4. Deviations (×100 in Å) from the least-squares plane of the four central nitrogen atoms.

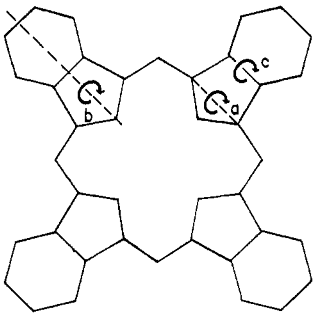

Figure 5. Rotation angles which describe the nonplanarity in phthalocyanin.

Packing forces can explain qualitatively some of the deviations from planarity of the Pc ring. The ruffling is in the proper direction to maximize the distance between overlapping groups in the "dimer." The closest intermolecular approach, between C(24) and C(7), governs the ruffling of groups C(2) through C(10) and C(22) through C(30), and the approach between atoms C(19) and C(36) twists those groups out of the plane. Benzene ring C(5)–C(10), the least planar of any of the benzene rings, is involved in the closest intermolecular approach.

The "radius of the central hole"[31] of a porphyrin may be defined as the distance from the pyrrole nitrogen to the center (Ct) of the molecule. Through a compilation of the results of many porphyrin and metalloporphyrin structures, Hoard[31] has shown that the metal atom lies

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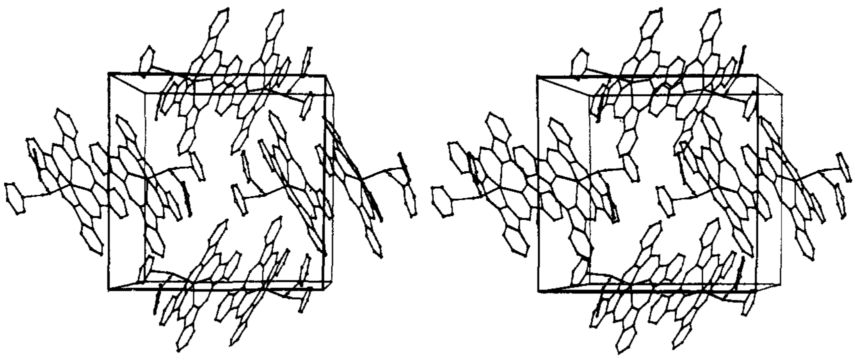

Figure 6. Stereoscopic view of the contents of the unit cell looking down the *c* axis. Except for the water molecule and its hydrogen bonds to pyridine, hydrogen atoms are omitted.

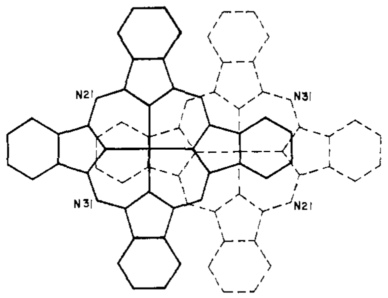

Figure 7. Normal projection of parallel phthalocyanins in the "dimer." One molecule is drawn with solid lines, the other with dashed lines.

in the plane of the four nitrogen atoms of porphyrin molecules only when the M–N distance is less than 2.01 Å. The M–N distance in porphyrins is usually 0.05–0.10 Å larger than in Pc's. Since the Mg–N distance in MgPc is 2.040 ± 0.003 Å, we expect that the Mg–N distance in magnesium porphyrins, when the magnesium atom is in a similar environment, will be at least 2.070 ± 0.02 Å. This distance is analogous to the largest metalloporphyrin M–N distance thus far reported, *i.e.*, in MeOFeMeso,[24] in which the iron atom is 0.46 Å out of the plane of the central nitrogens. From molecular orbital calculations Zerner, Gouterman, and Kobayashi[32] have predicted that the magnesium atom in porphyrins will have ~0.5 positive charge on it. For the chlorophyll molecule Katz, *et al.*, have shown[33,34] that intermolecular aggregation most likely involves the coordination of ketone and aldehyde oxygen atoms of one molecule with the central magnesium atom of the other. The central magnesium atom then would be in an environment similar to that in MgPc. This suggests the possibility that there is a similar nonplanar orientation of Mg in porphyrins in general and very likely chlorophyll in particular, when they are in a hydrated biological environment or when the chlorophyll is aggregated.

The existence of hydrated pentacoordinate magnesium atoms may help to explain the role of water in both the pyridine–magnesium porphyrin complexing reported by Seely[11] and the biosynthesis of magnesium porphyrins. Seely has reported at least a twofold enhancement of poly(vinylpyridine) complex formation when 0.016% H_2O was added to the nitromethane solutions of the magnesium porphyrins or MgPc. The water molecules might act as a pivot between the polymer and porphyrin molecules. This would allow more movement of the porphyrin molecules so that other pyridine molecules would be available for complexing.

Plane, *et al.*,[12] have studied the effect of pyridine as a catalyst in the insertion and removal of magnesium atoms in water solutions of deuteroporphyrins. When pyridine or some other catalyst is present, a complex similar to the $MgPc \cdot H_2O \cdot 2C_5H_5N$ might be formed. The hydrogen bonding of the bridging water molecule with its donation of positive charge to the pyridines would leave the oxygen more electronegative. The more electronegative oxygen, in turn, would attract the magnesium atom to form a stable complex with the magnesium atom halfway out of the plane. This would be in contrast to a more nearly planar molecule when pyridine is not present. From steric considerations alone, it would be more difficult to insert and remove the magnesium atom from the more planar configuration. In the biosynthesis of chlorophyll, a similar Mg coordination compound might be involved, with the imidazole of a histidine, for example, replacing the pyridine molecules. In fact, Baum and Plane[35] found that the imidazole as well as several other nitrogen bases can act as catalysts similar to pyridine.

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