# Lawrence Berkeley National Laboratory

**Recent Work** 

# Title

STRUCTURE AND CHEMISTRY OF THE PORPHYRINS. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE MONOHYDRATED DIPYRIDINATED MAGNESIUM PHTHALOCYANIN COMPLEX

# Permalink

https://escholarship.org/uc/item/0t78s8z6

# Authors

Fischer, Mark S. Templeton, David H. Zalkin, Allan <u>et al.</u>

# **Publication Date**

1970-02-01

Submitted to Journal American Chemical Society

UCRL-19554 Preprint

#### STRUCTURE AND CHEMISTRY OF THE PORPHYRINS. THE CRYSTAL AND MOLECULAR STRUCTURE OF THE MONOHYDRATED DIPYRIDINATED MAGNESIUM PHTHALOCYANIN COMPLEX

### RECEIVED LAWRENCE RADIATION LABORATORY

MAR 5 1970

February 1970

Mark S. Fischer, David H. Templeton,

Allan Zalkin, and Melvin Calvin

LIBRARY AND DOCUMENTS SECTION

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

LAWRENCE RADIATION LABORATORY

#### **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-19554

Structure and Chemistry of the Porphyrins. The Crystal and Molecular Structure of the Monohydrated Dipyridinated Magnesium Phthalocyanin Complex.<sup>1</sup>

-1-

Mark S. Fischer, David H. Templeton, Allan Zalkin and Melvin Calvin

Contribution from the Department of Chemistry, University of California and the Lawrence Radiation Laboratory, Berkeley, California 94720

The crystal and molecular structure of the monohydrated, Abstract: dipyridinated magnesium phthalocyanin, MgC32H16N8 H20.2C5H5N, has been determined by x-ray diffraction. The crystals are monoclinic, space group P2<sub>1</sub>/n, with cell parameters <u>a</u> = 17.098 ± 0.003 Å, <u>b</u> = 16.951 ± 0.003 Å,  $\underline{c} = 12.449 \pm 0.003$  Å, and  $\beta = 105.88 \pm 0.003$  °. The structure was solved by a combination of statistical and Fourier All hydrogen atoms were located, and least squares refinemethods. ment 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<sup>7,8</sup>, and by Vogt, Zalkin and Templeton<sup>9</sup>. 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 (See below.) studied by Robertson was the magnesium derivative<sup>4</sup> (MgPc). A 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  $\beta$ -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. detailed structure of a magnesium porphyrin, particularly if solvated, would help in understanding the chemistry of magnesium porphyrin complexes<sup>10-12</sup> and of chlorophyll<sup>13</sup>.



L

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), (101), and (210).

Weissenberg photographs of the O<u>k</u><sup>l</sup>, 1<u>k</u><sup>l</sup>, 2<u>k</u><sup>l</sup>, 3<u>k</u><sup>l</sup>, and 4<u>k</u><sup>l</sup> levels indicated Laue symmetry 2/m. The observed systematic absences (O<u>k</u>O, for <u>k</u>  $\neq$  2<u>n</u>; <u>h</u>O<u>l</u>, for <u>h</u>+<u>l</u>  $\neq$  2<u>n</u>) correspond to the monoclinic space group P2<sub>1</sub>/n, with the four general equivalent positions: <u>x,x,z</u>; -<u>x,-</u><u>x,-</u><u>z</u>; <u>k</u>+<u>x,k</u>-<u>x</u>,<u>k</u>+<u>z</u>; <u>k</u>-<u>x</u>,<u>k</u>+<u>x</u>,<u>k</u>-<u>z</u>. 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 <u>h</u>OO, OO<u>l</u>, O<u>k</u>O, <u>h</u>O<u>h</u>, and <u>h</u>O<u>h</u> reflections. The alpha doublet ( $\lambda$ =1.5405 Å for CuKa<sub>1</sub>) was resolved for those reflections of highest order. The cell dimensions are <u>a</u> = 17.098 ± 0.003 Å,

<u>b</u> = 16.951 ± 0.003 Å, <u>c</u> = 12.449 ± 0.003 Å, and  $\beta$  = 105.88 ± 0.03°. The observed density of 1.368  $\pm$  0.015 g cm<sup>-3</sup>, which was determined by flotation in an aqueous ZnBr, 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<sup>3</sup>. The calculated densities for one MgPc, 12 MgPc, and one MgPc and two pyridine molecules are 1.025, 1.539, and 1.329 g cm<sup>-3</sup>, 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 a axis coincided with the instrument  $\phi$  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  $\ge 1.006$  Å (20  $\le 100^{\circ}$ ) 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  $\varphi$  and  $\chi$ . 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 h00 reflections were observed as a function of the orystal orientation, and no absorption correction ( $\mu = 9.1 \text{ cm}^{-1}$ ) was

applied.

Atomic scattering factors of Cromer and Mann<sup>14</sup> for the non-hydrogen atoms and those of Stewart, Davidson, and Simpson<sup>15</sup> for the hydrogen atoms were used. The anomalous dispersion corrections given by Cromer<sup>16</sup>  $(\Delta f' = 0.15, \Delta f'' = 0.19)$  were used for magnesium. The function minimized by least squares was  $R_2^2 = \Sigma w (\Delta F)^2 / \Sigma w (F_0)^2$ . 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<sup>17</sup>; 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.<sup>18</sup>.

### Solution and Refinement of the Structure

Normalized structure factors,  $\underline{\underline{E}}_{\underline{\underline{n}}}$ , were calculated using Wilson's Method<sup>19</sup>. The phases of the highest 181 E values  $\geq 2.0$  were determined from Long's sign determination program<sup>17</sup> which iteratively applies the equation:  $\operatorname{sign}(\underline{\underline{E}}_{\underline{\underline{n}}}) = \operatorname{sign}(\underline{\Sigma}_{\underline{\underline{k}}} \underline{\underline{E}}_{\underline{\underline{k}}} \underline{\underline{n}}_{\underline{\underline{k}}})$ . The fixed positive phases of the 135, 014, and 132 reflections defined the origin, and the phases of an additional four reflections 024, 381, 192, and 115 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  $C = \sum_{\underline{\underline{n}}} \sum_{\underline{\underline{E}}} \underline{\underline{E}} \underline{\underline{E}} \underline{\underline{E}} \underline{\underline{L}} - \underline{\underline{k}} |$ 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  $\underline{\underline{F}}$  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  $\underline{\underline{F}}$  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 <u>F</u>-values (i.e. the normalized transform of the electron density) for the <u>hOl</u> data. This technique suggested that the orientation of the molecule in the plane agreed with the <u>E</u> 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  $\underline{E}$  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  $\exp(-\underline{h}^2\beta_{11}-\underline{k}^2\beta_{22})$  $-\underline{l}^2\beta_{33}-2\underline{h}^{1}\beta_{12}-2\underline{k}l\beta_{23}-2\underline{h}l\beta_{13}$ ) were used for the 54 atoms. A

diagonal least squares refinement of the 487 parameters including the scale factor k reduced  $R_{11}$  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  $|F_0/F_c|$  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  $F_0^i = F_0(1 + (EF)(I))$ , where the extinction factor EF is a constant = 5 x  $10^{-7}$ , 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  $|F_0/F_c|$  or  $w^{\frac{1}{2}}|4F|$  as a function of intensity or Brazz angle. In a Fourier synthesis of AF 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 <u>bc</u> 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  $|F_0|$  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<sup>2-9</sup> to within the respective standard deviations. The precision, however, is greater by at in this work least a factor of two for the MgPcAthan for the other Pc's.

The environment around the central magnesium atom is depicted A in Figure 2. The 2.022  $\pm$  0.003 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<sub>2</sub> distances for the six-

coordinate magnesium atom in the crystals  $Ce_2Mg_3(NO_3)_{12}^{24}H_2O$ (2.06 ± .01 Å)<sup>21</sup>,  $Mg(NH_4)_2(SO_4)_2^{6}H_2O(2.07 \pm .01 Å)^{22}$ , and  $MgSO_4^{6}H_2O(2.06 \pm .02 Å)^{23}$ .

Other five-coordinate metalloporphyrins whose crystal structures have been determined include methoxyiron-(III)-mesoporphyrin-IXdimethyl ester (MeOFeMeso)<sup>24</sup>, chlorohemin<sup>25</sup>, and vanadyldeoxophylloerythroetioporphyrin<sup>26</sup>. 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  $3.66 \pm .15^{\circ}$  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  $\pm$  .004 Å to N(41) and 2.753  $\pm$  .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  $\pm$  4° and 167  $\pm$  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  $C_{\downarrow\nu}$  (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 3 $\sigma$  of the respective bond length. The largest differences from the mean angles are 3.5 $\sigma$  for Mg-C(23)-C(24), 3.0 $\sigma$  for Mg-C(33)-C(34), and 3.0 $\sigma$  for Mg-C(13)-C(12). These are deviations of 0.6-0.7 $^{\circ}$ .

Because of the deviations from planarity, shown in Figure 4, the atomic positions in MgPc do not conform to  $C_{\downarrow\nu}$  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.<sup>28</sup> 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<sup>29</sup> and the 3.34 Å spacing of not involving hydrogen atoms  $\beta$ -CuPc<sup>7</sup>. The closest atomic approach between molecules is 3.239 Å which is the distance between atoms C(7) of one molecule and C(24) of the other. All C<sup>\*\*\*</sup>C and C<sup>\*\*\*</sup>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<sup>30</sup>, 3.38 Å in H<sub>2</sub>Pc<sup>3</sup> and NiPc<sup>5</sup>, and 3.39 Å in MeOFeMeso<sup>24</sup>, 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  $C(3_0)$ , 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"<sup>31</sup> 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<sup>31</sup> 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 A larger than in Pc's. Since the Mg-Nadistance 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<sup>24</sup>, 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<sup>32</sup> 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.

17

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<sup>10</sup> and the biosynthesis of Mg porphyrins. Seely has reported at least a twofold enhancement of poly(vinyl pyridine) complex formation when 0.016% H<sub>2</sub><sup>0</sup> 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<sup>12</sup> have studied the effect of pyridine as a catalyst and removal of magnesium atoms in water solutions of deuteroporphyrins. When pyridine or some other catalyst is present, a complex similar to the MgPc<sup>•</sup>H<sub>2</sub>O<sup>•</sup>2C<sub>5</sub>H<sub>5</sub>N 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 hrstidine, for example, replacing the pyridine molecules. In fact, Baum and Plane <sup>35</sup> 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
- 2 J.M. Robertson, <u>J.Chem.Soc.</u>, 615 (1935)
- 3 J.M. Robertson, <u>ibid.</u>, 1195 (1936)
- 4 R.P. Linstead and J.M. Robertson, ibid., 1736 (1936)
- 5 J.M. Robertson and I. Woodward, ibid., 219 (1937)
- 6 J.M. Robertson and I. Woodward, ibid., 36 (1940)
- 7 C.J. Brown, <u>ibid</u>, <u>A</u>, 2488 (1968)
- 8 C.J. Brown, <u>ibid.</u>, A, 2494 (1968)
- 9 L.H. Vogt, A. Zalkin and D.H. Templeton, <u>Inorg.Chem.</u>, <u>6</u>, 1725 (1967)
- 10 G.R. Seeley, <u>J.Phys.Chem.</u>, <u>71</u>, 2091 (1967)
- 11 N.A. Matwiyoff and H. Taube, J.Amer.Chem.Soc., 20, 2796 (1968)
- 12 R. Snellgrove and R.A. Plane, <u>ibid.</u>, <u>90</u>, 3185 (1968)
- 13 K. Sauer, E.A. Dratz and L. Coyne, <u>Proc.Nat.Acad.Sci.U.S.</u>, <u>61</u>, 17 (1968); K. Ballschmiter and J.J. Katz, <u>J.Amer.Chem.Soc.</u>, <u>91</u>, 2661 (1969)
- 14 D.T. Cromer and J.B. Mann, <u>Acta Cryst.</u>, <u>A24</u>, 321 (1968)
- R.F. Stewart, E.R. Davidson, and W.T. Simpson, <u>J.Chem.Phys.</u>,
   42, 3175 (1965).
- 16 D.T. Cromer, <u>Acta Cryst., 18</u>, 17 (1965)

- 17 R.E. Long, Ph.D. Thesis, University of California, Los Angeles, Calif., 1965.
- 18 C.K. Johnson, Oak Ridge National Report-3794, Revised, Oak Ridge, Tennessee, June, 1965.
- 19 A.J.C. Wilson, <u>Nature</u>, 150, 152 (1942).
- 20 C.A. Taylor and H. Lipson, "Optical Transforms," G. Bell and Sons, Ltd., London, 1964.
- 21 A. Zalkin, J. D. Forrester, and D. H. Templeton, <u>J. Chem. Phys.</u> <u>32</u>, 2881 (1963).
- 22 T.N. Margulis and D.H. Templeton, Z.Kristallogr, 117, 344 (1962).
- A. Zalkin, H. Ruben and D.H. Templeton, <u>Acta Cryst.</u>, <u>17</u>,
  235 (1964).
- 24 J.L. Hoard, M.J, Hamor, T.A. Hamor, and W.S. Caughey, <u>J.Amer.</u> Chem.Soc., <u>87</u>, 2312 (1965).
- 25 D.F. Koenig, <u>Acta Cryst.</u>, 18, 663 (1965).
- 26 R.C. Petterson and L.E. Alexander, <u>J.Amer.Chem.Soc.</u>, 20, 387 (1968).
- 27 G.C. Pimentel and A.L. McClellan, "The Hydrogen Bond," W.H. Freeman and Co., San Francisco, Calif., 1960, p 289.
- 28 A. Stone and E.B. Fleischer, <u>J.Amer.Chem.Soc.</u>, <u>20</u>, 2735 (1968).
- 29 J.B. Nelson and D.P. Riley, Proc. Roy. Soc., 57, 477,486 (1945).
- 30 L.E. Webb and E.B. Fleischer, <u>J.Chem.Phys.</u>, <u>43</u>, 3100 (1965).
- 31 J.L. Hoard in "Structural Chemistry and Molecular Biology,"
  - A. Rich and N. Davidson, Eds., W.H. Freeman and Co., San Francisco, Calif., 1968, pp 573-594.

- 32 M. Zerner, M. Gouterman, and H. Kobayashi, <u>Theor.Chim.Acta</u>,
  <u>6</u>, 363 (1966).
- J.J. Katz, G.L. Closs, F.C. Pennington, M.R. Thomas, and
   H.H. Strain, <u>J.Amer.Chem.Soc.</u>, <u>85</u>, 3801 (1963).
- 34 G.L. Closs, J.J. Katz, F.C. Pennington, M.R. Thomas, and H.H. Strain, <u>ibid.</u>, <u>85</u>, 3809 (1963).
- 35 S.J. Baum and R.A. Plane, <u>J.Amer.Chem.Soc.</u>, <u>88</u>, 910 (1966)

#### Table I.

Final Atomic Fractional Co-ordinates and Thermal

Parameters<sup>a</sup> of All Nonhydrogen Atoms in the

Asymmetric Unit<sup>b</sup>.

ATOM	X	Y	Z	811	822	833	B12	813	823
MG	-33142(6)	.01498(5)	.53984(7)	3,98(5)	3.13(5)	3.05(5)	17(4)	84( 4)	20[ 4]
01	.21951 11	*020A( I)	• 4024( 2)	<b>4.</b> 44(12)	4.0L(12)	3443(11)	• 3 3 ( 9 )	1.05(11)	- 02/11
N 1	-4600( 1)	.1644( 1)	.5118( 2)	9.011127	3.24(13)	9-19(13)	10(10)	-041107	
6 2	-4447( 2)	1069( 2)	-43511 27	3.3/(13)	3.00(10)	3.44(10)	- 22(10)	1 07( 0)	- 07(10)
N 3	•40291 11		-43081 21	3.72(14)	3 97(15)	3.54(12)	19(12)	76/171	- 12(14)
64	-9045( 2) 4/01/ 3V	0051( 2)	27051 21	3.43(14)	4.16(17)	3.53(15)	-43(13)	.89(12)	
	+4401( 2)	. 0324( 2)	.1749( 3)	4.28(17)	4.65(19)	4.20(18)	-38(15)	1.07(14)	.11(16)
		0220( 2)	17201 31	4.57(18)	6.33(23)	4.16(18)	.46(16)	1.71(15)	-64(18)
5 2	620241 21	1505( 2)	.18881 31	4.53(18)	5.40(21)	5,15(21)	28(16)	1.82(15)	1.07(18)
<b>č</b> o .	5160/ 71	.1651( 2)	.2920( 3)	4-20(17)	4.38(19)	4.52(19)	10(14)	.87(14)	.16(16)
č10	47351 21	10921 21	3352(2)	3.34(14)	4.13(17)	4.08(15)	.18(13)	.97(12)	.55(14)
NII	.3724(1)	0761( 1)	.3163( 2)	4.08(12)	3.69(13)	3.52(12)	.00(11)	.92(10)	00(10)
C12	-33611 21	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	.26001 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)
C 2 2	.2798( 2)	1049( 2)	.68881 21	3.63(14)	3.90(17)	3.41(15)	05(13)		•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)	20(13)
C25	.2929( 2)	0447( 2)	.8562( Z)	3.45(14)	4.13(16)	3.19(15)	-15(12)	.82(12)	-03(13)
C26	.2908( 2)	03501 Z1	.9660( 3)	4.28(17)	9.23(10)	3.09(10)	- 40(17)	+0/(1))	- 72/10)
C27	•2598( Z)	0961( 2)	1.0147( 3)	5.70(14)	6.2/1241	5.90(10)	-1 40(17)	2 20(14)	
C28	-2307( 2)	10451 21	9/4/1 31	4 49(17)	4 91/191	3.84(19)	58(15)	1.16(13)	22 (15)
629	•2323( 2)	- 1139( 2)	70761 21	3.56(15)	4.09(16)	3.40(15)	13(12)	89(12)	.07(14)
C30 .	+2000 21		.8103/ 21	4.34(13)	3, 38(13)	3-55(12)	.07(11)	.80(10)	30(10)
633	2005( 2)	.1197( 2)	.74581 21	3-88(15)	3.36(15)	3.64(16)	.32(12)	44(12)	11(13)
632 N33	30771 11	.1035( 1)	-6386( 2)	4,10(12)	3.53(12)	3.59(12)	27(10)	.87(10)	10(10)
r 36	-4381( 2)	-16051 21	.6071( 2)	3.87(15)	3.22(15)	3.91(16)	.08(12)	.81(13)	.05(13)
635	46261 23	2191( 2)	. 6961( 2)	4.04(15)	2.99(15)	4.36(16)	.03(13)	.54(13)	.11(13)
636	-5073( 2)	2885( 2)	.70661 31	5.21(19)	4.02(19)	5.41(21)	44(15)	1.10(16)	08(17)
637	-5217( 2)	.3295( 2)	.8050( 3)	6.02(20)	3.97(19)	6.33(23)	-1.01(16)	.81(17)	85(18)
638	4916( 2)	.3028( 2)	.8917( 3)	6.67(22)	4.51(21)	5.64(22)	62(17)	.44(18)	-1.04(18)
639	.4472( 2)	.2341( 2)	.8830( 3)	5.32(19)	4.17(19)	4.76(20)	25(15)	.65(15)	76(16)
C40	.4329( Z)	.1930( 2)	.7834( 3)	3,98(15)	3.06(15)	4.00(16)	.40(12)	.15(13)	35(14)
N41	-1310( Z)	.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)	-14201 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)
C 50	.0757(3)	1452( 3)	-1281( 5)	5.90(22)	8.09(33)	9.81(36)	.09(22)	-1 40(24)	
C51	+0940( 3)	-15/1(3)	-23861 6)	5.98(22)	5.18(26)	12.05(41)	-12/191	-1.401241	
				3. / 1 . / 1 .					

XBL 691-74

" note to Editor : a glossy print is enclosed to permit photographic reproduction of the body of This table.

a The form of the anisotropic thermal ellipsoid (expressed in units of  $\overset{2}{A}$ ) is:  $\exp(-0.25 \Sigma$ Σ i=1\_j=1  $B_{ij}b_{i}b_{j}h_{i}h_{j}$ , where  $b_{i}$  = ith reciprocal axis length and  $h_i = ith$  Miller index.  $\underline{b}$ 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	У	2	B( <sup>¥</sup> s)
HC1-1	.1932(19)	.0644(20)	.4984(27)	5.4(11)
H01-2	.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)	4.0C(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	•11/6(22)	•0972(23)	• 8993(33)	9.5(13)
H45	• 1667(21)	.2036(23)	.8082(30)	8.9(12)
H46	•1/59(20)	•1839(21)	• • • • • • • • • • • • • • • • • • • •	8.1(10)
H48	•1203(18)	•0418(18)	•1438(25)	5.83(86)
H49	•0762(27)	0581(27)	.0121(38)	12.5(17)
H50	•9680(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)

I te to Editor: Original copy is enclosed to permit photographic reproduction if desired.

Table III. Observed and Calculated Structure Factor Amplitudes of MgC<sub>32</sub>H<sub>16</sub>N<sub>8</sub> • H<sub>2</sub>O • 2C<sub>5</sub>H<sub>5</sub>N.

1.5

(Table to be reproduced photographically)



H   K,L+ 2   4   2	00 FC 0, 196 26 223 22 233 21	4 11 13 1 0 12 70 1 3 13 76 1 9 K,t= 11, 9 1 1	10 3 135 13 75 4 975 95 76 5 584 59 0 6 201 20 11 7 246 24	K K.L= 9,   7 -14 13 - 2 -13 27 2 3 -12 75 7 5 -11 38 1	1 3 30 30 4 54 46 5 4.L= 0, 2 -16 52 47 5 -14 19 14	2 39 42 3 75 49 4 107 112 5 72 71 4 218 211	-2 103 -1 0 0 72 1 56 2 72	97 4 94 5* 5 39 69 6 49 59 7 196 1 72 8 125 1	46 -12 37 -11 90 -10 99 -9 23 -6	0 16* 87 5- 17 24	-1 71 6 0 13 1 1 0 2 0	2* -1 4* 0 4	0 208 1 190 8 5 3 45	1 150 16 2 244 24 3 24 2 4 70 7 5 32 3		82 169 93 91 17 213 55 49 51 151	-2 62 6 -1 79 6 0 36 3 1 46 4 2 12 7	6 -12 (8 3 -11 59 2 -10 65 8 -9 72 2 -8 100	11 65 64 70 75
10 12 14	141 14 37 3 55 5 55 5	0 2 116 1 7 3 80 2 4 20 4 5 17	11 8 119 12. 74 9 65 6 18 10 66 6 16 11 27 2	-10 26 21 -9 61 5 -8 27 2 5 -7 52 5	-12 135 141 -10 172 174 -8 173 177 -6 218 206	7 162 170 8 247 251 9 265 284 10 178 18	3 44 4 49 5 82 6 13	4 9 0 93 10 17 77 11 10 1 12 101	120 -7	76 74 170 168 147 146 88 85	3 27 2 4 0 5 0 K.L = 16,	2 1 8 7• 2 25 3• 3 3• 4 2	6 84 3 251 0 10• 0 25	6 19 2 7 0 1 8 42 4 9 13 2	2 6 3 7	62 61 54 50 39 39 12 9	3 164 16 4 58 6 9 121 12 4 105 10	5 -7 8C 4 -6 26 6 -5 9 2 -4 126	28 25 129
R.L	42 1, 72 48 75 7	2 6 4L 0 7 46 9 7 8 85 9 3 9 67 0	37 12 78 74 52 13 32 3 93 14 73 7 65 15 40 3	6 -6 171 17 1 -5 66 61 1 -4 45 50 8 -3 67 8	-2 95 95 -2 95 95 0 743 773 2 838 836	11 55 45 12 95 90 13 44 81 14 13 19	8 79 9 50 10 48	50 13 23 54 14 42 50 K.L= 3, 51 -16 23 29 -15 43	35 -1 3 -1 14 0	365 398 0 30 138 105 72 75	-3 63 5 -2 62 5 -1 23 1	18 6 8 57 7 15 18 8 7 12 9 15	3 07 -1 3 154 -1 0 70 - 2 153 -	1 L3 L 0 45 4 9 60 5 8 59 5	9 1 10 9 11	5 75 56 36 56 63 50 50 23 26 4	7 17 8 62 6 9 46 3 10 79 8	9 -3 39 2 -2 114 6 -1 259 4 0 207 5 1 3	+2 178 247 : 200
	014 02 051 67 50 5	7 11 44 9 4 12 37 3 0 K,L= 12,	75 -16 23 L 39 -15 14 L 0 -14 27 24 34 -13 18 L	-1 98 9- 2 0 55 5. 4 1 356 34	6 82 84 2 8 259 260 10 44 45 12 28 33	-15 0 1 -14 0 1 -13 38 36	• K.L. 12, • -11 0 -10 71 0	2 -14 107 1 49 -13 53 4 -12 42 99 -11 31	07 2 51 1 42 4 23 1	58 56 66 64 30 32 65 62	L 19 1 2 108 1 K.L.= 0, -16 0	4 LO 4 2 11 5 4 LZ 4 7• L3 2	5 45 - 5 54 - 5 43 - 3 14 -	7 67 6. 6 142 14 5 46 5. 4 41 3	2 K.L. 1 -16 4 2 -15 7 -14	4, 5 - 57 60 - 6 30 -	13 13 12 52 5 11 13 10 23 2	9 2 47 0 3 111 9 4 93 2 5 51	43 120
10	26 2 200 20 103 10 30 2	5 L 17 8 2 17 8 3 103 10 9 4 33	13 -12 13 16 -11 159 15 05 -10 42 4 37 -9 142 14	1 3 14 1 5 4 121 13 5 72 7 6 11 1	14 42 38 14 14 2 14 14 18 1 -15 19 7	-11 33 30 -10 78 79 -0 10 14 -8 143 149	-8 33 -7 87 -6 84 -5 74	27 -10 79 7 -9 56 6 -8 63 78 -7 169 1	80 6 55 1 41 8 76 9	41 66 12 14 125 123 79 78	-14 83 8 -12 66 6 -10 19 1 -8 162 13	11 K.L. 13 -15 1 19 -14 1 73 -13 9	· · · ·	3 62 9 2 157 15 1 85 8 0 22 2	-13 7 -12 2 -11 3 -10	29 27 9 61 70 68 29 19	-9 111 11 -8 54 5 -7 47 4 -6 97 9	1 6 40 3 7 12 6 8 13 6 9 41	58 L6 6 38
17	45 4 3 47 4 47 4 47 4 47 4 47 4 47 4 47	2 5 45 4 5 6 13 6 7 0 4 8 56	47 -8 233 22 13 -7 29 2 99 -6 123 11 55 -5 43 3 94 -6 12 73	5 7 51 5 7 6 42 4 9 25 2 9 10 32 3	-14     14     6       1     -13     25     24       -12     17     7       -11     137     143	-7 102 9 -6 86 8 -5 45 40 -4 58 50			07 L1 24 L1 27 K.L	10 24 90 93 9, 3	-+ 310 24 -2 313 30 0 38 3	10 -10 10 10 -10 10 19 -9 1	5 34 9 110 1 13 9 90	2 39 4 5		10 122 19 107 12 129	-5 95 9 -4 32 2 -3 32 2 -7 12 1	7 10 C 9 11 52 4 K,L= 3, 7 -16 42	45 43
X,L- 0 4 1 2	2, 96 50 22 0 22	0 10 33 1 11 0 2 K,L= 13,	36 -3 69 9 20 -2 3 6 0 -1 12 1 15 0 239 24	1 12 30 2 1 13 13 1 2 K,L= 10, 0 -13 23 2	-9 14 9 -8 107 109 -7 115 113 -6 172 178	-2 174 177 -1 144 134 6 142 139 1 202 197	1 30 2 46 3 21	41 -1 154 1 40 0 57 22 1 341 3 14 2 57	58 -13 58 -12 31 -11 62 -10	103 103 14 3 79 79 18 4	4 86 4 47 5 4 14 1 10 77 5	1 -7 3 1 -6 9 18 -5 28 71 -4 12	2 31 1 49 9 273 9 132 Ku	6 60 60 7 13 8 60 61 L# 13	-4 2 7 -3 7 9 -2 1	4 218 29 29 11 123 17 91	0 16 7 1 69 7 2 196 15 3 73 7	5 -14 23 1 -13 13 3 -12 50 5 -11 102	22 11 44
30		1 2 84 0 0 3 49 0 4 4 18 0 6 5 61 0	03 L 347 35 08 2 L07 L0 18 3 56 5 03 4 52 5	-12 30 3 -11 45 4 -10 42 4 -9 18 1	-5 209 209 -6 15 8 -3 281 281 -2 305 335	2 0 3 102 100 4 99 99 5 469 45	5 73 6 99 L 7 53 8 65	72 3 14 26 6 22 82 5 216 2 72 6 335 3	18 -4 19 -8 10 -1 31 -4	110 111 49 69 150 150 234 227	12 42 5 K.L. 1, -16 30 2 -15 14	-3 16 2 11 -1 23 3 0 14	170 -1 24 - 1233 - 147 -	0 0 9 0 13 11 7 0		12 60 14 127 16 46 17 118	4 26 2 5 Q 6 19 2 7 80 8	7 -10 20 24 -9 41 -8 45 4 -7 36	25 42 62 40
10	77 8 26 2 138 13 130 13	L 6 0 5 7 68 0 6 8 57 5 6 9 13 8 10 13	12* 5 32 30 65 6 9L 9 56 7 3L4 32 9 8 558 56 7 9 108 10		-1 174 173 7 0 225 225 1 41 37 5 2 360 366 7 3 176 174	7 18 11 8 98 96 9 96 94 10 30 33	10 13 K.L. 13, -10 0	2	9 -4 84 -1 28 -2 04 -1	71 72 41 61 84 81 150 144	-13 51 5 -12 54 5 -11 100 13	10 2 330 13 3 20 16 4 8 16 5 2	316 - 13 - 46 - 21 -	5 135 131 4 13 14 3 135 13. 2 0 2	5 10 • 14 • 7	0 99 5 140 K 1 14 -	• 26 2 •L• 11, 12 0 11 13	5 -5 60 5 -4 10 24 -3 62 6 -2 200 1	51 13 44
12	12 L 40 3 71 7 46 4	0 K.L. L4, 9 0 75 6 1 30 6 2 40	0 10 59 51 72 11 0 28 12 37 5 37 13 79 8	-3 136 14 -3 136 14 -2 82 8 9 -1 35 3 0 70 7	6 12 11 9 120 117 6 72 75 9 7 60 60	11 68 70 12 159 16 13 62 60 14 32 34	-8 3 -7 62 -6 46 -5 32	24 12 51 5 51 13 38 55 14 30 52 K,L= 4,	42 G 39 1 20 2 3 3	103 90 131 126 58 60 41 40	-9 277 20 -8 45 4 -7 22 1 -6 102 10		5 124 - 00 24 37	1 66 6 0 96 96 1 29 21 2 26 24	10 11 12	19 73 - 10 29 18 60 14 38	10 43 4 -9 51 4 -8 46 4 -7 45 4	L -1 69 6 C 270 2 6 1 62 9 2 89	71 161 44 89
14 8.1-	19 1 3, 60 5 26 2	8 3 44 0 0 4 44 0 5 5 59 1 3 4 40 0	65 L4 63 6 66 15 54 5; 56 R,L= 3, 61 -15 30 3; 31 -14 23 2;	7 1 30 4 2 2 122 12 1 3 95 9 0 4 145 15	0         67         46           4         61         60           9         10         44         40           7         11         17         21           12         34         34         34	-15 15 34 -16 95 94 -13 52 54 -12 97 55	-3 0 -2 41 -1 31	$4^{\circ} -15 27$ $4^{\circ} -15 27$ $5^{\circ} -14 40$ 27 -13 43 $5^{\circ} -12 39$	20 9 33 6 46 1	20 20 12 10 22 24	-3 (5) (5) -4 (13) -3 294 20 -2 50 ( -1 87 4	10 10 10 11 11 30 10 12 0 10 K,L= 1 15 -15 11	30	3 10 14 6 13 14 5 44 43 6 113 114 7 32 31	-16   -15   -14	8 14 7 22 5 52	-6 C -5 65 6 -4 13 1 -3 31 2	1 3 52 0 4 134 1 3 5 24 4 6 59 0 7 22	51 29 24 61 26
5	346 34 117 12 154 15 201 20	4 8 42 4 9 0 4 K,L= 15, 2 1 95 1	46 -13 70 7 10 -12 73 70 0 -11 12 11 89 -16 88 7	0 12 7 30 2 8 0 78 8 9 94 9	13 54 51 2 14 30 32 1 15 56 48 5 K.L. 2, 2	-11 22 21 -10 111 111 -9 48 44 -8 36 34	1, 44 2, 16 3, 13 4, 52	66 -11 46 31 -10 96 1 -9 96 56 -8 42	54 9 99 10 88 11 45 12	49 50 65 74 19 20 116 117	0 58 5 1 135 1 2 57 5 3 52 4	17 -14 54 12 -13 82 18 -12 71 19 -11 50	55 K. 80 - 67 - 47 -	L= L4, 4 8 Q 1 7 38 34 6 59 51	-12 9 4 -11 1 -10 1	1 48 2 2 7 10	-1 58 5 0 24 2 1 28 2 2 60 6	9 81091 7 919 0 10 0 1 11 73	08 18 0* 71
10	37 3 142 14 62 6 184 19	7 2 38 5 3 36 9 4 96 1 5 75	34 -9 107 11 33 -8 249 24 94 -7 27 27 78 -6 15	1 10 0 9 11 13 10 7 12 35 3 7 R.L. 11, 1 9 112 18 3	$ \begin{bmatrix} 4 & -16 & 30 & 23 \\ 3 & -15 & 14 & 1 \\ 4 & -16 & 66 & 49 \\ 1 & -13 & 34 & 34 \\ -13 & 6 & 81 \end{bmatrix} $	-7 18 24 -6 121 111 -5 60 60 -6 106 106	5 53 6 75 7 23 8 23	40 -7 144 L 77 -6 180 L 17 -5 22 14 -4 107 1	43 K,L 74 -L3 14 -L3 08 -L3	10, 3 19 20 40 45 19 17	4 29 2 5 123 12 6 125 12 7 34 3	27 -10 101 24 -1 31 10 -0 51 14 -7 171 12 -4 124	1 106 - 29 - 58 - 1 176 -	5 19 14 4 30 35 3 90 81 2 105 104	-8 -7 2 -6 7 -5 30	0 3* 1 24 14 74 1 295	3 13 1 4 0 5 37 3 4 40 6	5 K.L. 4, 94 -lé 65 6 -l5 65 6 -l4 J0 7 -l3 34	70 63 24
13 14 15 16	13 1 13 1 0 1	7 64 1 K,L= 16, 0+ 0 131 1 7+ 1 99	71 -4 36 3 0 -3 263 26 23 -2 7 90 -1 214 21	5 -11 76 7 5 -10 27 2 5 -9 13 1 5 -6 63 8	-11 151 154 -10 124 126 -10 14 5 -0 14 5 -0 245 259	-2 75 7 -1 36 3 0 9 0 1 371 36	R,L= 14, -9 35 -8 14 -7 62	2 -2 86 34 -1 101 1 19 0 14 59 1 119 1	86 -6 00 -4 19 -1 14 -6	147 149 51 54 49 52 47 69	9 0 10 0 11 50 9	40 -5 40 50 -4 10 11 -3 70 11 -2 177	61 6 74 170	0 35 39 1 52 53 2 107 102 3 63 62	-3 17 -2 19 -1 12 0 3	1 170 5 148 K 7 124 -	8 32 3 ,L= 12, 11 13 - 16 23 2	1 -12 0 5 -11 12 6 -1C 78 5 -9 20	3+ 4 7+ 12
K,L= 0; 1 2		0 2 14 3 3 117 L 7 4 46 6 5 44	20 0 0 1 18 1 186 18 49 2 98 9 55 3 165 17	5* -7 25 2 8 -6 109 10 3 -5 44 4 0 -4 26 2	-7 27 23 74 11 4 -5 85 85 -4 332 330	2 138 133 3 164 165 4 113 113 5 63 63	-6 89 -5 81 -6 62 -3 153 1	2     106     1       16     3     8       13     4     27       14     5     1.45	11 -9 5 -0 30 -1 44 -4	131 130 16 18 89 93 58 58	13 0 K.L. 2, -16 61 0 -15 27 2	4* -L 0 4 0 73 3 1 0 25 2 40	15+ 73 3+ K, 85 -	4 42 41 5 40 44 L• 15, 4		4 50 17 90 16 52 17 99	-9 19 1 -8 52 5 -7 0 -6 23 3	6 -4 106 1 2 -7 67 1* -6 36 3 -5 77	96 69 35 74
4 1 5 1 7		<pre># -15 113 1 1 -13 31 0 -11 135 1 3 -9 184 1 </pre>	12 5 194 19 27 6 107 111 38 7 121 11 93 8 257 25	7 -2 23 2 7 -1 28 3 7 0 59 6 6 1 11	-2 89 90 -1 67 67 0 64 64 1 437 432	7 L6 L1 8 170 173 9 84 84 L0 28 24	-1 13 0 13 1 44 2 105 1	LL 7 L74 1 LL 8 90 41 9 0 06 10 43	82 ( 89 ) 20 2	31 31 147 140 99 97 12 2	-13 68 6 -12 71 1 -11 82 -10 131 12		4+ - 147 - 45 - 100 -	6 59 52 3 0 9 2 75 76 1 54 60	63 • 73 • • •	3 30 8 33 6 31	-4 73 7 -3 45 4 -2 22 2 -1 44 5	-3 76 5 -2 10 5 -1 42 6 134 1	77 9 39 30
10	255 26 42 3 126 12 71 6	4 -7 229 2 9 -5 31 6 -3 212 2 5 -1 196 1	34 9 84 8 30 10 20 1 24 11 80 8 83 12 75 7	7 2 44 8 9 3 38 3 8 4 76 4 7 5 44 6	5 2 231 225 5 3 39 40 4 110 112 5 44 45	11 59 5 12 155 16 13 66 6 KeL= 0, 2	3 70 4 60 5 0 4 13	76 11 13 67 12 55 64 13 0 15 16 29	20 4	138 140 103 108 25 26 0 20	-9 83 0 -0 204 20 -7 90 9 -6 79 0	1 0 01 6 0 20 6 10 13 67 11 11	68 24 16 8	0 27 24 1 100 107 2 102 96 3 13 6	10 19 11 4 12 1 *.L*	6 148 3 58 3 2 6, 5	0 48 4 1 32 3 2 19 2 3 32 3	1 20 2 2 144 1 3 15 4 47	17 -   81 14   88
13 14 15	41 3 40 3 40 3	3 1 452 6 8 3 271 2 7 5 273 2 6 7 55 0 9 135	52 13 40 4 82 14 27 3 68 15 54 5 54 K,L= 6, 41 -15 19 1		0 7 51 53 1 8 33 27 4 51 47	-13 93 93 -12 38 30 -11 39 43 -10 40 74	K,L+ 15, -7 19 -6 14 -5 19	2 -16 13 2 -16 13 21 -15 14 19 -14 19 14 -13 10	10 1 5 10 1 11	62 58 60 57 57 51	-9 225 22 -4 159 11 -3 63 6 -2 204 20 -1 41 5	12 13 13 K,L+ ( 14 -14 69 11 -13 13 19 -12 99	66 -1 14 -1 14 -1	5 27 22 3 179 140 1 67 67	-13 3 -14 1 -13 1 -12 1	C 26 3 7 4 13 3 12 4 17 E	5 27 L 5 27 L 6 145 140 7 C 1	5 33 6 30 7 13 8 8 13 8 13	
1 2 3	74 7 20 2 120 12 109 10	7 11 48 5 13 0 6 15 90 6 K <sub>2</sub> L= 1,	40 -14 36 3 13* -13 42 3 66 -12 13 1 1 -11 20 2	11 82 8 9 X.L. 12. 7 -11 13 1 2 -10 95 9	1 11 37 36 1 12 96 88 7 13 13 9 56 0 110	-8 48 90 -8 48 70 -7 87 83 -6 189 185	-6 27 -3 33 -2 88 -1 33	25 -12 34 29 -11 27 86 -10 16 33 -9 57	34 -12 28 -11 7 -10 60 -1	0 6* 0 5* 56 60 76 77	0 20 2 1 0 2 5 6 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	5 -11 22 5• -10 11 55 -9 117 17 -8 27	22 - 115 - 115 - 24 -	7 47 45 3 18 24 5 383 343 1 296 284	-10 5 -9 8 -8 7 -7 8	1 56 4 85 4 73 6 90	9 37 30 6 23 1 7 13 4 23 1	IC 0 11 47 K.L. 5. I -15 56	47 62 6
7	33 3 114 11 213 21 312 33 214 21	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	40 -10 160 16 23 -9 35 3 72 -8 39 4 34 -7 227 22 12 -6 139 14	G -9 33 3 6 -8 13 1 -7 134 13 5 -8 22 1 0 -5 41 5	6 15 0 30 8 K.L. 3, 2 2 -14 23 18 9 -15 30 24 9 -14 23 14	-5 61 5 -6 39 33 -3 249 239 -2 40 3 -1 94 93	1 78 2 27 3 50 4 27	0 -0 47 1 0 -7 44 1 16 -6 13 51 -5 77 19 -1 17	• • • • • • • • • • • • • • • • • • •	160 161 171 176 0 36 51 51	6 70 7 5 54 9 6 47 4 7 21 1 8 16 1	1 -7 4 13 -6 191 14 -5 11 14 -4 24 14 -3 44	138	1 77 174 3 177 174 3 177 174 5 20 19 7 233 233	-5 2	0 17 - 56 - 1 51 -	-3 73 61 -4 13 1 -3 48 41 -2 32 2 -1 10 3	-14 0 -13 90 -12 13 7 -11 18 -10 27	48 E 1 7 - 1 16 30
10 11 12 13	32 3 12 10 47 4	2 -11 20 • -10 28 • -9 24 • -8 47	16 -5 121 12 23 -4 77 8 25 -3 8 48 -2 0	-4 130 12 3 -3 37 3 -2 103 9 • -1 24 2	-13       34       36         -12       24       21         -11       86       86         -10       45       45	0 L02 9 L 9 2 96 9 3 31 2	5 35 6 43 K.L. 16, -5 13	38     -3     104     1       97     -2     51       2     -1     96       12     0     117	01 -1 54 -2 97 -1 13 0	130 137 20 21 33 30 23 19	9 50 0 10 71 0 11 57 9 12 13	19 -2 99 14 -1 137 14 0 41 1 121	49 1 134 1 43 1 122 K.	0 1 1 33 2 3 0 2	<ul> <li>-1 32</li> <li>0 3</li> <li>1 16</li> <li>2 4</li> </ul>	6 325 1 26 8 166 2 41	0 13 14 1 53 54 2 88 90 3 56 50	-9 84 -8 16 -7 54 -8 102	83 4 16 5 53 7
15 K.L.	4L9 40	1 -7 35 1 -8 72 0 -5 293 2' 7 -4 60 6 2 -1 398 1	35         -1         55         5           76         0         40         7           93         1         103         10           60         2         11         1           60         2         11         1	5 0 73 5 6 1 17 2 0 2 93 9 4 3 47 4 4 3 47 4	-7 0 1 95 -7 0 0 0 -6 105 112	5 60 60 6 0 19 7 100 L02	-3 13 -2 110 1 -1 70 0 27	12 2 84 20 3 59 62 4 112 1	85 2 63 1 LV 4	44 43 97 104 28 30	K.L.= 3. -16 0 -15 35 3	4 3 50 24 4 23 12 5 24	60 -1 25 -1 26 -1 50 -1	0 23 22 5 40 41 6 43 43 5 48 45 7 40 34	33 48 52 46	0 24 0 83 0 21 1 61 K.	4 23 24 5 37 44 6 13 24 14 14, 5	-3 77 -4 25 -3 25 -2 44	79
	28 2 35 3 189 19 185 18	5 -2 140 1 0 -1 43 0 0 484 4 6 1 146 1	50 4 116 11 47 5 54 5 79 6 0 39 7 88 9	5 55 5 6 10 1 7 0 1 0 35 3	-4 20 25 2 -3 51 51 0 -2 22 10 3 -1 35 38	0 134 10 10 66 8 11 35 40 12 65 6	1 13 2 0 3 37 4,L= 0,	16 6 25 5° 7 79 3° 8 106 1 3 ° 12	25 4 82 1 08 4 13 9	22 21 37 34 70 71 79 82	-13 0 -12 12 1 -11 124 12 -10 27 1	5• 7 0 11 8 45 25 • 130 30 10 0	10+ -1 +7 -10 129 - 5+ -1	45 42 0 36 35 708 212 155 163	4 4 9 3 10 3	0 42 2 34 3 36 9 10	7 4C 4 6 65 5 5 33 3	C 10 1 L10 1 2 89 3 77	3 12 62 79
***	30 2 104 10 33 5	L 2 126 L 7 3 208 20 6 4 484 50 5 5 20 5 6 256 20	25 8 89 9 00 9 23 2 06 10 43 4 26 11 69 6 51 12 64 6	4 9 57 6 7 10 42 4 5 11 78 8 7 K+L= 13, 6 -19 13 1	0 0 53 53 0 1 66 61 0 2 184 180 1 3 26 24 1 4 351 349	13 87 93 K.L. 9, 3 -14 40 43 -13 39 43 -12 27 33	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	16 13 107 1 00 11 58 7 70 12 33 55 13 0	08 10 61 K,L 34 -L1 44 -L0 3 -4	97 5L 12, 3 0 40 14 15 57 58	-7 71 4 -8 0 -7 43 4 -6 208 21 -5 249 20	10 11 42 10K,L= 9 14 -16 42 11 -13 44 12 -12 42	42 - 42 - 32 - 39 -	102 105 5 381 360 6 179 181 5 201 194	-15 2 -14 1 -13 -12 1	7, 5 - 6 29 - 3 12 - 0 10	-3 L3 1 -2 262 101 -1 42 42 0 84 83	5 84 5 84 2 6 96 7 38	90 92 34
	17 12 10 5è10 57 5	8 7 67 6 8 136 1 1 9 60 3 10 11	65 13 60 5 51 14 19 1 62 K,L. 7, 9 -15 19 1	9 -9 14 1 8 -8 91 9 1 -7 0 1 3 -6 62 8	5 245 244 2 6 185 187 5 7 224 224 3 8 81 79	-11 62 64 -10 146 144 -9 28 29 -8 32 31	-5 175 1 -3 109 1 -1 135 1 1 11	61 -15 66 08 -14 45 37 -13 52 4 -12 87	45 -1 34 -1 54 -4 91 -5	14 20 64 67 183 183 83 83	-4 18 1 -3 149 11 -2 158 10 -1	• -11 39 11 -10 22 15 -9 52 • -0 17	32 -; 16 -1 54 ( 16 1	2 96 103 1 24 24 7 16 10 1 42 40	-11 1 -10 6 -9 6 -8	8 15 6 60 8 71 0 2* K	2 08 81 3 37 41 4 13 4 L= 19, 5	9 18 10 13 11 29 K,L= 6,	5 13 30
15 K.L. 1 2	13, 77, 7	9 11 22 0 12 41 19 13 43 8 14 44 4 5 15 50	22 -14 19 1 41 -13 73 7 36 -12 32 2 62 -11 53 5 64 -10 41 6	3 -3 G L 6 -4 50 4 7 -3 L3 L 7 -2 65 6 1 -L 28 2	3 10 64 64 3 11 58 61 5 12 32 27 5 13 12 10	-7 84 8 -6 42 40 -5 107 107 -4 52 57 -1 25 30	3 39 5 67 7 162 1 9 102 1	37 -11 21 71 -10 84 47 -9 53 07 -8 15 4 -7 39	17 -4 05 -1 51 -2 0 -1 34 0	10 72 100 72 65 65	0 71 0 1 40 9 2 8 1 3 139 13 4 22 3	18 -7 0 14 -6 44 12 -5 136 17 -4 49 12 -1 15	42 134 51 17	01 01 01 05 110 07 07	-7 1 -6 4 -5 1 -4 3	6 14 - 9 51 - 1 5 - 6 39 -	-5 96 52 -4 0 3 -3 23 21 -2 121 122	-15 44 -14 43 -13 0 -12 91 -11 97	*8 39 5*
	16 3 156 16 16	9 K.L. 2, 8 -16 23 4 -15 73 7* -14 90	1 -9 64 6 22 -8 16 71 -7 95 9 56 -6 51 5	0 18 9 1 104 10 9 2 80 7 1 3 44 4	5 14 13 21 0 15 35 41 6 K.L. 4, 2 7 -16 62 59	-2 126 121 -1 17 11 0 31 30 1 22 21	L3 23 K.L. L. -16 36 -15 56	22 -6 19 3 -5 62 36 -6 36 47 -3 160 1	8 56 34 74	208 205 152 148 28 24 43 45	5 125 11 6 289 21 7 48 4 6 149 1	11 -2 0 11 -1 78 9 0 0	90 150 50 10	7 49 44 12 4 50 45 57 56	-2 9 -1 3 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	3 89 4 32 9 32 Ka 2 34 -1	0 49 49 1 49 54 L= 0, 4	-10 63 -9 39 -8 165 1 -7 42	43 33 68 43
10	23 2 75 7 37 6	4 -12 61 7 -11 131 1 5 -10 19 1 -9 17	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	5 10 1 5 10 1 5 6 35 3 1 7 27 3 6 8 100 10	0 -13 14 10 0 -14 19 3 5 -13 13 2 0 -12 63 62 3 -11 26 22	3 65 92 6 85 81 5 11 14 6 46 44	-12 88 -11 16 -10 26	19 -2 224 2 95 -1 40 8 0 139 1 25 1 279 2 32 2 84	64 6 31 1 74 6 62 1	103 (00 53 53 14 30 23 21 0 40 42	10 13 11 91 9 12 19 1	8 3 197 51 4 29 13 5 17	03 11 201 12 36 13 24 K.C	1 13 17 2 23 21 9 35 30 .• 2, 5	2 12	9 132 -1 1 23 -1 6 87 -1 6 36 -	4 104 102 2 155 153 10 16 4 9 52 49 16 109 107	-6 34 -5 14 -6 139 1 -3 57 -2 69	29 19 38 59
13 14 8.L.	53 5	30 -8 106 1 1 -7 151 1 0 -6 100 10 8 -5 80	10 0 121 12 55 1 33C 32 03 2 91 9 79 3 113 11	5 <b>9</b> 68 7 5 K,L= 14, 3 -9 42 4 1 -8 69 7,	2 -10 02 92 -9 107 111 -8 167 170 2 -7 132 131	7 12 10 8 66 60 9 26 20 10 66 41	-8 91 -7 32 -6 26 -5 13	5 3 117 1 5 4 6 27 5 204 2 2 6 78 2 6 78	16 E.L 100 - 10 05 -1 76 -1	• 13, 3. 38 40 14 10 19 24	K,L+ 4, -16 50 4 -15 23 2 -14 33 2	4 7 57 67 8 72 10 9 13 27 10 33	62 -19 72 -14 20 -13 30 -12	23 20 13 3 83 78 27 28	7 6 9 9 10	0 40 - 7 56 - 6 97 0 130	4 214 214 2 224 231 0 321 323 2 44 40	-1 82 C 32 1 58 2 116 1	75 30
23	30 4 754 26 77 7	3 -2 72 1 -1 121 1 7 0 114 1	73 5 165 16. 74 6 35 3. 22 7 71 7 13 8 80 7		-0     28     25       0     -5     14     10       5     -4     29     24       1     -3     243     237       7     -2     15     15	11 00 01 12 19 11 RaL= 10, 2 -13 52 51 -12 54 51	-3 47 -2 45 -1 165 L	7         7         22           6         8         55           13         9         25           55         10         13           78         11         113	27 -0 94 -0 33 -9 15 -0	57 50 19 19 19 15	-13 44 4 -12 18 1 -11 17 1 -10 92 9	11 0 15 K.L. 10 14 -13 37 20 -12 23	2+ -11 , 4 -10 35 -1 17 -1	93 95 54 56 96 91 24 23	11 3 K,L= 1 -14 5 -13 6	7 34 8, 5 9 54 9 67 1	4 75 71 6 159 160 8 62 85 0 56 58	3 90 6 0 5 12 6 52	•3 5• 1• 51 5
*	43 6 56 4 46 10 17 1	6 1 348 33 G 2 243 24 1 3 476 44 2 41484154	39         9         5C         4           48         10         35         3           62         11         13         15           64         12         117         11	-2 27 2 5 -1 23 1 5 0 74 7 1 55 5	2 -1 136 138 9 0 21 13 2 1 284 285 2 163 162	-11 129 132 -10 59 63 -9 22 19 -8 33 31	1 89 2 140 1 3 25 4 115 1	00 12 80 34 13 27 25 K.L= 7. 12 -15 27	89 -2 27 -1 3 C 20 1	107 103 123 123 106 106 22 20	-8 18 1 -7 9 1 -6 204 20 -5 182 11	3 -10 23 10 -9 32 18 -8 42 12 -7 43	30 -4 34 -9 38 -4 61 -3	38 38 86 87 258 247 37 39	-11 2 -10 8 -9 4 -8 3	29 K, 79 -1 34 -1	L= 1, 4 6 23 20 5 13 15 4 19 14	0 443 10 19 8,1 7,	40 17
11	41 LO 35 3 44 4 91 9	0 6 44 4 9 7 132 1 5 8 140 10 0 9 330 32	14 13 85 8 14 15 3 32 K,L= 8, 52 −14 38 3 78 −13 0 13	2 20 3 3 49 4 4 68 7 5 23 1 2 4 23 1	4 137 142 4 137 142 5 79 45 6 49 50 7 46 47	-7 12 3 -6 191 185 -5 66 49 -6 34 34 -3 232 220	6 200 2 7 41 8 105 1 9 47	0 -14 84 04 -13 43 4 44 -12 19 05 -11 28 45 -10 54	47 3 10 4 30 9	32 27 23 20 42 48 35 40 74 74	-6 20 1 -3 171 11 -2 162 16 -1 117 10	18 -6 32 71 -5 12 67 -4 41 66 -3 61 67 -2 102	20 -2 4 -L 40 0 42 L 102 2	27 27 185 182 1 41 41 9 3 78 71	-7 31 -8 11 -5 30 -4 12	1 12 -1 1 12 -1 38 -1 5 120 -1	3 18 99 2 25 23 1 24 27 0 23 23	-14 0 -13 0 -12 53 4 -11 18	2*
1 1 2 3 1	4. 11 74 7 107 19	0 10 0 7 11 176 1 2 12 97 1 13 50	5* -12 100 9 78 -11 13 1 97 -10 77 71 56 -9 6 1	7 8C 7 8 44 3 7 K.L- L5, 1 8 -7 60 5	8 405 418 9 55 59 1 10 92 92 11 18 19	-2 24 24 -1 49 42 0 44 49 1 140 144	10 108 10 11 13 12 0 13 52	6 -9 80 6 -8 78 14* -7 193 1 15 -6 25	84 1 78 8 15 8,L	13 4 37 4 14, 3 19 13	1 92 9 2 36 3 3 176 17 4 121 12	1 -1 0 18 0 20 14 L 0 23 2 50	11+ 3 24 4 4+ 5 47 4	130 129 52 50 61 60 86 84	-2 4 -1 180 0 72 1 9	44 - 183 - 75 -	8 6L 56 7 202 204 6 17 L9 5 268 256	-9 28 2 -8 95 9 -7 89 0	
****	50 4 78 7 47 4 75 7	0 14 50 7 15 27 3 4 K,L= 3, 2 -16 23 2	51 -6 66 83 33 -7 103 96 1 -6 21 19 20 -5 93 95 5 -6 16 16	-5 27 2 -6 0 L	L* L2 37 42 2 13* 62 65 3* 14 23 25 1 K.L* 5, 2	2 11 4	14 0 X.L. 2, -16 23 -15 14	1° -5 20 3 -4 43 15 -3 45 5 -2 57	L3 -0 30 -1 43 -4 60 -9	14 14 19 14 38 36 96 94	5 159 15 6 11 7 79 1 8 39 3	18 3 149 7 4 30 12 5 174 19 4 45	174 7 27 8 173 9 43 10	12 5 24 26 0 3 23 22	2 0	27 - 37 - 40 -	4 105 98 3 106 105 2 128 128 1 322 303	-5 186 1 -4 11 -3 22 2 -2 106 10	93 4 17 13
10	41 4 26 2 0 19 1	2 -14 19 1 0 -13 0 1• -12 179 1 2 -11 57	11 -3 52 50 1• -2 190 18 76 -1 46 4 55 0 252 23	-t 51 4 0 65 6 1 19 1 2 65 6	-15 27 28 -14 30 26 -13 29 25 -12 74 73	7 0 4 8 46 44 9 19 31 10 50 42	-13 66 -12 47 -11 71 -10 93	71 0 73 55 L 26 70 2 27 75 3 31	72 -3 23 -2 32 -1 29 0	103 L02 95 90 13 23 56 59	10 110 10 11 19 1 12 53 5 13 13	17 8 19 4 9 44 1 10 107 1 X-L- 11	26 12 51 K,L 107 -16 4 -15	33 33 • 3, 5 • 4• 65	7 73	80 26 38 10	- 13 13 1 57 57 2 81 78 3 196 198 4 143 140	-1 102 0 42 1 51 5 2 12 3 77	16 11 14
13 #,L 0 1 1	33 3 10, 1 133 12 0	8 -10 50 0 -9 106 10 6 -8 66 7• -7 7• 1	1         1         157         156           28         2         45         45           45         3         161         155           75         4         31         21           10         4         3         21	3 19 1 4 0 19 5 103 9 6 23 2	-11 34 33 -10 98 99 -9 19 11 -8 85 87 -7 114 197	11 23 22 12 49 50 K,L- 11, 2 -12 14 5	-9 240 2 -8 67 -7 89 -6 83	37     4     35       43     5     0       92     6     16       82     7     43	35 1 10• 2 27 3 44 4	46 49 0 20 19 11 19 17	K.L. 5. -16 37 3 -15 0 -14 27 3	4 -12 13 12 -11 13 41-10 62 10 -9 53	6 -16 10 -13 67 -12 52 -11	L3 7 48 46 99 96 52 51	R.L. 9 -14 12 -13 51 -12 50	20 50 62	5 e3 45 6 35 33 7 111 116 6 13 26	• 3• 3 5 85 8 6 58 8 7 62 5	
31	88 8 45 4 45 4		14 6 11 9 12 7 11 9 14 8 66 66	-3 27 22 -4 28 8 -3 27 20 -2 66 6	-6 99 95 -5 12 5 -4 24 20 -3 266 202	-10 47 55 -9 10 31 -8 82 85 -7 13 1	-3 22 1 -3 22 1 -2 103 1 -1 127 12	4 9 40 14 10 41 16 13 13 1 16 12 44	34 4 52 7 52 8.L 54 -7	13 20 0 70 15, 3 23 22	-12 13 -11 149 16 -10 47 6	3 -7 13 7 -6 66 6 -5 86 12 -4 60	-10 2 -9 71 -8 89 -7 55 -4	11 12 26 23 50 52 67 60 63 50	-10 45	41   12   13   1	14 L4 0 66 67 1 33 24 2 16 16	4 23 2 4 14 1 16 44 4	3
10	12 L1 56 51 0 1	5 -1 223 22 7 0 61 5 9 1 852 90 1 2 326 32	25 10 97 98 19 11 35 34 18 12 86 91 12 13 67 61	-1 23 20 0 110 121 1 55 42 2 23 25	-2 e3 e2 -1 65 e7 0 12 19 1 468 168	-6 12 11 -5 30 31 -4 151 145 -3 26 23	0 62 0 1 25 1 2 23 1 3 43 4	4 13 108 10 16 K,L- 8, 16 -14 43 1 13 -13 19 1	17 -6 3 -5 12 -4 18 -3	38 32 59 50 14 14 51 47	-8 13 1 -7 81 6 -6 55 5 -5 148 14	1 -3 80 2 -2 80 2 -1 821 5 0 24	75 -5 79 -6 120 -3 37 -2	336 320 41 43 258 249 173 177	-6 12 -5 31 -6 51 -3 0	15 -1 31 -1 54 -1 12 <sup>9</sup> -1	27 17 19 22 43 61 13 1		

11

MAGNESTUN PHEMALOCYANEN.

OUSERVED AND CALCULATED STRUCTURE FACTORS DF PCATO.0.01 = 5353

\*1173477 \$4 602779 \$ 27 0 27 0 27 128 \$ 41 87 86 42 87 77 78 148 421 88 613 8298 829 829 81 122 118 8 444 9 94 1 22179000071878869402496174779781842424748210898436254492551400278449878988449572944 4512,072204504570257554077251207267212041505754405144050675504070285440455554414655645554414555271 \$2004001 \$ 960 67110557116774244246254 6 4953410 6802 9619 424801 58174 59562353212360620 74126571744269763 11 1100222747575700×00952094511586595520579738457551175122959778607514141946845455010222757597360751414555209572 0+43133003804518130164712547735484709977184318243089824330 400013712994088401717110148073003 1344463341714748420000173447734884734134477908888390841079833687747074427423234734487187187484718719 4543447784705972057728754914778554914778214276255498080848558946555059041482587144554546882592 1111820 40232367161616084049532012398513934055139240453449742031649110332642454461222538432701103340495 45 67890L54321109876543

XBL 691-72

-27-

Table IV. Intramolecular Bond Distances (in Å) of MgPc  $^{\circ}$  H<sub>2</sub>O  $^{\circ}$ 2 C<sub>5</sub>H<sub>5</sub>N. 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<sub>2</sub>O, and 0.03-0.05 Å for C-H in the pyridine rings.

-28-

Atoms	Distance	Atoms	Distance	Atoms	Distance
Mg-0(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)1-0(1)	0.73
Mg-N(33)	2.039	C(24)-N(31)	1.335	H(01)2-0(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)	.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)	.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
<b>C(9)</b> -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
<b>C(18)</b> -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 <sup>o</sup>) of MgPc • H<sub>2</sub>O • 2 C<sub>5</sub>H<sub>5</sub>N. Standard deviations are 0.1<sup>o</sup> for all angles involving Mg, 0.2-0.3<sup>o</sup> for all angles in the Pc ring, and 0.4-0.6<sup>o</sup> for all angles in the pyridine rings.

-30-

Atoms	Angle	Atoms	Angle
O(1) - Mg - N(3)	106.5	N(11)-C(12)-N(13)	127.2
0(1) - Mg - N(13)	101.2	N(11)-C(12)-C(20)	123.8
0(1)-Mg-N(23)	101.5	N(13)-C(12)-C(20)	109.0
0(1)-Mg-N(33)	107.0	$M_{g-N(13)-C(12)}$	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)	ã <b>86.8</b>	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	<b>C(16)</b> -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
$M_{g-N(3)-C(2)}$	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
<b>C(5)-C(6)</b> -C(7)	118.0	Mg-N(23)-C(22)	125.3
<b>C(6)-C(7)-</b> C(8)	121.2	Mg=N(23)=C(24)	126.2
C(7)-C(8)-C(9)	1211.2	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
<b>C(5)-</b> 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

-31-

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	<b>C(37)-C(38)-</b> 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	<b>C(35)</b> -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

-32-

Table VI. Intermolecular Spacing Less Than 3.5 Å for C<sup>\*\*</sup>C and C<sup>\*\*\*</sup>N Approaches and Less Than 3.0 Å for C<sup>\*\*\*</sup>H and N<sup>\*\*\*</sup>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	Atom	Atom	Distance
Adjacent Molecule 2	01 1	01' 2	(A)
1- <u>x</u> ,-y,1- <u>2<sup>8</sup></u>	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 <u>b</u>	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
t-x, t+y, t-2	N(1)	H(50)	2.66
	C(9)	H(51)	2.80
	C(5)	H(17)	2.84
È-X, È+Y, 3-Z	<b>C(</b> 40)	H(29)	2.80
<u>2</u> -x,- <u>2</u> +y, <u>3</u> -2	N(21)	H(45)	2.61
	C(29)	H(46)	2.84

<sup>B</sup>Position of the other molecule in the "dimer." <sup>b</sup>Only the closest pyridine-MgPc distances are listed.

-34-

Table VII. Rotation Angles (in <sup>0</sup>) for Nonplanarity of MgPc.

Atoms	uan	<u>nPu</u>	n <sup>Ghi</sup>
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 <u>bc</u> plane.
Figure 2. The central region of the MgPc molecule. The equivalent Mg-N and N<sup>\*\*</sup>N distances have been averaged.

-36-

Figure 3. Averaged bond distances (in Å) and bond angles (in <sup>o</sup>) of MgPc. Standard deviations of the bond distances and angles are 0.006 Å and 0.4<sup>o</sup>.

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 <u>c</u> 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 <u>bc</u> plane.

-37-



XBL 691-18





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

-40-

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 <u>c</u> axis. All  $C_N, O_n$  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.



-43-

#### LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor. TECHNICAL INFORMATION DIVISION LAWRENCE RADIATION LABORATORY UNIVERSITY OF CALIFORNIA BERKELEY, CALIFORNIA 94720

. **X**