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

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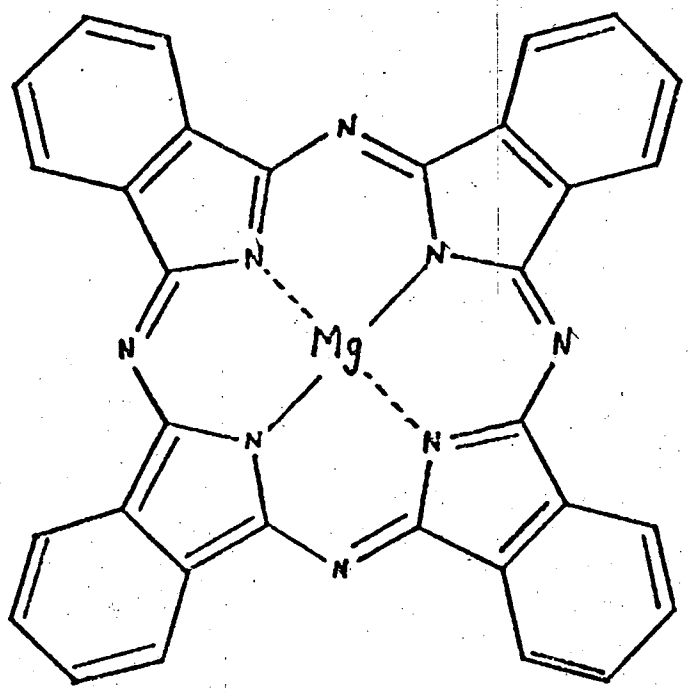
Abstract: The crystal and molecular structure of the monohydrated, dipyridinated magnesium phthalocyanin, $MgC_{32}H_{16}N_8 \cdot H_2O \cdot 2C_5H_5N$, has been determined by x-ray diffraction. The crystals are monoclinic, space group $P2_1/n$, with cell parameters $\underline{a}$ = 17.098 ± 0.003 Å, $\underline{b}$ = 16.951 ± 0.003 Å, $\underline{c}$ = 12.449 ± 0.003 Å, and β = 105.88 ± 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, non-zero 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 towards 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 non-planarity of chlorophyll are discussed.

Several phthalocyanin (Pc) structures have been determined previously, notably those 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 was the magnesium derivative[4] (MgPc). (See below.) Through a comparison of cell parameters and qualitative intensity data, Robertson showed that MgPc, when synthesized and 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 non-anhydrous environment, had different cell dimensions from 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 porphyrin, particularly if solvated, would help in understanding the chemistry of magnesium porphyrin complexes[10-12] and of chlorophyll[13].



Magnesium phthalocyanin

Experimental Procedure

The MgPc used in this structural analysis was obtained from E.I. duPont Co., duPont Code No. DD 1383. Although the bottle was labeled Magnesium Phthalocyanin, the analysis of nitrogen written on the bottle (N_{calc} = 20.88%, N_{obs} = 19.5%) and an independent assay of the hydrogen present (H_{calc} = 2.98%, H_{obs} = 3.53%) imply 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 $0k\ell$, $1k\ell$, $2k\ell$, $3k\ell$, and $4k\ell$ levels indicated Laue symmetry 2/m. The observed systematic absences ($0k0$, for $k \neq 2n$; $h0\ell$, for $h+\ell \neq 2n$) correspond to the monoclinic space group $P2_1/n$, with the four general equivalent positions: x,y,z; $-x,-y,-z$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$. A General Electric XRD-5 x-ray diffractometer equipped with a copper x-ray tube, a manual quarter-circle Eulerian-cradle goniostat, and a .0005 inch 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 alpha doublet (λ=1.5405 Å for $CuK\alpha_1$) was resolved for those reflections of highest order. The cell dimensions are a = 17.098 ± 0.003 Å,

$\underline{b}$ = 16.951 ± 0.003 Å, $\underline{c}$ = 12.449 ± 0.003 Å, and β = 105.88 ± 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 one MgPc, 1½ MgPc, and one MgPc and two 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 x 0.1 x 0.15 mm so aligned that the reciprocal $\underline{a}$ 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 ≧ 1.006 Å ($2\theta \leqq 100°$) were counted for ten seconds 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 (±2%) random variations in intensity. Variations of only 5% in the intensities of the $\underline{h}$00 reflections were observed as a function of the crystal orientation, and no absorption correction (μ = 9.1 cm^{-1}) was

applied.

Atomic scattering factors of Cromer and Mann[14] for the non-hydrogen 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 $\sigma^2(I) = I + 2I_b + (cI)^2$: $\sigma(F^2) = (LP)^{-1}\sigma(I)$, $\sigma(F) = [\sigma(F^2)]^{\frac{1}{2}}$ if $I \leq \sigma(I)$, and $\sigma(F) = F - [F^2 - \sigma(F^2)]^{\frac{1}{2}}$ 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 of the 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, $\underline{E}_{\underline{h}}$, were calculated using Wilson's Method[19]. The phases of the highest 181 E values ≧ 2.0 were determined from Long's sign determination program[17] which iteratively applies the equation: $\mathrm{sign}(\underline{E}_{\underline{h}}) = \mathrm{sign}(\Sigma_{\underline{k}}\, \underline{E}_{\underline{k}} \underline{E}_{\underline{h}-\underline{k}})$. 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 sixteen computer runs in which they were allowed to have all combinations of positive and negative phases. A consistency index defined as $C = \Sigma_{\underline{h}} \Sigma_{\underline{k}} \underline{E}_{\underline{h}} \underline{E}_{\underline{k}} \underline{E}_{\underline{h}-\underline{k}} / \Sigma_{\underline{h}} \Sigma_{\underline{k}} |\underline{E}_{\underline{h}} \underline{E}_{\underline{k}} \underline{E}_{\underline{h}-\underline{k}}|$ was calculated for each combination. Two of the sixteen possibilities had C = 0.68, whereas C = 0.47-0.55 for the other fourteen.

Fourier maps were calculated from the $\underline{E}$ 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 (.30,.00,.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 $\underline{E}$ 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

transform with the E-values (i.e. the normalized transform of the electron density) for the $h0\ell$ data. This technique suggested that the orientation of the molecule in the plane agreed with the E map orientation to within five degrees.

Conventional least squares and Fourier calculations were used to distinguish between the two possibilities. The positions of the twenty-two 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 twelve highest peaks, in the form of two 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 $\exp(-h^2\beta_{11}-k^2\beta_{22}-\ell^2\beta_{33}-2hk\beta_{12}-2k\ell\beta_{23}-2h\ell\beta_{13})$ 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 non-zero 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 non-linearity of the scintillation counter was not responsible. Therefore an extinction correction of the form $F_o' = F_o(1 + (EF)(I))$, where the extinction factor EF is a constant $= 5 \times 10^{-7}$, 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 non-zero 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 $w^{\frac{1}{2}}|\Delta F|$ 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 e $Å^{-3}$.

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 non-hydrogen atoms are listed in Table I, 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 in Table III.

The MgPc molecule itself is non-planar, and the magnesium atom is 0.496 Å out of the plane of the central nitrogen atoms directed towards 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 IV and V 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 two for the MgPc in this work than for the other Pc's.

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 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 $Ce_2Mg_3(NO_3)_{12}\cdot 24\ H_2O$ (2.06 ± .01 Å)[21], $Mg(NH_4)_2(SO_4)_2\cdot 6\ H_2O$ (2.07 ± .01 Å)[22], and $MgSO_4\cdot 6\ H_2O$ (2.06 ± .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 vanadyldeoxophyllo-erythroetioporphyrin[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 ± .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 ± .004 Å to N(41) and 2.753 ± .004 Å to N(47) are somewhat shorter than the average hydrogen bonded O··N distance of 2.80 Å. 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 VI. The relatively short O··N distances and the stability of the air-exposed crystals indicate that the hydrogen bonds are relatively strong.

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 (in 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 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 thirty 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 VII.

The packing arrangement of the unit cell is shown in Figure 6. The MgPc molecules are close together in pairs about the centers of symetry at ($\frac{1}{2}0\frac{1}{2}$) and ($0\frac{1}{2}0$). 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 VI. 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.

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 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 ± .003 Å, we expect that the Mg-N distance in Mg-porphyrins, when the magnesium atom is in a similar environment, will be at least 2.070 ± .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 non-planar 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-Mg porphyrin complexing reported by Seely[10] and the biosynthesis of Mg porphyrins. Seely has reported at least a twofold enhancement of poly(vinyl pyridine) complex formation when 0.016% H_2O was added to the nitromethane solutions of the Mg 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 half-way 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.

Footnotes

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, Washington, March, 1969

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

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
MG	.33142(6)	.01498(5)	.53984(7)	3.98(5)	3.13(5)	3.05(5)	-.17(4)	.84(4)	-.20(4)
O1	.2195(1)	.0569(1)	.4624(2)	4.44(12)	4.81(12)	3.45(11)	.33(9)	1.05(11)	.21(9)
N 1	.4600(1)	.1644(1)	.5118(2)	4.01(12)	3.54(13)	4.14(13)	-.16(10)	.84(10)	-.02(11)
C 2	.4447(2)	.1069(2)	.4351(2)	3.57(15)	3.66(16)	3.94(16)	.13(13)	.74(12)	.28(14)
N 3	.4029(1)	.0386(1)	.4368(2)	3.91(12)	3.57(13)	3.54(12)	-.23(10)	1.07(9)	-.07(10)
C 4	.4045(2)	-.0051(2)	.3447(2)	3.22(14)	3.87(16)	3.69(15)	.19(12)	.76(12)	.12(14)
C 5	.4481(2)	.0384(2)	.2785(2)	3.43(14)	4.16(17)	3.53(15)	.43(13)	.89(12)	.31(13)
C 6	.4637(2)	.0228(2)	.1769(3)	4.28(17)	4.65(19)	4.20(18)	.38(15)	1.07(14)	.11(16)
C 7	.5024(2)	.0800(2)	.1320(3)	4.57(18)	6.33(23)	4.16(18)	.44(16)	1.71(15)	.64(18)
C 8	.5282(2)	.1505(2)	.1888(3)	4.53(18)	5.40(21)	5.15(21)	-.28(16)	1.82(15)	1.07(18)
C 9	.5159(2)	.1651(2)	.2920(3)	4.20(17)	4.38(19)	4.52(19)	-.10(14)	.87(14)	.16(16)
C10	.4735(2)	.1092(2)	.3352(2)	3.34(14)	4.13(17)	4.08(15)	.18(13)	.97(12)	.55(14)
N11	.3724(1)	-.0761(1)	.3163(2)	4.08(12)	5.69(13)	3.52(12)	.00(11)	.92(10)	-.00(10)
C12	.3361(2)	-.1186(2)	.3789(2)	3.72(15)	3.62(16)	3.22(15)	.01(12)	.73(12)	-.07(13)
N13	.3237(1)	-.0975(1)	.4789(2)	4.13(12)	3.33(12)	3.26(12)	-.48(10)	.86(10)	.00(10)
C14	.2872(2)	-.1587(2)	.5165(2)	4.09(15)	3.33(15)	3.24(15)	.18(12)	.54(12)	.04(13)
C15	.2729(2)	-.2229(2)	.4362(2)	4.01(15)	3.40(16)	3.44(15)	.15(12)	.37(12)	-.19(13)
C16	.2356(2)	-.2965(2)	.4328(3)	4.72(17)	3.78(17)	4.26(18)	-.43(14)	.66(14)	-.26(15)
C17	.2292(2)	-.3426(2)	.3390(3)	5.95(19)	3.92(18)	5.12(20)	-.81(15)	1.01(15)	-1.02(17)
C18	.2600(2)	-.3163(2)	.2520(3)	6.16(20)	4.28(19)	4.34(18)	-.20(16)	.91(15)	-1.44(16)
C19	.2973(2)	-.2445(2)	.2552(3)	4.76(17)	4.16(19)	4.15(18)	.30(14)	1.26(14)	-.33(15)
C20	.3035(2)	-.1975(2)	.3493(2)	3.89(15)	3.38(15)	3.51(15)	.44(12)	.80(12)	-.16(13)
N21	.2658(1)	-.1628(1)	.6125(2)	4.34(13)	4.06(13)	3.12(12)	-.34(10)	.86(10)	-.37(11)
C22	.2798(2)	-.1049(2)	.6888(2)	3.63(14)	3.90(17)	3.41(15)	-.05(13)	.71(11)	.13(13)
N23	.3129(1)	-.0324(1)	.6814(2)	4.25(12)	3.32(12)	3.34(12)	-.18(10)	.75(9)	-.03(10)
C24	.3223(2)	.0057(2)	.7812(2)	3.81(15)	3.77(16)	3.08(15)	.51(13)	.42(12)	-.26(13)
C25	.2929(2)	-.0447(2)	.8562(2)	3.46(14)	4.13(16)	3.19(15)	.15(12)	.82(12)	.05(13)
C26	.2908(2)	-.0350(2)	.9660(3)	4.28(17)	4.53(18)	3.69(17)	-.37(14)	.87(13)	-.22(15)
C27	.2598(2)	-.0961(2)	1.0147(3)	5.70(19)	6.57(24)	3.90(18)	-.68(17)	1.64(15)	-.22(18)
C28	.2307(2)	-.1645(2)	.9560(3)	6.33(20)	5.98(23)	4.41(20)	-1.40(17)	2.20(16)	.40(18)
C29	.2323(2)	-.1750(2)	.8466(3)	4.68(17)	4.91(19)	3.84(18)	-.58(15)	1.16(13)	-.22(15)
C30	.2653(2)	-.1138(2)	.7976(2)	3.56(15)	4.09(16)	3.40(15)	-.13(12)	.89(12)	.07(14)
N31	.3563(1)	.0763(1)	.8103(2)	4.34(13)	3.38(13)	3.55(12)	.07(11)	.80(10)	-.30(10)
C32	.3895(2)	.1197(2)	.7458(2)	3.88(15)	3.36(15)	3.64(16)	.32(12)	.44(12)	-.11(13)
N33	.3927(1)	.1035(1)	.6386(2)	4.10(12)	3.53(12)	3.59(12)	-.27(10)	.87(10)	-.10(10)
C34	.4381(2)	.1605(2)	.6071(2)	3.87(15)	3.22(15)	3.91(16)	.08(12)	.81(13)	.05(13)
C35	.4626(2)	.2191(2)	.6961(2)	4.04(15)	2.99(15)	4.36(16)	.03(13)	.54(13)	.11(13)
C36	.5073(2)	.2885(2)	.7066(3)	5.21(19)	4.02(19)	5.41(21)	-.44(15)	1.10(16)	-.08(17)
C37	.5217(2)	.3295(2)	.8050(3)	6.02(20)	3.97(19)	6.33(23)	-1.01(16)	.81(17)	-.85(18)
C38	.4916(2)	.3028(2)	.8917(3)	6.67(22)	4.51(21)	5.64(22)	-.62(17)	.44(18)	-1.04(18)
C39	.4472(2)	.2341(2)	.8830(3)	5.32(19)	4.17(19)	4.76(20)	-.25(15)	.65(15)	-.76(16)
C40	.4329(2)	.1930(2)	.7834(3)	3.98(15)	3.06(15)	4.00(16)	.40(12)	.15(13)	-.35(14)
N41	.1310(2)	.0761(2)	.6137(2)	6.61(16)	5.85(17)	5.69(16)	.23(14)	2.05(13)	-.37(15)
C42	.1031(2)	.0185(3)	.6650(4)	6.30(21)	5.47(23)	6.92(26)	-.36(17)	1.69(18)	-.86(21)
C43	.0955(2)	.0237(3)	.7703(4)	6.63(23)	8.29(31)	6.77(28)	-.14(21)	2.67(20)	.94(26)
C44	.1177(3)	.0911(4)	.8279(4)	6.87(24)	11.00(39)	5.03(25)	2.46(24)	1.91(20)	-.51(28)
C45	.1465(3)	.1524(3)	.7776(4)	6.70(23)	6.34(26)	7.67(30)	1.52(20)	.41(20)	-1.65(25)
C46	.1513(2)	.1420(3)	.6704(4)	6.93(22)	5.59(23)	7.06(26)	-.05(18)	1.91(19)	.38(21)
N47	.1301(2)	-.0224(2)	.2762(3)	5.50(15)	5.37(18)	6.38(19)	-.09(12)	.47(13)	-.99(14)
C48	.1117(2)	-.0118(3)	.1670(4)	7.65(24)	6.57(26)	7.11(27)	-.94(20)	2.80(20)	-.97(24)
C49	.0834(3)	-.0709(4)	.0897(4)	7.93(26)	10.01(36)	7.38(30)	-1.52(24)	3.13(22)	-2.71(30)
C50	.0757(3)	-.1452(3)	.1281(5)	5.90(22)	8.09(33)	9.81(36)	.09(22)	1.41(23)	-4.11(32)
C51	.0940(3)	-.1571(3)	.2386(6)	5.98(22)	5.18(26)	12.05(41)	-.07(19)	-1.40(24)	-.54(31)
C52	.1199(2)	-.0948(3)	.3098(4)	5.71(21)	6.70(27)	8.07(29)	.13(19)	-1.10(19)	.17(25)

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[a] The form of the anisotropic thermal ellipsoid (expressed in units of Å^2) is: $\exp(-0.25 \sum_{i=1}^{3} \sum_{j=1}^{3} B_{ij} b_i b_j h_i h_j)$, where b_i = ith reciprocal axis length and h_i = ith Miller index.

[b] The numbers in parenthesis here and in succeeding tables are the estimated standard deviations of the least significant digit(s).

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

ATOM	x	y	z	B(Å²)
HO1-1	.1932(19)	.0644(20)	.4984(27)	5.4(11)
HO1-2	.1921(23)	.0354(22)	.3934(33)	9.5(13)
H 6	.4466(15)	-.0286(16)	.1380(21)	3.84(68)
H 7	.5107(17)	.0713(17)	.0612(25)	4.99(79)
H 8	.5569(16)	.1896(16)	.1579(22)	4.22(71)
H 9	.5336(16)	.2126(17)	.3314(23)	4.17(74)
H16	.2172(15)	-.3157(16)	.4956(22)	4.00(71)
H17	.2052(17)	-.3967(18)	.3370(23)	4.91(75)
H18	.2502(15)	-.3461(16)	.1843(22)	4.00(68)
H19	.3209(16)	-.2256(16)	.1971(22)	4.30(72)
H26	.3110(14)	.0135(15)	1.0058(19)	2.59(59)
H27	.2605(18)	-.0924(18)	1.0928(28)	6.51(89)
H28	.2104(17)	-.2066(18)	.9920(24)	5.19(80)
H29	.2112(15)	-.2228(16)	.8035(22)	3.87(68)
H36	.5302(15)	.3060(15)	.6496(21)	2.97(65)
H37	.5534(20)	.3819(22)	.8118(27)	7.8(10)
H38	.5014(18)	.3326(19)	.9602(25)	6.18(91)
H39	.4257(17)	.2154(17)	.9468(24)	5.15(79)
H42	.0905(19)	-.0261(20)	.6223(27)	7.0(10)
H43	.0763(24)	-.0185(24)	.8020(33)	10.0(14)
H44	.1176(22)	.0972(23)	.8993(33)	9.5(13)
H45	.1667(21)	.2036(23)	.8082(30)	8.9(12)
H46	.1759(20)	.1839(21)	.6336(28)	8.1(10)
H48	.1203(18)	.0418(18)	.1438(25)	5.83(86)
H49	.0762(27)	-.0581(27)	.0121(38)	12.5(17)
H50	.0680(23)	-.1907(25)	.0713(33)	11.1(13)
H51	.0827(26)	-.2016(26)	.2727(35)	10.8(16)
H52	.1311(22)	-.0981(21)	.3931(31)	8.8(12)

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Table III. Observed and Calculated Structure Factor Amplitudes of $MgC_{32}H_{16}N_8 \cdot H_2O \cdot 2C_5H_5N$.

(Table to be reproduced photographically)

OBSERVED AND CALCULATED STRUCTURE FACTORS OF MAGNESIUM PHTHALOCYANIN.
FCA(0,0,0) = 5355

H	FOB	FCA
K,L=	0,	0
2	256	263
4	223	220
6	233	219
8	141	140
10	37	37
12	55	52
14	55	54
16	42	42
K,L=	1,	0
1	472	487
2	75	73
3	117	115
4	814	827
5	851	874
6	50	50
7	168	171
8	26	25
9	200	208
10	103	108
11	30	29
12	45	42
13	28	35
14	47	46
15	89	84
16	59	55
K,L=	2,	0
0	496	501
1	220	222
2	121	125
3	648	661
4	860	910
5	63	66
6	88	86
7	77	81
8	26	25
9	138	138
10	130	136
11	28	18
12	12	10
13	40	39
14	77	76
15	46	46
16	19	18
K,L=	3,	0
1	60	55
2	26	23
3	172	176
4	346	344
5	117	124
6	154	156
7	201	202
8	37	37
9	142	145
10	62	69
11	184	191
12	76	78
13	39	38
14	13	11
15	0	10*
16	0	7*
K,L=	4,	0
0	222	233
1	48	47
2	16	16
3	41	39
4	114	118
5	40	41
6	103	110
7	96	93
8	255	264
9	42	39
10	126	126
11	71	65
12	22	13
13	41	38
14	40	37
15	40	38
K,L=	5,	0
1	74	77
2	20	25
3	120	126
4	109	106
5	53	51
6	118	116
7	213	217
8	312	330
9	216	219
10	32	32
11	12	9
12	18	9
13	47	48
14	53	61
15	0	1*
K,L=	6,	0
0	419	407
1	107	112
2	28	25
3	35	30
4	189	190
5	185	186
6	47	51
7	30	27
8	104	106
9	55	55
10	26	25
11	124	128
12	105	106
13	84	81
14	57	53
15	13	9
K,L=	7,	0
1	0	1*
2	77	78
3	54	55
4	36	39
5	156	160
6	14	4
7	0	7*
8	47	51
9	23	24
10	75	77
11	57	65
12	105	111
13	0	3*
14	53	51
K,L=	8,	0
0	53	48
1	70	70
2	0	3*
3	38	43
4	254	261
5	77	77
6	63	66
7	56	60
8	96	101
9	17	12
10	12	4
11	91	100
12	35	39
13	44	45
14	91	90
K,L=	9,	0
1	118	117
2	74	72
3	187	191
4	50	46
5	78	77
6	47	44
7	75	72
8	63	66
9	41	42
10	26	20
11	0	1*
12	19	18
13	31	38
K,L=	10,	0
0	133	126
1	0	7*
2	11	8
3	143	142
4	88	89
5	45	45
6	44	45
7	12	15
8	56	57
9	0	8*
10	0	2*
11	13	10
12	78	75
13	76	76
K,L=	11,	0
1	11	11
2	116	111
3	80	76
4	20	18
5	17	16
6	41	37
7	44	52
8	85	93
9	67	65
10	68	73
11	48	55
12	37	39
K,L=	12,	0
0	142	134
1	17	13
2	17	16
3	103	105
4	33	37
5	45	47
6	13	13
7	0	9*
8	54	55
9	30	34
10	33	36
11	0	2*
K,L=	13,	0
1	13	15
2	84	83
3	49	68
4	18	18
5	61	63
6	0	12*
7	68	69
8	57	56
9	13	9
10	13	7
K,L=	14,	0
0	75	72
1	30	28
2	40	37
3	64	65
4	64	66
5	59	56
6	60	61
7	119	131
8	42	46
9	0	1*
K,L=	15,	0
1	95	89
2	38	34
3	36	33
4	96	94
5	75	78
6	59	56
7	64	71
K,L=	16,	0
0	131	123
1	99	90
2	14	20
3	117	118
4	46	49
5	64	55
K,L=	0,	1
-15	113	112
-13	31	27
-11	135	138
-9	184	193
-7	229	234
-5	31	30
-3	212	224
-1	196	183
1	652	652
3	271	282
5	273	268
7	55	54
9	135	141
11	48	48
13	0	13*
15	90	86
K,L=	1,	1
-16	36	40
-15	27	23
-14	74	72
-13	38	34
-12	17	12
-11	20	16
-10	28	23
-9	26	25
-8	47	48
-7	35	35
-6	72	78
-5	293	293
-4	60	60
-3	398	388
-2	148	150
-1	43	47
0	484	479
1	146	139
2	128	125
3	208	200
4	484	506
5	29	26
6	258	251
7	67	65
8	156	151
9	60	42
10	11	9
11	22	22
12	41	41
13	43	36
14	66	62
15	50	44
K,L=	2,	1
-16	23	22
-15	73	71
-14	50	56
-13	54	55
-12	61	59
-11	131	138
-10	19	17
-9	17	11
-8	106	110
-7	151	155
-6	100	103
-5	80	79
-4	766	759
-3	477	473
-2	72	74
-1	121	122
0	114	113
1	348	339
2	243	248
3	476	462
4	1484	1564
5	452	454
6	44	46
7	132	132
8	160	162
9	330	328
10	0	5*
11	176	178
12	97	97
13	58	56
14	50	51
15	27	33
K,L=	3,	1
-16	23	20
-15	0	5*
-14	19	11
-13	0	1*
-12	179	176
-11	57	55
-10	50	51
-9	106	108
-8	46	45
-7	74	75
-6	8	10
-5	115	114
-4	685	692
-3	122	119
-2	120	127
-1	223	225
0	61	59
1	852	908
2	326	322
3	135	134
4	975	957
5	584	592
6	201	203
7	244	244
8	119	123
9	65	68
10	66	63
11	27	25
12	78	74
13	32	31
14	73	71
15	40	38
K,L=	4,	1
-16	23	16
-15	14	12
-14	27	24
-13	18	18
-12	13	1
-11	159	155
-10	42	40
-9	142	140
-8	230	223
-7	29	27
-6	123	118
-5	43	39
-4	202	203
-3	89	91
-2	0	4*
-1	12	12
0	239	240
1	347	350
2	107	106
3	56	54
4	52	58
5	32	30
6	91	91
7	314	328
8	558	568
9	108	105
10	59	58
11	0	6*
12	57	59
13	79	80
14	65	67
15	54	52
K,L=	5,	1
-15	30	30
-14	23	28
-13	70	71
-12	73	70
-11	12	15
-10	88	79
-9	107	111
-8	249	249
-7	27	27
-6	15	7
-5	27	29
-4	36	35
-3	263	265
-2	7	6
-1	214	215
0	0	5*
1	186	188
2	98	93
3	165	170
4	78	77
5	194	197
6	107	110
7	121	117
8	257	256
9	84	87
10	20	19
11	80	88
12	75	77
13	40	47
14	27	34
15	54	56
K,L=	6,	1
-15	19	18
-14	36	34
-13	42	39
-12	13	17
-11	28	22
-10	160	160
-9	35	34
-8	39	41
-7	227	225
-6	139	140
-5	121	124
-4	77	83
-3	8	8
-2	0	8*
-1	55	53
0	80	78
1	183	180
2	11	14
3	173	178
4	116	114
5	54	56
6	0	4*
7	88	91
8	89	94
9	23	27
10	43	45
11	69	67
12	64	66
13	60	59
14	19	18
K,L=	7,	1
-15	19	13
-14	19	13
-13	73	76
-12	32	27
-11	53	57
-10	61	61
-9	64	64
-8	16	9
-7	95	93
-6	51	51
-5	28	28
-4	77	79
-3	227	210
-2	24	21
-1	20	24
0	121	125
1	330	325
2	91	93
3	113	111
4	93	90
5	165	163
6	35	32
7	71	74
8	80	79
9	50	45
10	35	35
11	13	15
12	117	118
13	63	63
14	35	33
K,L=	8,	1
-14	38	33
-13	0	12*
-12	100	97
-11	13	13
-10	77	77
-9	0	8*
-8	86	85
-7	103	96
-6	21	19
-5	93	95
-4	148	145
-3	52	56
-2	190	187
-1	46	45
0	252	233
1	157	156
2	45	45
3	161	159
4	31	23
5	82	80
6	11	5
7	11	5
8	66	66
9	17	5
10	97	98
11	35	34
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-6	102	108
-5	151	158
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-2	58	60
-1	87	85
0	58	57
1	135	132
2	57	58
3	52	49
4	29	27
5	123	124
6	125	120
7	34	34
8	65	62
9	0	6*
10	0	5*
11	50	51
12	19	11
13	0	4*
K,L=	2,	4
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-11	12	6
-10	131	124
-9	85	81
-8	204	206
-7	90	94
-6	79	87
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-4	159	153
-3	63	64
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-1	41	39
0	28	25
1	0	5*
2	58	55
3	34	37
4	70	71
5	94	93
6	47	46
7	21	18
8	16	14
9	50	49
10	71	66
11	57	54
12	13	8
13	35	34
K,L=	3,	4
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-12	12	11
-11	124	123
-10	27	30
-9	71	68
-8	0	1*
-7	43	44
-6	208	211
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-4	18	19
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-1	8	9
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1	60	54
2	8	12
3	139	137
4	22	22
5	125	131
6	289	281
7	48	49
8	149	144
9	81	74
10	13	8
11	91	51
12	19	15
13	44	40
K,L=	4,	4
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-15	23	20
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-12	18	15
-11	17	14
-10	92	90
-9	214	211
-8	18	13
-7	9	10
-6	204	208
-5	182	172
-4	20	18
-3	171	171
-2	162	167
-1	117	108
0	144	147
1	92	91
2	38	38
3	176	174
4	121	123
5	159	158
6	11	7
7	79	72
8	39	39
9	35	30
10	110	107
11	19	14
12	53	51
13	13	1
K,L=	5,	4
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-13	18	12
-12	13	3
-11	149	167
-10	67	64
-9	86	82
-8	15	11
-7	61	62
-6	55	52
-5	148	145
-4	0	1*
-3	210	208
-2	181	190
-1	8	5
0	43	45
1	86	84
2	253	251
3	0	10*
4	20	25
5	73	76
6	83	87
7	158	154
8	78	78
9	152	153
10	45	45
11	56	54
12	46	43
13	23	19
K,L=	6,	4
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-14	19	12
-13	93	91
-12	39	35
-11	35	34
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-9	11	13
-8	92	90
-7	32	31
-6	91	89
-5	289	273
-4	128	132
-3	165	170
-2	18	24
-1	237	233
0	149	147
1	74	70
2	350	316
3	20	13
4	85	84
5	21	21
6	125	124
7	94	88
8	30	24
9	38	39
10	96	98
11	30	30
12	0	4*
K,L=	7,	4
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-14	52	55
-13	82	80
-12	71	67
-11	50	47
-10	109	106
-9	35	29
-8	57	58
-7	177	176
-6	126	125
-5	60	61
-4	10	6
-3	76	74
-2	177	170
-1	0	15*
0	73	73
1	0	3*
2	86	85
3	62	65
4	0	4*
5	163	167
6	44	45
7	100	100
8	67	68
9	26	24
10	13	16
11	13	8
12	13	7
K,L=	8,	4
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-13	13	14
-12	95	98
-11	22	22
-10	113	115
-9	117	115
-8	27	24
-7	46	48
-6	131	138
-5	11	4
-4	26	19
-3	66	69
-2	99	99
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1	121	122
2	81	73
3	58	60
4	23	25
5	29	28
6	45	50
7	0	10*
8	45	47
9	130	129
10	0	5*
11	42	42
K,L=	9,	4
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-13	44	32
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-11	35	32
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-9	52	54
-8	17	16
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-6	44	42
-5	136	134
-4	49	51
-3	15	17
-2	0	9*
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0	0	15*
1	0	5*
2	63	63
3	197	201
4	29	36
5	17	24
6	99	106
7	57	62
8	72	72
9	13	20
10	33	38
11	0	2*
K,L=	10,	4
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-12	23	17
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-10	23	30
-9	32	34
-8	42	38
-7	63	61
-6	32	26
-5	12	6
-4	41	40
-3	61	62
-2	102	102
-1	0	11*
0	20	24
1	0	8*
2	50	47
3	169	174
4	30	27
5	174	173
6	45	43
7	0	4*
8	19	26
9	46	51
10	107	107
K,L=	11,	4
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-11	13	10
-10	62	62
-9	53	52
-8	45	46
-7	13	2
-6	66	71
-5	86	89
-4	40	55
-3	80	75
-2	80	79
-1	121	120
0	24	32
1	159	161
2	244	247
3	24	21
4	70	72
5	32	38
6	19	22
7	0	14*
8	42	42
9	13	23
K,L=	12,	4
-11	13	11
-10	45	41
-9	60	59
-8	59	58
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-6	142	141
-5	46	52
-4	41	37
-3	62	58
-2	157	157
-1	85	82
0	22	23
1	18	0
2	39	41
3	54	51
4	0	7*
5	35	38
6	60	60
7	13	7
8	40	40
K,L=	13,	4
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-9	0	5*
-8	13	11
-7	0	5*
-6	84	80
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-4	13	18
-3	135	133
-2	0	2*
-1	66	65
0	96	96
1	29	27
2	26	24
3	19	14
4	13	14
5	44	42
6	113	116
7	32	31
K,L=	14,	4
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-7	38	38
-6	59	53
-5	19	16
-4	30	35
-3	90	87
-2	108	104
-1	75	78
0	35	35
1	52	53
2	107	102
3	63	62
4	42	43
5	40	44
K,L=	15,	4
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-4	59	56
-3	0	9*
-2	75	78
-1	56	60
0	27	28
1	108	107
2	102	98
3	13	8
K,L=	0,	5
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-9	60	60
-7	47	45
-3	18	24
-5	383	363
-1	296	286
1	55	55
3	177	174
3	177	174
5	20	15
7	233	233
9	0	1*
11	33	28
13	0	2*
K,L=	1,	5
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-15	40	41
-14	43	43
-13	98	95
-12	40	36
-11	45	42
-10	34	35
-9	208	212
-8	155	163
-7	25	23
-6	102	105
-5	381	360
-4	179	181
-3	201	194
-2	96	103
-1	24	24
0	16	10
1	42	40
2	180	191
3	91	91
4	105	110
5	67	69
6	69	67
7	69	66
8	12	9
9	50	45
10	57	56
11	13	17
12	23	21
13	35	30
K,L=	2,	5
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-15	23	20
-14	13	3
-13	83	78
-12	27	28
-11	93	95
-10	54	56
-9	96	91
-8	26	23
-7	83	85
-6	38	38
-5	86	87
-4	258	247
-3	37	39
-2	27	27
-1	185	182
0	41	41
1	9	3
2	78	71
3	130	129
4	52	50
5	61	60
6	86	84
7	12	5
8	24	26
9	0	3*
10	23	22
11	23	23
12	33	33
K,L=	3,	5
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-15	13	3
-14	13	7
-13	48	46
-12	99	96
-11	52	51
-10	11	12
-9	26	23
-8	50	52
-7	67	66
-6	63	59
-5	336	320
-4	41	43
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-2	173	177
-1	182	169
0	93	91
1	217	213
2	55	49
3	151	151
4	62	61
5	54	50
6	39	39
7	12	9
8	73	74
9	36	36
10	64	63
11	48	50
12	23	24
K,L=	4,	5
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-15	0	3*
-14	19	17
-13	29	27
-12	69	61
-11	70	68
-10	20	19
-9	31	32
-8	130	122
-7	109	107
-6	132	129
-5	107	105
-4	214	218
-3	29	29
-2	131	123
-1	97	91
0	62	60
1	124	127
2	46	46
3	127	118
4	18	15
5	100	99
6	145	140
7	21	14
8	21	21
9	79	73
10	30	29
11	58	60
12	44	38
K,L=	5,	5
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-15	27	22
-14	55	52
-13	64	69
-12	51	48
-11	12	2
-10	17	10
-9	91	94
-8	0	3*
-7	21	24
-6	74	74
-5	301	295
-4	23	21
-3	171	170
-2	155	168
-1	127	124
0	36	36
1	54	50
2	87	90
3	56	52
4	97	99
5	67	62
6	33	30
7	38	33
8	36	31
9	71	64
10	156	148
11	63	58
12	13	2
K,L=	6,	5
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-14	13	7
-13	14	13
-12	13	12
-11	18	17
-10	51	56
-9	84	85
-8	74	73
-7	86	90
-6	118	125
-5	20	17
-4	54	56
-3	51	51
-2	14	9
-1	326	325
0	31	26
1	168	166
2	42	41
3	30	24
4	80	83
5	20	21
6	61	61
7	80	84
8	60	62
9	32	34
10	33	36
11	19	10
K,L=	7,	5
-15	26	29
-14	13	12
-13	0	1*
-12	13	3
-11	18	15
-10	66	60
-9	68	71
-8	0	2*
-7	16	14
-6	49	51
-5	11	5
-4	36	39
-3	16	13
-2	93	89
-1	34	32
0	29	32
1	32	34
2	129	132
3	31	23
4	86	87
5	34	36
6	70	67
7	0	6*
8	57	56
9	94	97
10	0	13*
11	37	36
K,L=	8,	5
-14	58	56
-13	65	67
-12	44	41
-11	29	29
-10	84	79
-9	41	39
-8	38	34
-7	37	32
-6	11	12
-5	38	38
-4	125	128
-3	0	6*
-2	44	44
-1	180	183
0	72	75
1	95	96
2	0	16*
3	16	27
4	34	37
5	39	40
6	88	92
7	73	80
8	26	26
9	0	3*
10	13	10
K,L=	9,	5
-14	18	20
-13	51	50
-12	58	62
-11	13	12
-10	45	41
-9	13	10
-8	115	113
-7	0	1*
-6	12	15
-5	31	31
-4	51	54
-3	0	12*
-2	62	66
-1	79	83
0	36	32
1	46	48
2	12	22
3	168	165
4	58	64
5	121	124
6	105	102
7	17	9
8	62	62
9	46	36
10	79	84
K,L=	10,	5
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-12	52	50
-11	13	9
-10	23	22
-9	111	111
-8	54	53
-7	47	46
-6	97	96
-5	95	97
-4	32	29
-3	32	24
-2	12	17
-1	38	42
0	76	75
1	69	71
2	156	153
3	73	75
4	26	27
5	0	2*
6	19	24
7	80	84
8	27	30
9	26	25
K,L=	11,	5
-12	0	2*
-11	13	8
-10	63	61
-9	51	44
-8	46	46
-7	45	49
-6	0	1*
-5	65	60
-4	13	13
-3	31	26
-2	61	60
-1	58	59
0	24	27
1	28	20
2	60	61
3	13	15
4	0	9*
5	30	30
6	60	66
7	80	77
8	32	31
K,L=	12,	5
-11	13	4
-10	23	25
-9	19	16
-8	52	52
-7	0	1*
-6	23	33
-5	43	40
-4	73	78
-3	45	45
-2	22	25
-1	48	54
0	48	46
1	32	32
2	19	23
3	32	33
4	44	42
5	27	13
6	145	140
7	0	3*
K,L=	13,	5
-9	37	36
-8	23	17
-7	13	7
-6	23	17
-5	73	68
-4	13	8
-3	48	48
-2	32	27
-1	10	37
0	13	19
1	53	56
2	88	90
3	50	50
4	23	24
5	37	48
6	13	24
K,L=	14,	5
-8	23	15
-7	40	42
-6	65	57
-5	33	31
-4	60	62
-3	13	13
-2	102	101
-1	42	42
0	84	83
1	86	82
2	68	81
3	37	41
4	13	9
K,L=	15,	5
-5	56	52
-4	0	3*
-3	23	27
-2	121	122
-1	13	8
0	49	49
1	49	54
K,L=	0,	6
-16	49	66
-14	104	102
-12	155	155
-10	16	8
-8	52	49
-6	109	107
-4	214	214
-2	226	231
0	321	323
2	64	68
4	75	77
6	159	160
8	82	85
10	56	58
12	26	27
K,L=	1,	6
-16	23	20
-15	13	15
-14	19	16
-13	98	99
-12	25	23
-11	24	27
-10	23	23
-9	58	57
-8	61	56
-7	202	204
-6	17	19
-5	268	256
-4	105	98
-3	106	105
-2	128	128
-1	322	303
0	13	13
1	57	57
2	81	78
3	196	198
4	143	140
5	63	65
6	35	33
7	111	116
8	13	26
9	18	19
10	68	67
11	33	29
12	18	16
K,L=	2,	6
-16	27	17
-15	19	22
-14	63	61
-13	13	1
-12	18	11
-11	53	68
-10	65	68
-9	72	70
-8	100	96
-7	80	78
-6	26	24
-5	9	9
-4	126	129
-3	39	42
-2	178	178
-1	259	247
0	207	200
1	26	21
2	42	43
3	111	139
4	93	91
5	51	51
6	60	58
7	12	16
8	13	6
9	41	38
10	0	5*
11	52	45
K,L=	3,	6
-16	42	43
-15	33	32
-14	23	22
-13	13	11
-12	50	44
-11	102	102
-10	20	25
-9	41	42
-8	65	62
-7	36	40
-6	41	39
-5	60	53
-4	10	13
-3	42	44
-2	200	198
-1	69	71
0	270	261
1	42	44
2	89	89
3	52	51
4	134	129
5	26	24
6	59	61
7	22	26
8	109	108
9	19	18
10	0	0*
11	73	71
K,L=	4,	6
-16	65	70
-15	65	63
-14	30	24
-13	26	23
-12	0	3*
-11	12	4
-10	78	74
-9	20	12
-8	106	106
-7	47	49
-6	36	35
-5	77	74
-4	124	117
-3	76	77
-2	10	9
-1	42	39
0	134	130
1	20	17
2	184	181
3	15	14
4	87	88
5	33	31
6	30	27
7	13	1
8	13	9
9	13	10
10	0	4*
11	67	62
K,L=	5,	6
-15	56	56
-14	0	4*
-13	90	88
-12	13	7
-11	18	16
-10	27	30
-9	84	83
-8	16	16
-7	54	53
-6	102	99
-5	77	79
-4	25	28
-3	25	22
-2	44	40
-1	112	112
0	10	3
1	110	112
2	89	82
3	77	79
4	36	37
5	84	80
6	96	92
7	38	34
8	54	51
9	13	5
10	13	13
11	29	30
K,L=	6,	6
-15	44	48
-14	43	39
-13	0	5*
-12	91	96
-11	57	59
-10	63	63
-9	39	33
-8	165	168
-7	42	43
-6	34	29
-5	19	19
-4	139	138
-3	57	59
-2	69	67
-1	82	75
0	32	30
1	58	64
2	118	124
3	90	93
4	0	5*
5	12	16
6	52	51
7	41	41
8	0	6*
9	40	40
10	19	17
K,L=	7,	6
-14	0	13*
-13	0	2*
-12	53	48
-11	18	13
-10	18	19
-9	28	26
-8	95	95
-7	89	88
-6	46	40
-5	186	193
-4	11	4
-3	22	27
-2	106	103
-1	102	99
0	42	36
1	53	51
2	12	4
3	77	75
4	34	34
5	85	84
6	58	61
7	62	59
8	23	27
9	19	13
10	44	42

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| | | |

Table IV. Intramolecular Bond Distances (in Å) of MgPc · H_2O · 2 C_5H_5N. Standard deviations are 0.002 Å for Mg-N, 0.003 Å for Mg-O, 0.003-0.004 Å for C-N in the Pc ring, 0.004-0.005 Å for C-C in the Pc ring, 0.006 Å for C-N in the pyridine rings, 0.007-0.010 Å for C-C in the pyridine rings, 0.02-0.03 Å for C-H in the Pc ring, 0.03-0.04 Å for O-H in the H_2O, and 0.03-0.05 Å for C-H in the pyridine rings.

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

Table V. Intramolecular Bond Angles (in ^{o}) of MgPc $\cdot$ H_2O $\cdot$ 2 C_5H_5N. Standard deviations are 0.1^{o} for all angles involving Mg, 0.2-0.3^{o} for all angles in the Pc ring, and 0.4-0.6^{o} for all angles in the pyridine rings.

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

Table VI. Intermolecular Spacing Less Than 3.5 Å for C···C and C···N Approaches and Less Than 3.0 Å for C···H and N···H Approaches. Standard deviations are 0.02-0.04 Å for distances involving hydrogens and 0.004-0.006 Å for those not involving hydrogen.

Position of Adjacent Molecule 2	Atom of 1	Atom of 2	Distance (Å)
$1-x,-y,1-z$[a]	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[b]	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
$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$	N(1)	H(50)	2.66
	C(9)	H(51)	2.80
	C(5)	H(17)	2.84
$\frac{1}{2}-x,\frac{1}{2}+y,\frac{3}{2}-z$	C(40)	H(29)	2.80
$\frac{1}{2}-x,-\frac{1}{2}+y,\frac{3}{2}-z$	N(21)	H(45)	2.61
	C(29)	H(46)	2.84

[a]Position of the other molecule in the "dimer."

[b]Only the closest pyridine-MgPc distances are listed.

Table VII. Rotation Angles (in °) 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

Figure Captions

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

Figure 2. The central region of the MgPc molecule. The equivalent Mg-N and N···N distances have been averaged.

Figure 3. Averaged bond distances (in Å) and bond angles (in °) of MgPc. Standard deviations of the bond distances and angles are 0.006 Å and 0.4°.

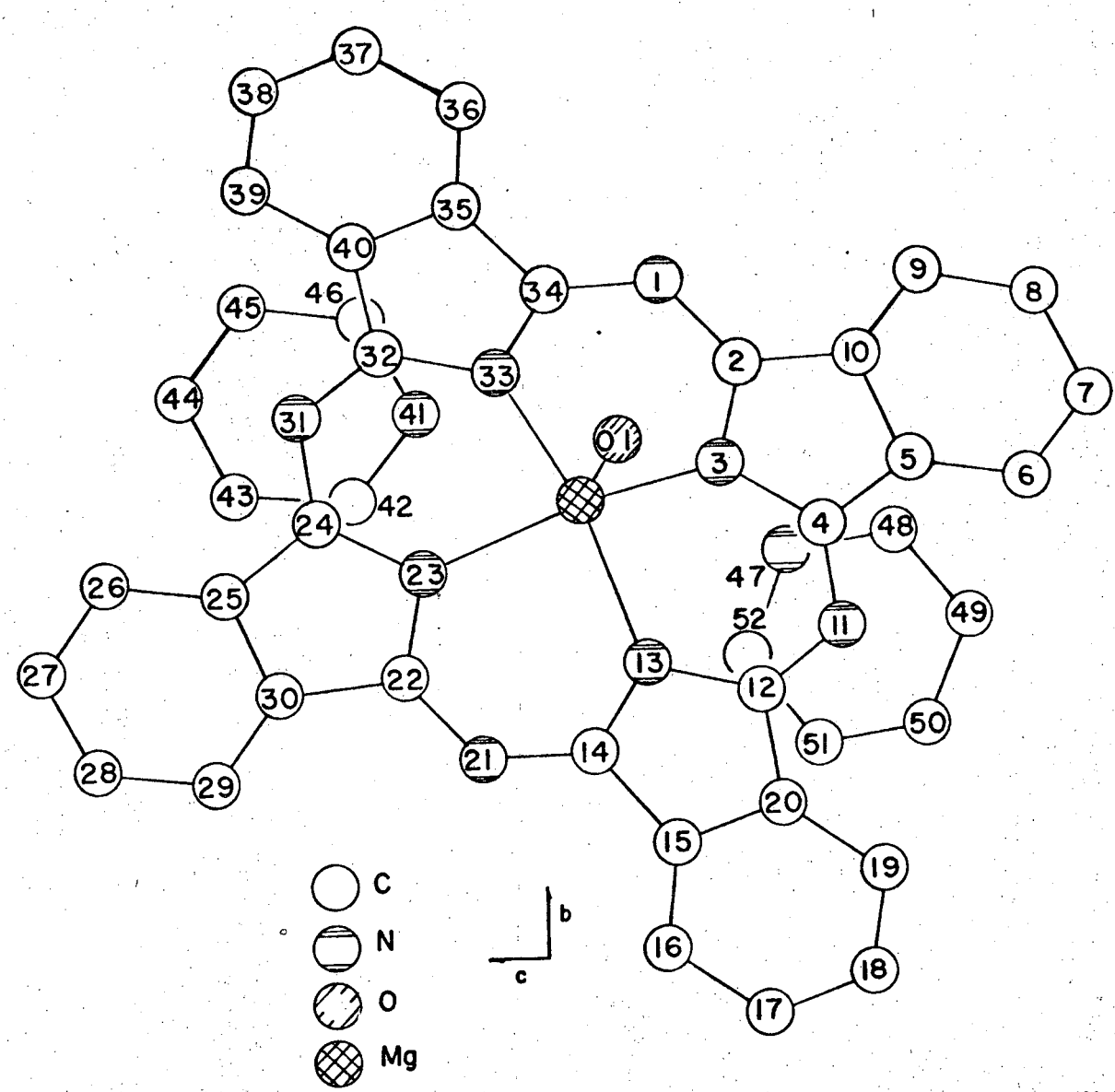
Figure 4. Deviations (x 100 in Å) from the least squares plane of the four central nitrogen atoms.

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

Figure 6. Stereoscopic view of the contents of the unit cell looking down the c axis. All C, N, O, and Mg atoms as well as the two hydrogens of the water molecule are shown. The hydrogen bonds connecting the water molecyle to the two pyridine molecules are drawn in.

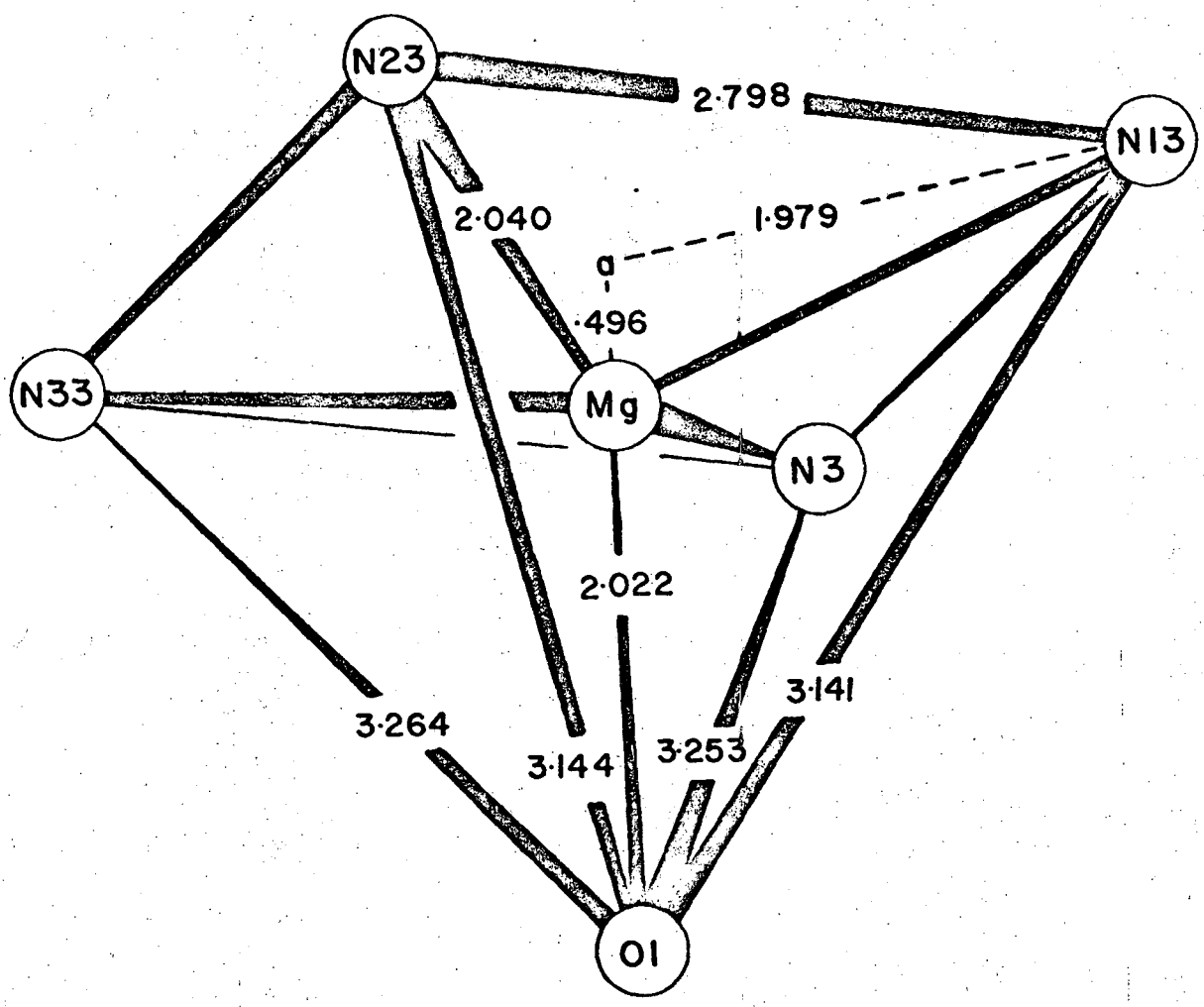
Figure 7. Normal projection of parallel phthalocyanins in the dimer. One molecule is drawn with solid lines, the other with dashed lines.

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



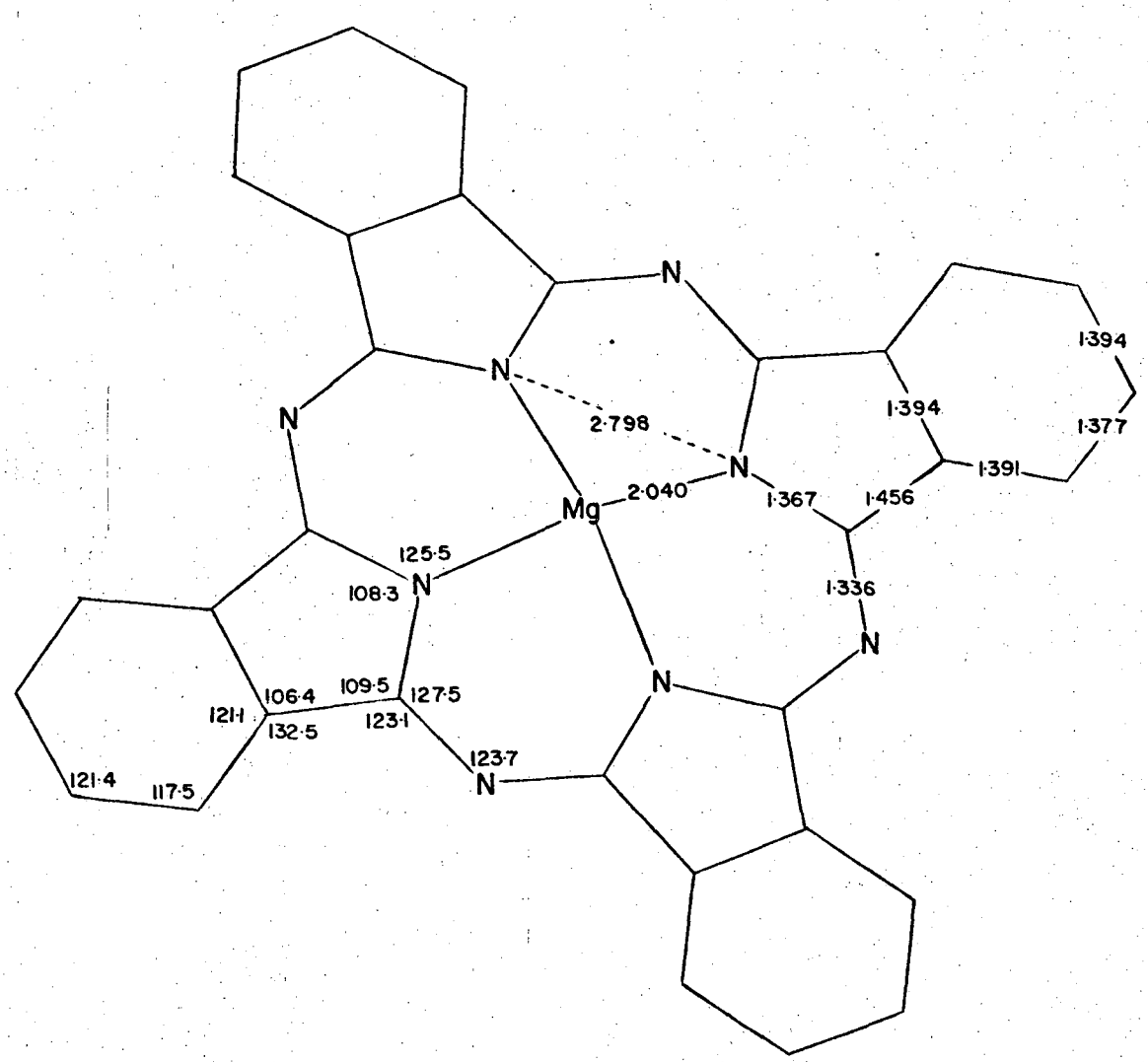
XBL 691-18

Figure 2. The central region of the MgPc molecule. The equivalent Mg-N and N•••N distances have been averaged.



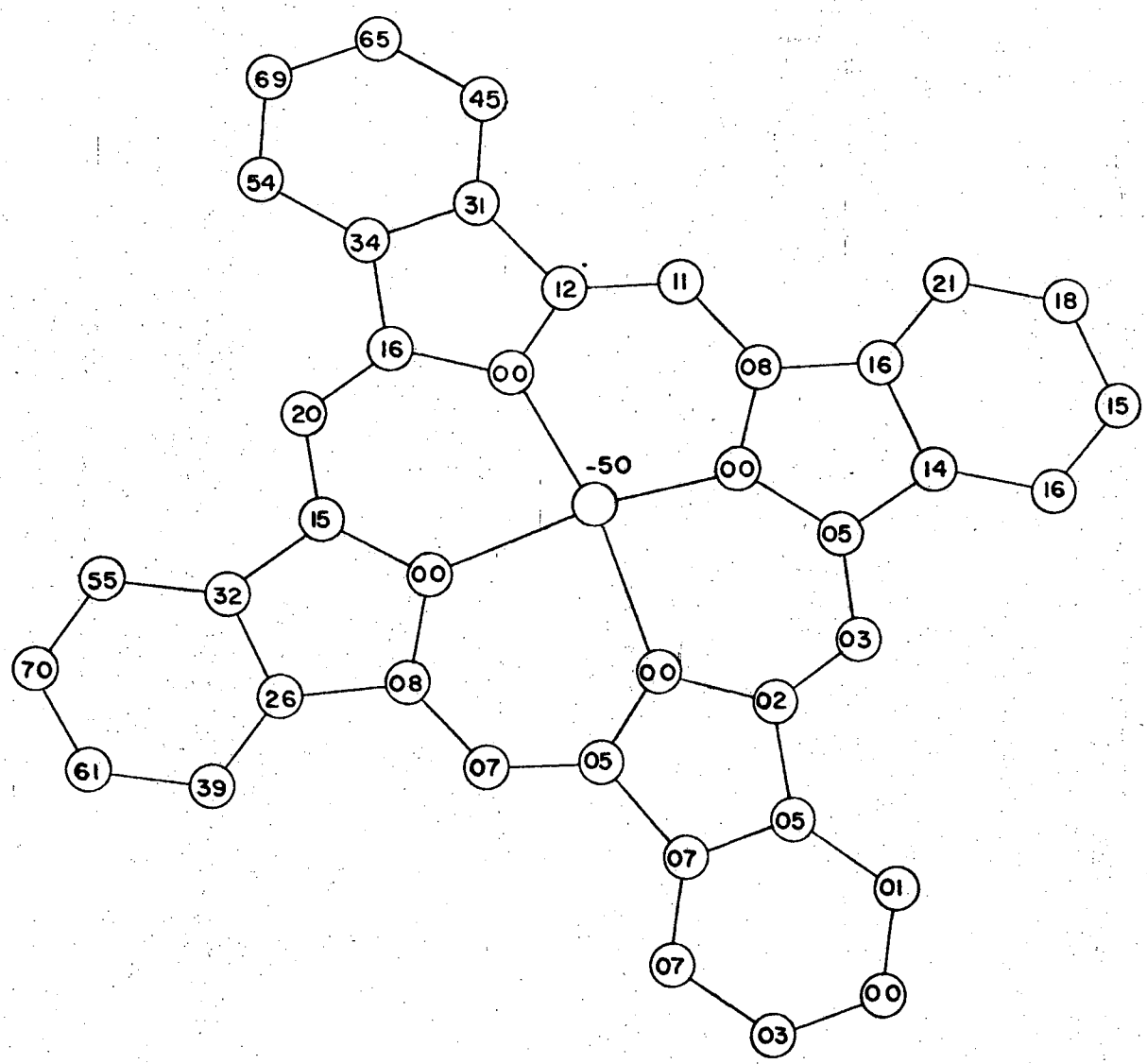
XBL 691-15

Figure 3. Averaged bond distances (in Å) and bond angles (in °) of MgPc. Standard deviations of the bond distances and angles are 0.006 Å and 0.4°.



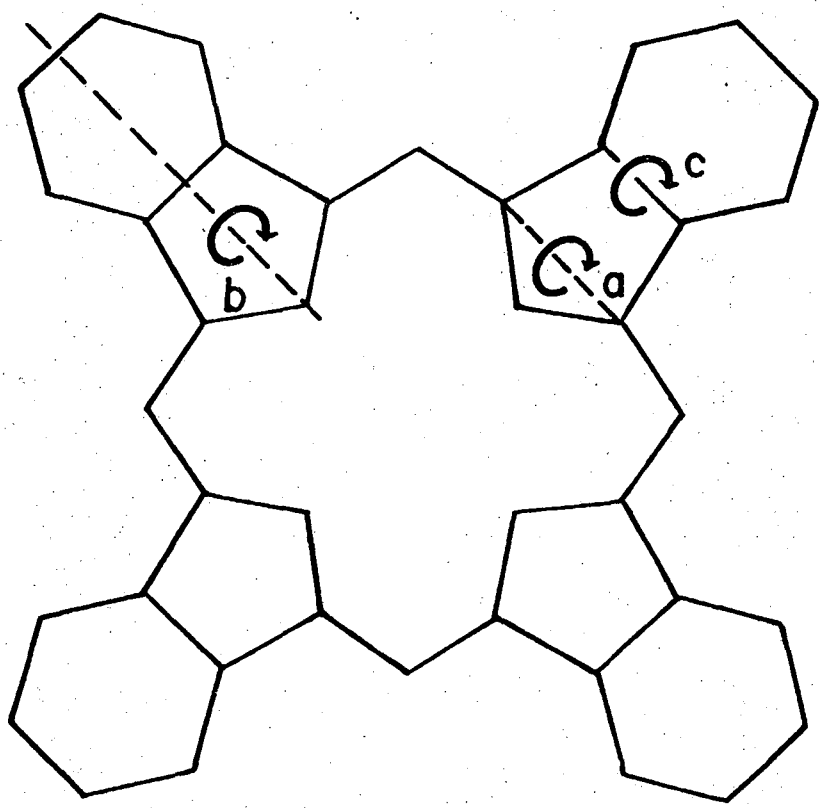
XBL 691-17

Figure 4. Deviations (x100 in Å) from the least squares plane of the four central nitrogen atoms.



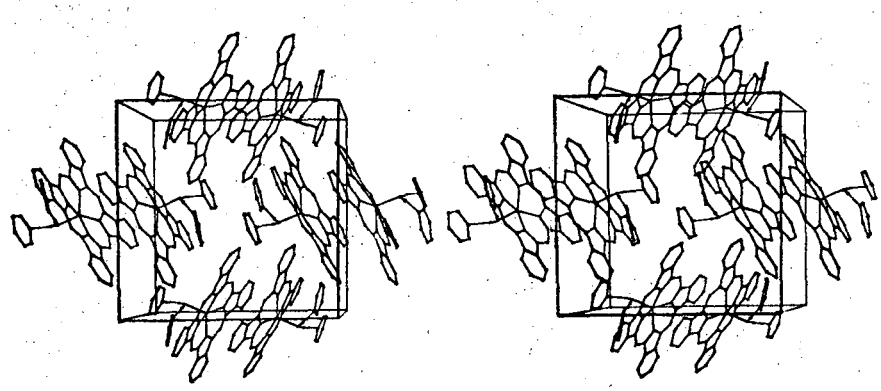
XBL 691-16

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



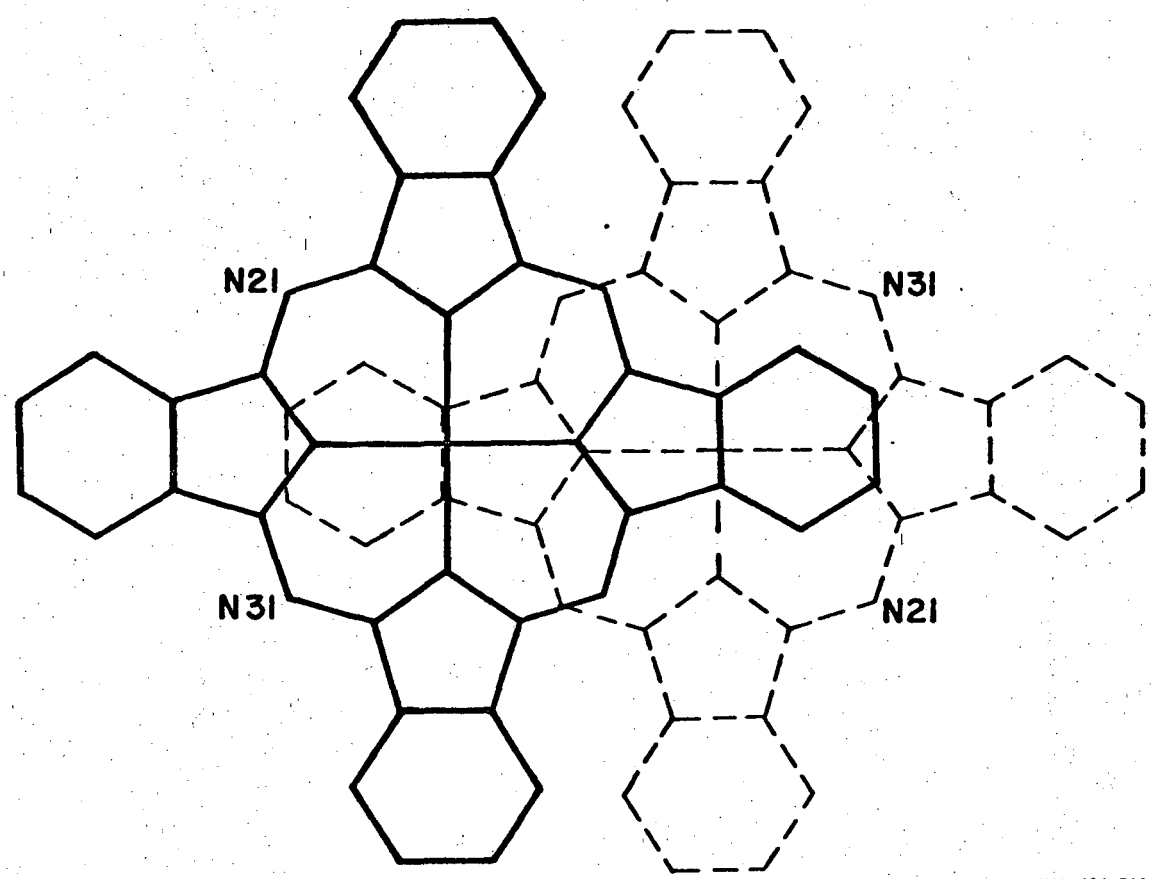
XBL 695-461

Figure 6. Stereoscopic view of the contents of the unit cell looking down the c axis. All C,N,O, and Mg atoms as well as the two hydrogens of the water molecule are shown. The hydrogen bonds connecting the water molecule to the two pyridine molecules are drawn in.



XBL 691-162

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



XBL 694-368

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