Nuclear magnetic resonance spectra of bis(dimethylamino)beryllium show two resonances in benzene (τ 7.55 and 6.96) and in cyclohexane (τ 7.55 and 7.40). In both solvents, the resonance associated with the protons on the terminal groups is shifted downfield with respect to the resonance associated with the bridge groups. The C^{13}–H coupling constants, redetermined in benzene from HA-100 data and taken at room temperature, are 129 ± 1 cps for the terminal group and 133 ± 1 cps for the bridge group. Drago and Matwiyoff[16] have drawn a correlation between $J(C^{13}\text{–H})$ and τ from a number of observations. This relationship affords a means of determining the existence of large nonlocal contributions to the proton chemical shifts. While a quantitative comparison of the two environments in bis(dimethylamino)beryllium cannot be made, the anisotropic contribution appears to be larger for the terminal groups than for the bridge groups. The fact that τ values of the terminal protons are solvent shifted upfield in benzene relative to cyclohexane implies that a significant portion of the anisotropic contribution may be due to the interaction of the benzene molecules with the terminal amino group. We were unable to obtain C^{13}–H coupling constants in cyclohexane.

The reaction of trimethylaluminium with bis(dimethylamino)beryllium[6] in various molar ratios, and subsequent sublimation at low temperatures, yields a mixture of materials. Principal among these are two crystalline substances (multiple plates and very small needles) and an amorphous solid. The plate-like material can be initially separated, but upon successive sublimations a variety of compounds are again obtained. Attempts to mount fragments of the plates for X-ray structural analysis did not produce satisfactory results. However, single crystals of the needle-like substance were mounted and preliminary X-ray data were taken. Space group and unit cell determination showed that this compound was dimethylberyllium.[17] The presence of dimethylberyllium could be accounted for by a reaction such as

$$2Al(CH_3)_3 + Be[N(CH_3)_2]_2 \rightleftharpoons Be(CH_3)_2 + [(CH_3)_2AlN(CH_3)_2]_2 \qquad (1)$$

Previous studies with this system indicated that neutral addition complexes such as $Al(CH_3)_3 \cdot Be(N(CH_3)_2)_2$ and $(Al(CH_3)_3)_2 \cdot Be(N(CH_3)_2)_2$ were formed.[6] However, the expected severe steric interaction for these compounds together with the complex spectra reported (three to four resonances in the Al–CH_3 area and three resonances in the –$N(CH_3)_2$ area) shed doubt as to their actual nature. If one views the spectra as the result of a redistribution equilibrium process,[18] then compounds with more favorable stereochemistries may be expected. Indeed, we have found that in a typical nmr spectrum of the plate-like substance, two of the resonances may be assigned to the $[(CH_3)_2AlN(CH_3)_2]_2$ compound. It is believed that by a systematic study of compounds related to the parent species in eq 1, the nature of the redistribution equilibrium could be fully understood.

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The Structure of Aquomagnesium Tetraphenylporphyrin[1]

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Abstract: The crystal and molecular structure of aquomagnesium tetraphenylporphyrin, $(H_2O)MgTPP$, has been solved using X-ray crystallographic techniques. The crystals are tetragonal (a = 13.46, c = 9.68 Å) and the space group was fixed to be I4/m with two molecules per unit cell. Since the magnesium atom does not lie in the mirror plane (±0.273 Å), the crystal structure was concluded to be disordered, similar to that of ClFeTPP and $(H_2O)ZnTPP$. The magnesium atom proved to be hydrated and possesses approximate square-pyramidal coordination. The porphyrin molecule is characteristic of other porphyrins and metalloporphyrins.

Most of the metalloporphyrin structures that have been reported thus far consist of metals of the first transition series or beyond.[3] Of the metalloporphyrins preceding the first transition series, magnesium-containing porphyrins are probably of the most interest because of their possible relationship to chlorophyll and its related compounds. Thus, during the course of a continuing study of the structure of porphyrin molecules, we have determined the crystal and molecular structure of magnesium tetraphenylporphyrin (MgTPP), which we now wish to summarize here.

Experimental Section

Crystals of MgTPP suitable for X-ray study and displaying pseudo-octahedral morphology were grown by slow evaporation of chloroform solutions seeded with very small crystals of MgTPP

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(2) NSF Undergraduate Summer Participant, 1967, 1968.

(3) For extensive reviews of structural studies of porphyrins, see T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Am. Chem. Soc.*, 87, 2305 (1965); L. E. Webb and E. B. Fleischer, *J. Chem. Phys.*, 43, 3100 (1965), and references contained therein.

that were grown previously.[4] Preliminary X-ray examination of the crystals showed them to be tetragonal (a = 13.46, c = 9.68 Å, ±0.02 Å), and systematic extinctions narrowed the space group to one of three possibilities: I4, I$\bar{4}$ (noncentric), and I4/m (centric), with two molecules per unit cell. Density measurements carried out by flotation in aqueous silver nitrate solutions indicated a molecular weight of 669 ± 20 (d_o = 1.267, d_c = 1.205 g cm^{-3}) per half-cell. This molecular weight is 33 g mole^{-1} higher than that of MgTPP and, within the limits of error of the density measurements, suggests the presence of one or possibly two molecules of water per molecule of MgTPP.

X-Ray intensity data were collected with Cu Kα radiation and a General Electric XRD-5 equipped with a single-crystal orienter and a scintillation counter assembly. The intensities were obtained using the stationary crystal–stationary counter technique with balanced Ni–Co filters. The intensities of three convenient reflections were monitored periodically throughout the data collection and showed no fall-off as a function of X-ray exposure to the crystal. Before converting the measured intensities to relative structure amplitudes, they were corrected empirically for absorption as a function of azimuthal orientation of the crystal on the orienter. The correction was small and the average curve employed over the complete 2θ range ($2\theta_{mx}$ = 110°) had a maximum:minimum ratio of about 1.05. Of the 657 reflections accessible in this range ($d_{\min}$ = 0.94 Å), 431 (65.6%) were taken to be observable.

Structure Analysis

The space group of MgTPP was fixed to be I4/m from Wilson statistics and Karle E statistics. The result was anticipated since the molecule inherently must be approximately centrosymmetrical, and large deviations from this symmetry were not expected. All of which raises an interesting point: since the molecules would be situated at special positions in the noncentric space group possibilities (on 4 and $\bar{4}$), only large deviations from a centrosymmetrical arrangement would lead to an indication of a noncentric intensity distribution. However, the latter is inherently precluded by the molecule. Thus, it is to this extent only that we have fixed the arrangement to correspond to a center of symmetry.

Since the structure of MgTPP appeared to be isomorphous with that of disordered ClFeTPP and disordered (H_2O)ZnTPP, these structures were employed as the starting point of the structure analysis.[5] Structure factors of MgTPP were calculated using average coordinates of the carbon and nitrogen atoms of the assumed isomorphous structures with the magnesium atom in the mirror plane (R = 0.30). An electron density based on the structure factor calculation confirmed the isomorphism and additionally revealed a peak (approximately 4.0 e Å^{-3}) stituated on the fourfold rotation axis. This peak was assumed to be an oxygen of a water molecule. It was included in a weighted (Hughes' scheme) least-squares calculation as a 0.75 weight oxygen atom (midway between an ordered and disordered atom) and its weight was varied as one of the parameters. The weight changed to 0.60 so that it was concluded that this peak was a disordered oxygen atom of a water molecule.

The structure was then refined through successive least-squares computations with intermittent difference electron density calculations until anisotropic thermal parameters were included and hydrogen atoms located. During the latter stages of refinement, it became clear that it would be difficult, if not impossible, to approximate the observed magnesium atom satisfactorily on the basis of thermal parameters alone. In addition, the B_{33} thermal parameter of magnesium had become unreasonably large (13.4 Å^2). Therefore, it was suspected that the magnesium might not be in the mirror plane but rather displaced out of the plane in a similar way as the central atoms of ClFeTPP and (H_2O)ZnTPP.[5] By analogy, the magnesium was included in at least-squares calculation as a half-weight atom displaced ±0.25 Å along the fourfold rotation axis and its parameters were varied. The magnesium moved slightly to about ±0.27 Å out of the plane and its B_{33} parameter reduced significantly (to 4.8 Å^2). Thus, it was concluded that we were dealing with a disordered approximately square-pyramidal structure of aquo MgTPP.

Additional refinement of this structure gave a final R value of 0.085, hydrogen atoms included. The final atomic parameters are given in Table I and the bond distances and bond angles of MgTPP are shown in Figure 1. The errors in the bond distances are about ±0.01 Å toward the center of the molecule and increase to about ±0.02 Å further away. The errors in the bond angles are about 0.5–0.8°.

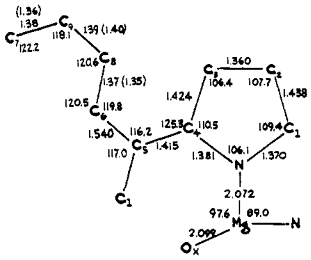

Figure 1. Bond distances and bond angles.

Discussion[6]

Although the crystal structure of MgTPP is disordered, the disorder is fairly precise in the mirror plane (see the B_{11} and B_{22} thermal parameters of Table I). The same is not true, however, in the z direction (the B_{33} parameters are consistently and significantly larger). If it were not for the fact that the magnesium atom is not in the mirror plane, it would have been practically impossible to differentiate between the disordered square-pyramidal structure and an octahedrally coordinated magnesium structure. A similar situation obtains for ClFeTPP and (H_2O)ZnTPP.[5] Thus, although the porphyrin moiety is determined to be in the mirror plane, it does not imply that the porphyrin is strictly planar since small deviations from planarity cannot be detected unambiguously and would lead to similar results (larger B_{33} parameters). The following possibilities cannot be

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(4) We wish to thank Dr. Alan D. Adler of the New England Institute for Medical Research, Ridgefield, Conn., for kindly furnishing us with a sample of MgTPP.

(5) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967); M. D. Glick, G. H. Cohen, and J. L. Hoard, *ibid.*, **89**, 1996 (1967).

(6) For a table of the observed and calculated structure factors, order NAPS Document No. NAPS-00409 from ASIS, National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001, remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

Table I. Final Atomic Parameters[a] (B_{ij}'s × 10^4)

Atom	x	y	z	β_{11}	B_{11}^b	β_{22}	B_{22}^b	β_{33}	B_{33}^b	β_{12}	β_{13}	β_{23}
Mg	0	0	0.0282 (16)	54 (2)	3.90	54 (2)	3.90	129 (32)	4.85	0	0	0
Ox	0	0	0.2448 (22)	121 (10)	8.80	121 (10)	8.80	183 (28)	6.89	0	0	0
N	0.0355 (4)	0.1484 (4)	0	48 (4)	3.48	53 (4)	3.85	184 (10)	6.90	3 (3)	0	0
C_1	−0.0294 (6)	0.2268 (5)	0	60 (5)	4.35	53 (5)	3.85	179 (13)	6.71	4 (4)	0	0
C_2	0.0257 (7)	0.3183 (6)	0	70 (6)	5.04	58 (5)	4.23	252 (17)	9.48	−6 (5)	0	0
C_3	0.1240 (6)	0.2950 (6)	0	60 (5)	4.35	56 (5)	4.09	197 (14)	7.39	1 (4)	0	0
C_4	0.1296 (6)	0.1894 (6)	0	59 (5)	4.30	59 (5)	4.30	160 (12)	6.02	1 (4)	0	0
C_5	0.2186 (5)	0.1333 (6)	0	52 (4)	3.77	67 (5)	4.87	160 (11)	6.02	−18 (4)	0	0
C_6	0.1361 (6)	0.1932 (5)	0	55 (5)	3.96	62 (5)	4.47	185 (13)	6.96	2 (4)	0	0
C_7	0.4906 (7)	0.2958 (6)	0	65 (6)	4.71	62 (6)	4.47	335 (24)	12.6	3 (5)	0	0
C_8	0.3592 (5)	0.2181 (6)	0.1208 (8)	83 (5)	6.02	128 (6)	9.30	188 (11)	7.05	−34 (4)	−2 (6)	−43 (6)
C_9	0.4490 (5)	0.2702 (6)	0.1228 (9)	88 (5)	6.36	121 (6)	8.76	245 (14)	9.19	−29 (4)	−12 (7)	−27 (7)

[a] Anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. Standard errors are in parentheses. [b] $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$.

distinguished from our results: (a) a planar porphyrin with large B_{33}'s; (b) a nonplanar porphyrin with small deviations from planarity and normal B_{33}'s; (c) as in (b) but with larger B_{33}'s.

From Figure 1, it can be seen that the behavior of the TPP moiety is similar to that of other porphyrins and metalloporphyrins. There is the characteristically short C–C distance of the pyrrole ring (1.36 Å) and the abnormally long bridge-to-phenyl distance (1.54 Å). In the present instance, the latter seems to be somewhat enhanced and could be due to the phenyl ring being oriented at right angles to the porphyrin ring so that the phenyl groups cannot enter into conjugation with the π-bonding system of the porphyrin.

The magnesium atom approximates closely square-pyramidal coordination with the pyrrole nitrogen atoms and the hydrating water molecule. The major deviation from square-pyramidal coordination comes from the magnesium being 0.273 Å (7.6°) out of the plane of the nitrogen atoms. It should be mentioned here that the water molecule is probably bound fairly firmly to the magnesium, since it was not introduced by us in the process of crystallization and must have been introduced at the time of preparation of the molecule.

Finally, in obtaining the bond distances and bond angles of the phenyl group, the atomic coordinates were corrected for a rigid body libration of the phenyl group in and perpendicular to its plane. The librations are clearly indicated by the B_{11}, B_{22}, β_{12}, and β_{23} parameters of C_8 and C_9 (plane of the phenyl ~30° from the *a* axis). The corrections were of the order of 0.02 Å (root-mean-square angle of libration of about 10°), and the uncorrected bond distances are shown in Figure 1 in parentheses.

Comparative Studies of the Catalytic Fluorination of Carbon Monoxide with Elementary Fluorine

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Abstract: In spite of a lack of good understanding, the process called catalytic fluorination has been used in the past for synthesis of many volatile fluorides. The procedure involves mixing fluorine with a reactant in the presence of a mass of catalyst which may be a finely divided metal coated with a film of metal fluoride. By comparing the behavior of various "catalysts," it has now been shown that a film of silver fluoride(s) on copper truly is a catalyst for the reaction $CO + F_2 = CF_2O$ (1) and for subsequent changes producing CF_3OOCF_3 and CF_3OF. Copper alone is much less active, and aluminum appears not to be a catalyst for reaction 1. The behavior of cesium fluoride as a catalyst for the reaction $CF_2O + F_2 = CF_3OF$ (2) has been confirmed and the salt has been shown not to help reaction 1. Possible mechanisms are discussed.

Although the process called catalytic fluorination has been used frequently in the past by many persons, including the senior author, little has been done to evaluate the relative activities of different catalysts or even in some cases to establish that without question catalysis occurs. The present paper answers some of the need for definite information.

Catalytic fluorination was first used by Fredenhagen and Cadenbach,[1] who allowed fluorine diluted by nitrogen to react with the vapors of several organic compounds. Fluorine contacted the organic material within the pores of a mass of copper gauze. The reaction proceeded smoothly without combustion or explo-

[1] K. Fredenhagen and G. Cadenbach, *Ber.*, 67, 928 (1934).