Crystal and Molecular Structure of Dimethoxyporphinatogermanium(IV)

ARISTIDES MAVRIDIS and A. TULINSKY*

The crystal and molecular structure of dimethoxyporphinatogermanium(IV), $(MeO)_2Ge(P)$, has been determined by x-ray crystallographic methods. The compound crystallizes in the monoclinic system, $a = 15.013$ (5), $b = 14.441$ (5), $c = 8.414$ (4) Å., $\beta = 91.85$ (2)°, space group $P2_1/c$ with four molecules per unit cell. The structure was solved through the application of Sayre's equation. The crystal structure is unusual in that the asymmetric unit consists of two crystallographically independent half-molecules located at centers of symmetry. The germanium coordination corresponds to that of a slightly distorted octahedron with the methoxy groups in apical positions. The averaged structures of the independent molecules are the same except for the orientation of the methoxy groups and the structures closely approximate D_{4h} symmetry. The independent pyrrole rings have a geometry similar to that of the azapyrrole of free base porphine and there is a general "squaring-up" and overall contraction of the central core region of $(MeO)_2Ge(P)$ compared to the free base. The density of $(MeO)_2Ge(P)$ is the largest of all porphyrins, especially when normalized with respect to the central ion. The abnormally large density is probably due to the fact that the molecular centers are located at face centered positions so that the packing is based upon a close packed arrangement.

Introduction

Although the octahedral nature of germanium in germanium porphyrins has been known for some time on the basis of NMR studies,[1,2] recently there has been a surge of general interest in the molecular and electronic structures of group 4 metalloporphyrins. Thus, independent x-ray crystallographic structure determinations have been reported for dichloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatotin(IV), $(Cl)_2Sn(TPP)$,[3] and dichloro-1,2,...,8-octaethylporphinatotin(IV), $(Cl)_2Sn(OEP)$,[4] and extended Hückel calculations have been carried out with Si, Ge, Sn, and Pb porphyrin structures.[5,6] In the case of the latter, the influence of the geometry of the molecule on the electronic spectrum of the macrocycle was the point of principal interest. In a continuation of our program of studying the effects of metallo substitution on the free base structure of the porphine ring system,[7] the present study includes the octahedral geometry of a germanium-substituted porphine and thus also quantitates the structural parameters of the geometry suggested by the NMR work. This x-ray structure determination is essentially an extension of our $\alpha,\beta,\gamma,\delta$-tetra-$n$-propylporphinatocopper(II), Cu(TPrP), work[7] since the radius of the germanium atom is small enough to also be accommodated in the central hole of the porphine core with minimal perturbation. In addition, the electron content of germanium is sufficiently small so as to permit an accurate structure determination and therefore the assessment of the effects of the germanium substitution on the free base structure[8,9] and with respect to the Cu(II) derivative.

Experimental Section

The dihydroxyporphinatogermanium(IV), $(HO)_2Ge(P)$, used in the x-ray crystallographic structure determination was prepared according to published procedures.[1] Well formed purple crystals exhibiting a rectangular-prismatic morphology of $(MeO)_2Ge(P)$ were obtained by allowing methanol to diffuse into a nearly saturated solution of $(HO)_2Ge(P)$ in chloroform. The structure determination of crystals grown in this manner showed that the $(HO)_2Ge(P)$ had been converted to $(MeO)_2Ge(P)$ during the crystallization process.[2]

Preliminary x-ray studies of a single crystal of $(MeO)_2Ge(P)$ using photographic and diffractometric methods showed the crystal system to be monoclinic and systematic absences fixed the space group to be $P2_1/c$. A suitable crystal fragment with approximate dimensions of $0.08 \times 0.10 \times 0.35$ mm was used for recording diffracted intensities. The lattice parameters were obtained from diffractometric measurements by the least-squares fit of the angular coordinates of 12 reflections in the range $52° < 2\theta < 90°$. The density of the crystal and unit cell data are summarized in Table I.

The intensity data collection was carried out with Cu Kα radiation (1.5418 Å) using a Picker four-circle diffractometer controlled by a Digital Equipment Corporation (DEC) 8K PDP-8 computer (FACS I system) coupled to a DEC 32K disc file and an Ampex TMZ 7-track

Table I. Crystal and Unit Cell Data of $(MeO)_2Ge(P)$

$a = 15.013$ (5) Å	$d_c = 1.61$ g cm^{-3}
$b = 14.441$ (5) Å	$d_o = 1.60$ g cm^{-3}
$c = 8.414$ (4) Å	Mol wt = 443.0 amu
$\beta = 91.85$ (2)°	$Z = 4$
$V = 1823.2$ Å^3	$F(000) = 904$ electrons
$\mu = 27.33$ cm^{-1}	
$\mu l_{mx} = 0.96$ (longest direction)	

tape transport. Intensities of reflections were measured by a wandering ω-step-scan procedure using balanced Ni/Co filters.[10] The step scan was performed in 0.03° increments of the ω angle and extended $\pm 0.075°$ on either side of the calculated peak position. Each step was measured for a duration of 4 s and the four largest measurements were summed to obtain the intensity of the reflection.[11] When the observed peak position did not coincide with the calculated ω value, one or two additional steps were taken to assure centering of the scan. The background was measured with a Co filter at the ω value of the maximum intensity for a time interval of 4 s and this count was multiplied by four to give the total background intensity. Since the step scan procedure is essentially a stationary crystal–stationary counter measurement, in order to avoid Kα splitting effects, the intensity data collection was confined to $2\theta < 110°$.

During the intensity data collection, the alignment of the crystal was monitored with the use of an automatic realignment subroutine by measuring the intensities of three standard reflections: (006) at $\chi = 90°$ and two ϕ values 100° apart, and the (842) reflection.[10] The standard reflections also served to monitor x-ray damage to the crystal; no decrease in the intensities of the standards was observed. Before the onset of intensity data collection, the mosaic spreads of two reflections were measured to ensure crystal quality and to help select the quadrant to be used for intensity data collection.

The intensities of the reflections were corrected for absorption and for lack of balance. A semiempirical method was used for the absorption correction based on the variance of the relative transmission (T) with the azimuthal angle (ϕ).[12] The $T(\phi)$ curves were constructed by measuring the variation of the absorption of reflections at $\chi = 90°$. Since the c^* axis occurred at $\chi = 90°$, $(00l)$ reflections were used to correct general reflections for absorption in terms of ϕ, 2θ, and reciprocal lattice level (l index). The absorptions of three reflections were measured: (002), (004), and (006), with $2\theta = 21.31$, 43.02, and 66.73°, respectively (maximum/minimum absorption ratios of 1.2, 1.2, and 1.3, respectively). The lack of balance was measured empirically and corrected in a manner described elsewhere.[13]

The intensities of a total of 2396 independent reflections were recorded of which 598 were taken to be absent. The observable limit was fixed from the average value of the measured intensities of the 120 systematically absent reflections and gave 1798 observable reflections for the structure determination; this corresponds to an observation/parameter ratio of 7:1 with general thermal vibrations but excluding hydrogen atoms.

Last, the corrected intensities were converted to relative structure amplitudes by application of the usual Lorentz and polarization factors.

Structure Analysis

A sharpened, origin removed, three-dimensional Patterson ($|E^2 - 1|$) map was synthesized. The map was characterized by large peaks at $(0, {}^1/_2, {}^1/_2)$, $({}^1/_2, {}^1/_2, 0)$, and $({}^1/_2, 0, {}^1/_2)$. Because of the ambiguity in the Harker section at $v = {}^1/_2$ of the Patterson map, two sets of fractional coordinates (a and b) were found for the germanium atom:

$$x = 0 \quad x = {}^1/_2 \quad x = {}^1/_4$$
$$y = {}^1/_2 \quad y = {}^1/_2 \quad y = 0$$
$$z = {}^1/_2 \quad z = 0 \quad z = {}^1/_4$$

$$\underbrace{\hspace{3cm}}$$
$$\text{a} \qquad\qquad \text{b}$$

A Fourier map based on the phase angles obtained from the coordinates (b) and coordinates deduced from ensuing maps did not lead to reasonable progress nor results. Since two crystallographically independent molecules per unit cell seemed unlikely at that time, a Fourier synthesis based on the coordinates (a) was never calculated. Instead, we decided to proceed via direct methods of phase determination.

Since almost all of the largest normalized structure amplitudes were of the type (hkl) = (even, even, even) or (odd, odd, odd), it was not possible to find three appropriate origin determining reflections with which to initiate a direct method of sign determination. In an effort to circumvent the problem, the E distribution was altered to correspond approximately to that of the free base macrocycle. This was carried out by subtracting the amplitude of the germanium atom contribution from the 590 germanium atom affected observed structure amplitudes, $|F_o(hkl)|$ (the amplitude of the contribution is the same for both sets of coordinates). These new structure amplitudes, $|F'(hkl)|$, where

$$|F'(hkl)| = ||F_o(hkl)| - |F_{Ge}(hkl)|_c|$$

and $|F_{Ge}(hkl)|_c$ is the calculated structure amplitude of the germanium atom were then converted to normalized values. Although the foregoing difference is only correct for in-phase scattering of the germanium atom and the porphine macrocycle, nevertheless, it proved to be an excellent approximation for the largest structure amplitudes (since the germanium scattering is constant and always at maximum by virtue of its geometrical contribution).

The phase angles of the largest $|E|$'s were obtained by iteratively applying Sayre's equation. The $|E|$'s with values greater than 1.5 were used in a sign determination computer program written by Long.[14] All 200 phases were determined and an E map revealed the positions of all the nonhydrogen atoms *except that of the metal*. The solution proved to be that of the two independent molecules centered around the independent centers of symmetry and subsequent refinement verified the correctness of the structure. Such unusual behavior has been previously observed with other metalloporphyrins.[15,16]

The coordinates of the 26 nonhydrogen atoms corresponding to $(HO)_2Ge(P)$ were determined from the E map. A structure factor calculation based on these with an average isotropic thermal parameter gave an R value of 0.21 ($R = \sum ||F_o| - |F_c||/\sum|F_o|$). At this stage, full-matrix, unit weight[9] least-squares refinement was initiated and another electron density map was computed ($R = 0.15$). This map revealed additional density near that of each of the independent oxygen atoms which proved to be the methyl groups. A difference electron density, with $R = 0.108$, displayed all the expected hydrogen atoms including those of the methyl groups. The hydrogen atoms were assigned isotropic temperature factors which were 1.25 greater than the isotropic temperature factors of the carbon atoms to which they were bonded and the resulting structure factor calculation had an R of 0.094.
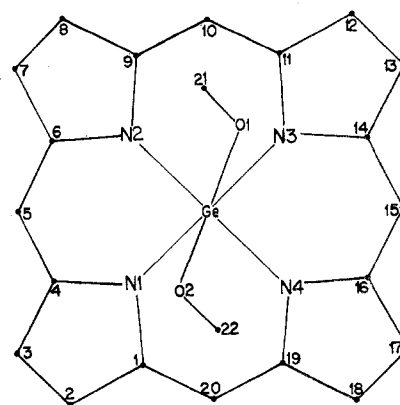

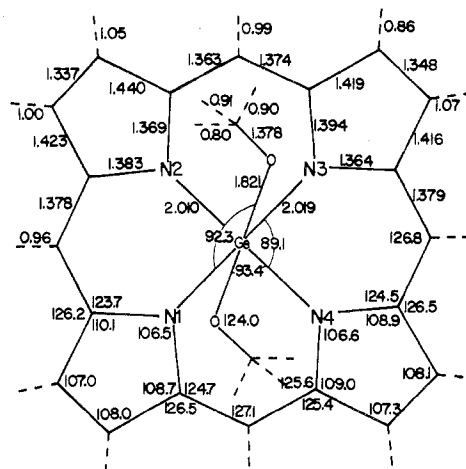**Figure 1.** Numbering system of $(MeO)_2Ge(P)$.

Figure 2. Molecule A; bond distances (Å) and angles (deg); broken lines indicate C–H bonds.

Relocation of the hydrogen atoms from a new difference electron density map and three more cycles of refinement gave an R value of 0.043. Another cycle of refinement on the coordinates of nonhydrogen atoms showed that the parameter shifts were insignificant compared to estimated standard deviations and that the R factor did not change, so that refinement of the structure was terminated. The final difference Fourier synthesis was featureless except for small regions of 0.1–0.2 eÅ^{-3} in the neighborhood of the germanium atoms.

Results[17]

Table II lists the final atomic parameters of the nonhydrogen atoms of the two independent centrosymmetrical molecules of the asymmetric unit and Table III lists the final parameters of isotropic hydrogen atoms. The atom notation is according to that of Figure 1. The standard deviations of the atomic parameters are in parentheses and are those of the final cycle of least-squares refinement; the errors in the hydrogen atom coordinates are about ten times greater than those of the atom to which they are bonded. The interatomic bond distances and angles of $(MeO)_2Ge(P)$ are shown in Figures 2 and 3 and are listed in Table IV along with their estimated standard deviations. The average standard deviations of the nonhydrogen atom bond distances and angles, based on the standard deviations of the atomic coordinates, are 0.008 Å and 0.5°, respectively. Best least-squares planes were calculated using unit weights for all the atoms of the porphine macrocycle of each molecule. The deviations of the atoms from these least-squares planes are listed in Table V. Best least-squares planes were also computed for the atoms of each pyrrole ring separately; these proved to be planar within the error of their

Table II. Final Atomic Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Peak height, $e\text{Å}^{-3}$
					Molecule A					
Ge	0.5	0.5	0	347 (4)	479 (5)	925 (13)	−44 (4)	−17 (6)	−22 (7)	49.0
N(1)	0.4436 (3)	0.6268 (3)	−0.0122 (5)	50 (3)	49 (3)	131 (8)	0 (2)	−16 (4)	−6 (4)	6.7
N(2)	0.4042 (2)	0.4552 (3)	0.1427 (4)	42 (3)	66 (3)	111 (8)	−10 (2)	4 (3)	−5 (4)	6.5
C(1)	0.3673 (3)	0.6539 (4)	0.0685 (6)	50 (4)	59 (4)	152 (11)	9 (3)	−27 (5)	−23 (5)	4.9
C(2)	0.3527 (4)	0.7496 (4)	0.0382 (7)	62 (4)	80 (5)	205 (13)	16 (4)	−41 (6)	−36 (7)	4.7
C(3)	0.4190 (4)	0.7812 (4)	−0.0517 (6)	77 (5)	55 (4)	179 (12)	9 (3)	−52 (6)	−22 (6)	4.9
C(4)	0.4743 (4)	0.7043 (4)	−0.0850 (6)	63 (4)	57 (4)	136 (10)	−7 (3)	−32 (5)	−3 (5)	5.1
C(5)	0.3177 (3)	0.5969 (4)	0.1593 (6)	46 (4)	77 (5)	157 (11)	0 (4)	0 (5)	−30 (6)	5.2
C(6)	0.3972 (3)	0.3684 (4)	0.2107 (6)	48 (3)	73 (5)	115 (10)	−21 (3)	−2 (4)	−2 (5)	5.0
C(7)	0.3226 (4)	0.3675 (4)	0.3106 (6)	68 (4)	86 (5)	140 (11)	−33 (4)	−1 (5)	−14 (6)	4.7
C(8)	0.2841 (3)	0.4509 (5)	0.3033 (6)	49 (4)	105 (6)	119 (10)	−24 (4)	16 (5)	−29 (6)	5.0
C(9)	0.3350 (3)	0.5068 (4)	0.1972 (6)	43 (3)	92 (5)	110 (9)	−14 (4)	−5 (4)	−24 (6)	5.2
C(10)	0.4524 (4)	0.2948 (4)	0.1796 (6)	63 (4)	67 (4)	118 (10)	−14 (3)	−14 (5)	6 (5)	5.1
C(21)	0.5754 (4)	0.5020 (4)	0.3129 (6)	51 (3)	80 (4)	114 (9)	−14 (3)	−12 (4)	−1 (6)	5.2
O(1)	0.5698 (2)	0.5430 (2)	0.1650 (3)	49 (2)	57 (2)	87 (6)	−14 (2)	−18 (3)	2 (3)	7.9
					Molecule B					
Ge	0	0.5	0.5	336 (4)	338 (4)	878 (12)	15 (4)	50 (6)	0 (6)	58.0
N(1)	−0.0948 (2)	0.5888 (2)	0.4181 (4)	38 (2)	36 (3)	111 (7)	3 (2)	4 (3)	0 (3)	7.4
N(2)	−0.0592 (2)	0.3976 (2)	0.3738 (4)	40 (2)	34 (3)	102 (7)	0 (2)	1 (3)	−4 (3)	7.2
C(1)	−0.1664 (3)	0.5685 (3)	0.3171 (6)	40 (3)	53 (4)	113 (9)	3 (2)	8 (4)	11 (5)	5.7
C(2)	−0.2109 (3)	0.6512 (4)	0.2956 (6)	44 (3)	57 (4)	159 (11)	10 (3)	7 (5)	20 (5)	5.7
C(3)	−0.1809 (3)	0.7185 (3)	0.3796 (6)	47 (3)	48 (4)	171 (11)	11 (3)	17 (5)	16 (5)	5.9
C(4)	−0.1022 (3)	0.6807 (3)	0.4589 (5)	40 (3)	44 (3)	125 (9)	6 (3)	13 (4)	14 (5)	5.9
C(5)	−0.1847 (3)	0.4832 (4)	0.2516 (6)	42 (3)	61 (4)	134 (10)	−2 (3)	−4 (4)	1 (5)	6.1
C(6)	−0.0306 (3)	0.3081 (3)	0.3631 (5)	48 (3)	43 (3)	109 (9)	−5 (3)	15 (4)	−6 (4)	5.6
C(7)	−0.0891 (3)	0.2577 (4)	0.2563 (6)	56 (4)	52 (4)	134 (10)	−15 (3)	20 (5)	−13 (5)	5.8
C(8)	−0.1537 (3)	0.3161 (4)	0.2056 (6)	54 (4)	56 (4)	146 (10)	−9 (3)	−5 (5)	−15 (5)	5.6
C(9)	−0.1350 (3)	0.4046 (3)	0.2775 (6)	45 (3)	47 (3)	121 (9)	−2 (3)	3 (4)	6 (5)	6.0
C(10)	0.0450 (3)	0.2720 (3)	0.4398 (6)	55 (4)	40 (3)	131 (10)	3 (3)	22 (5)	−3 (5)	6.3
C(21)	0.0594 (4)	0.5067 (4)	0.1814 (6)	57 (3)	78 (4)	99 (9)	−11 (3)	18 (4)	−1 (5)	4.7
O(1)	0.0732 (2)	0.5330 (2)	0.3410 (3)	38 (2)	45 (2)	83 (5)	−3 (2)	16 (2)	4 (3)	9.0

[a] Anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; estimated standard deviations in parentheses. The anisotropic thermal parameters have all been multiplied by 10^4, except those for the metal atom, which have been multiplied by 10^5.

Table III. Final Hydrogen Atom Parameters

Atom	x	y	z	B, Å^2	Peak height, $e\text{Å}^{-3}$
		Molecule A			
HC(2)	0.314	0.782	0.087	5.7	0.41
HC(3)	0.431	0.850	−0.091	5.2	0.50
HC(5)	0.267	0.625	0.213	5.3	0.38
HC(7)	0.323	0.308	0.369	5.7	0.36
HC(8)	0.231	0.484	0.360	5.3	0.45
HC(10)	0.451	0.233	0.221	5.0	0.39
HC(21)	0.606	0.530	0.374	4.4	0.40
HC(21)	0.520	0.494	0.353	4.4	0.51
HC(21)	0.597	0.443	0.300	4.4	0.48
		Molecule B			
HC(2)	−0.273	0.649	0.229	4.6	0.44
HC(3)	−0.195	0.777	0.397	4.6	0.54
HC(5)	−0.241	0.475	0.193	4.4	0.41
HC(7)	−0.102	0.207	0.243	4.7	0.44
HC(8)	−0.199	0.298	0.136	4.8	0.43
HC(10)	0.059	0.209	0.416	4.5	0.49
HC(21)	0.101	0.537	0.113	4.4	0.51
HC(21)	0.001	0.515	0.151	4.4	0.44
HC(21)	0.073	0.438	0.169	4.4	0.51

Figure 3. Molecule B; bond distances (Å) and angles (deg); broken lines indicate C–H bonds.

determination ($\sigma = \pm 0.002$, 0.003, 0.006, 0.007, respectively). Finally, Table VI lists corresponding equivalents of the principal mean-square displacements of the nonhydrogen atoms from equilibrium positions along the principal vibration directions. In addition, an average isotropic temperature factor is listed for each atom based on the principal mean-square displacements. From Table VI, it can be seen that molecule A is considerably more disordered than molecule B of the asymmetric unit. This can also be seen from the peak heights of the atoms 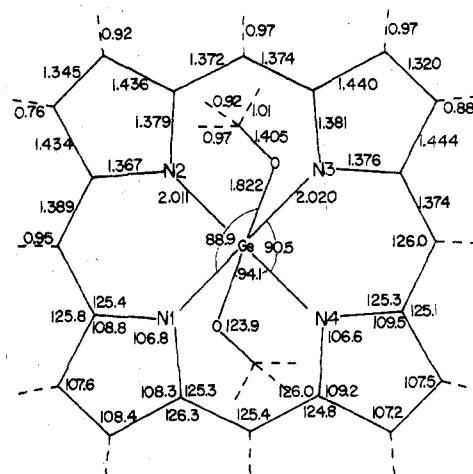listed in Table II and is the reason for the generally larger standard deviations of the atomic coordinates of molecule A.

Discussion

The crystal structure consists of two structurally nonequivalent $(\text{MeO})_2\text{Ge(P)}$ molecules, with a crystallographically imposed center of symmetry, located at face centered positions of the unit cell. The packing of $(\text{MeO})_2\text{Ge(P)}$ is exceptionally efficient compared to other porphyrin systems. As far as we are aware, the physical density of $(\text{MeO})_2\text{Ge(P)}$ is the highest of all porphines and porphyrins for which a structure has been determined or unit cell dimensions have been measured. This is achieved with no unusually close intermolecular contacts;

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Table IV. Bond Distances (Å) and Angles (deg) of $(MeO)_2Ge(P)$

Atoms	Molecule A	Molecule B	Atoms	Molecule A	Molecule B
Ge–N(1)	2.019 (4)	2.020 (4)	N(1)–Ge–N(2)	89.1 (2)	90.5 (1)
Ge–N(2)	2.010 (4)	2.011 (4)	N(1)–Ge–O(1)	92.3 (2)	88.9 (2)
Ge–O(1)	1.821 (3)	1.822 (3)	N(2)–Ge–O(1)	93.4 (2)	94.1 (2)
N(1)–C(1)	1.394 (6)	1.381 (6)	Ge–O(1)–C(21)	124.0 (3)	123.9 (3)
N(1)–C(4)	1.364 (7)	1.376 (6)	C(1)–N(1)–C(4)	106.5 (4)	106.8 (4)
N(2)–C(6)	1.383 (7)	1.367 (6)	C(6)–N(2)–C(9)	106.6 (4)	106.6 (4)
N(2)–C(9)	1.369 (7)	1.379 (6)	N(1)–C(1)–C(2)	108.7 (4)	108.3 (4)
C(1)–C(2)	1.416 (8)	1.440 (7)	N(1)–C(4)–0C(3)	110.1 (4)	108.8 (4)
C(3)–C(4)	1.419 (8)	1.444 (7)	N(2)–C(6)–C(7)	108.9 (5)	109.5 (4)
C(6)–C(7)	1.423 (8)	1.434 (7)	N(2)–C(9)–C(8)	109.0 (5)	109.2 (4)
C(8)–C(9)	1.440 (8)	1.436 (7)	N(1)–C(1)–C(20)	124.7 (5)	125.3 (4)
C(2)–C(3)	1.348 (8)	1.320 (7)	N(1)–C(4)–C(5)	123.7 (5)	125.4 (4)
C(7)–C(8)	1.337 (9)	1.345 (7)	N(2)–C(6)–C(5)	124.5 (4)	125.3 (4)
C(1)–C(20)	1.374 (8)	1.374 (7)	N(2)–C(9)–C(10)	125.6 (4)	126.0 (4)
C(4)–C(5)	1.379 (8)	1.374 (7)	C(20)–C(1)–C(2)	126.5 (5)	126.3 (4)
C(5)–C(6)	1.378 (8)	1.389 (7)	C(5)–C(4)–C(3)	126.2 (5)	125.8 (4)
C(9)–C(10)	1.363 (9)	1.372 (7)	C(5)–C(6)–C(7)	126.5 (4)	125.1 (4)
O(1)–C(21)	1.378 (7)	1.405 (6)	C(10)–C(9)–C(8)	125.4 (5)	124.8 (4)
			C(1)–C(2)–C(3)	108.0 (5)	108.4 (4)
			C(4)–C(3)–C(2)	107.0 (5)	107.6 (4)
			C(6)–C(7)–C(8)	108.1 (5)	107.5 (4)
			C(9)–C(8)–C(7)	107.3 (5)	107.2 (4)
			C(4)–C(5)–C(6)	126.8 (5)	126.0 (4)
			C(9)–C(10)–C(11)	127.1 (5)	125.4 (4)

Table V. Deviations of Porphine Skeleton From Least-Squares Plane

Molecule A		Molecule B	
Atom	d, Å	Atom	d, Å
Ge	0	Ge	0
N(1)	−0.05	N(1)	−0.03
N(2)	−0.02	N(2)	0.02
C(1)	−0.06	C(1)	−0.01
C(2)	0.01	C(2)	0.01
C(3)	0.09	C(3)	0.01
C(4)	0.03	C(4)	−0.01
C(5)	−0.07	C(5)	0.00
C(6)	0.03	C(6)	0.01
C(7)	0.07	C(7)	−0.02
C(8)	0.03	C(8)	0.00
C(9)	−0.03	C(9)	0.01
C(10)	−0.01	C(10)	−0.01
$\sigma = \pm 0.05$ Å		$\sigma = \pm 0.02$ Å	

the closest van der Waals approach in $(MeO)_2Ge(P)$ is about 3.49 Å [methyl(A)–methyl(B)]. The compact packing might be related to the location of the molecules on independent centers of symmetry in the unit cell and the concomitant freedom derived thereof. Four molecules in general positions in space group $P2_1/c$ are related to each other by the symmetry elements of the space group. However, in the present case, the orientation of the one pair of molecules is not dependent on the orientation of the other pair and the only

restrictions between the two pairs are of a "chemical and/or physical" nature. The plane of molecule B is tilted about 75° with respect to the plane of molecule A.

The coordination of the germanium atom in $(MeO)_2Ge(P)$ corresponds to that of a slightly distorted centrosymmetrical octahedral complex with the methoxy oxygen atoms at the apical positions. As can be expected from its radius (1.22 Å)[18] and coordination, the germanium atom is located in the plane of the porphine macrocycle (Table V). Both molecules are essentially planar although molecule B shows a higher degree of planarity; the angle between adjacent pyrroles in molecule B is 1.2° whereas the same angle in molecule A is 6.2°.

From Figures 2 and 3, it can be seen that the bond distances and bond angles of the crystallographically independent molecules are not exactly the same except in the region close to the germanium atom. However, from Table VII it will be seen that the averaged independent molecules are identical within the errors of their determination. This is so even though molecule B, in general, shows better internal consistency and larger peak heights for the atoms than its counterpart of the asymmetric unit (Tables II and VI). The Ge–N distances are essentially the same in both molecules as are the Ge–O distances. The latter (1.822 ± 0.001 Å) agrees well with the sum of the covalent radii of germanium and oxygen (0.60 Å);[18] moreover, it agrees well with a recent structure determination of a germanium hemiporphyrazine,[19] where a Ge–O distance of 1.804 Å is reported.

Table VI. Principal Mean-Square Displacements (Å²) in "Isotropic B" Notation

Molecule A	$8\pi^2\bar{\mu}_1{}^2$	$8\pi^2\bar{\mu}_2{}^2$	$8\pi^2\bar{\mu}_3{}^2$	$\langle B \rangle$	Molecule B	$8\pi^2\bar{\mu}_1{}^2$	$8\pi^2\bar{\mu}_2{}^2$	$8\pi^2\bar{\mu}_3{}^2$	$\langle B \rangle$
Ge	2.53	3.08	4.13	3.24	Ge	2.43	2.77	3.20	2.80
N(1)	3.04	4.07	4.93	4.01	N(1)	2.93	3.13	3.56	3.20
N(2)	3.13	3.37	5.86	4.12	N(2)	2.66	3.05	3.64	3.12
C(1)	2.90	4.10	6.89	4.63	C(1)	2.94	3.48	4.70	3.71
C(2)	3.53	4.98	9.75	6.09	C(2)	3.30	4.02	5.88	4.40
C(3)	2.97	4.34	9.44	5.58	C(3)	3.15	3.92	6.00	4.36
C(4)	2.73	4.79	6.89	4.80	C(4)	2.89	3.15	4.76	3.60
C(5)	3.64	4.20	7.17	5.00	C(5)	3.48	4.10	5.11	4.23
C(6)	2.99	3.47	7.21	4.56	C(6)	2.80	3.34	4.72	3.62
C(7)	3.27	4.44	9.55	5.75	C(7)	3.28	3.40	6.37	4.35
C(8)	2.97	3.54	9.97	5.49	C(8)	3.28	4.83	5.55	4.55
C(9)	2.50	3.91	8.23	4.88	C(9)	3.26	3.90	4.20	3.79
C(10)	3.07	4.53	7.07	4.89	C(10)	2.96	3.49	5.47	3.97
C(21)	2.85	4.46	7.20	4.84	C(21)	2.52	4.89	7.01	4.81
O(1)	2.00	3.72	5.99	3.90	O(1)	1.90	3.65	3.89	3.15
	$\langle$Molecule A$\rangle = 4.79$					$\langle$Molecule B$\rangle = 3.84$			

Table VII. Comparison of Averaged $(MeO)_2Ge(P)$ with Free Base[a]

	Molecule A	Molecule B	Averaged (A–B)	Porphine
Ge–N	2.015 (6)	2.016 (6)	2.015 (5)	2.029[b]
N–C_a	1.378 (14)	1.376 (6)	1.377 (10)	1.376 (1)
C_a–C_b	1.425 (10)	1.439 (5)	1.432 (10)	1.452 (11)
C_b–C_b	1.343 (8)	1.333 (18)	1.338 (13)	1.345 (1)
C_a–C_m	1.374 (7)	1.377 (8)	1.375 (7)	1.382 (9)
N–C_a–C_m	124.6 (8)	125.5 (3)	125.1 (7)	125.0 (6)
C_a–C_m–C_a	127.0 (2)	125.7 (4)	126.3 (8)	127.1 (5)
N–C_a–C_b	109.2 (6)	109.0 (5)	109.1 (6)	109.8 (5)
C_a–C_b–C_b	107.9 (6)	107.7 (5)	107.8 (5)	107.1 (8)
C_m–C_a–C_b	126.2 (5)	125.5 (7)	125.8 (6)	125.1 (8)
C_a–N–C_a	106.6 (1)	106.7 (1)	106.6 (1)	106.1 (2)

[a] C_a, C_b, and C_m notation is that of J. L. Hoard, ref 22; observed standard deviation from averaged value in parentheses. [b] Half of cross azapyrrole distance.
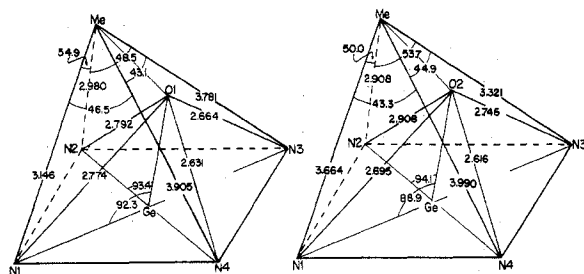

Figure 4. Geometry of the germanium coordination; distances (Å); angles (deg); molecule A on left.

The independent molecules differ from one another in the exact positioning of the methoxy groups with respect to the porphine macrocycle (Figure 4). The Ge–O direction differs by about 1–2° in the two molecules and the O–Me orientations with respect to the macrocycle are also different. The plane which contains the atoms Ge, O, and C of the methoxy group forms the following angles with respect to N(2)–N(4): molecule A, 33.9°; molecule B, 16.8°. These differences might be due to the relatively close intermolecular contact already mentioned between the methyl groups of independent molecules.

The fourfold averaged structure of the independent molecules of $(MeO)_2Ge(P)$ is compared with the averaged structure of the azapyrrole of free base porphine in Table VII. The comparison of the bond angles of this ring in the two porphyrin systems, which is more sensitive than a comparison of bond distances, reveals that the rings are the same within experimental error (±0.6°); the same can be said of the bond distances. Such a behavior is consistent with the general idea that the substitution of the inner pyrrolic hydrogen atoms by an atom of optimal size can be accommodated in the porphine core without distortion and essentially leads only to changes in the reduced pyrrole rings.[20] The Ge–N distance is 0.042 Å shorter than half the nitrogen separation between reduced pyrroles in the free base but it is only 0.014 Å shorter than the corresponding separation of the azapyrroles. Consequently, the reduced pyrrole rings are altered more in stereochemistry during the D_{4h} symmetry derivative formation.

The geometry of the central core region of $(MeO)_2Ge(P)$ is compared with that of porphine in Table VIII. From Table VIII, it will be seen that the pyrrolic nitrogen atoms "square-up" [N(1)N(2)N(3), N(2)N(1)N(4)], and this is accompanied by an overall contraction (~0.08 Å, N_1–N_3, N_2–N_4). Similar observations have been made with $Cu(TPrP)^5$ and $Ni(OEP)^{21}$ even though the metals Ge, Cu, and Ni differ significantly in character. The geometrical constraints of the porphyrin system are so overwhelming that metals with a relatively low electron content are easily ac-

Table VIII. Comparison of Central Core Region of $(MeO)_2Ge(P)$ with Free Base

Atom	Molecule A	Molecule B	Average (A–B)	Porphine
N(1)–N(2)	2.828 (6)	2.862 (5)	2.85	2.88
N(1)–N(4)	2.871 (6)	2.839 (5)	2.86	2.89
N(1)–N(3)	4.039 (6)	4.040 (5)	4.04	4.12
N(2)–N(4)	4.021 (5)	4.021 (5)	4.02	4.04
C(5)–C(10)	4.809 (8)	4.831 (7)	4.82	4.83
C(5)–C(20)	4.809 (8)	4.826 (7)	4.82	4.84
C(5)–C(XX)	6.825 (8)	6.804 (6)	6.82	6.84
C(10)–C(20)	6.777 (7)	6.853 (7)	6.82	6.83
∠N(1)–N(2)–N(3)	90.3 (2)	90.3 (1)	90.3	91.0
∠N(2)–N(1)–N(4)	89.7 (2)	89.7 (1)	89.7	88.7
∠C(10)–C(5)–C(20)	89.6 (1)	90.4 (1)	90.0	89.9
∠C(5)–C(10)–C(15)	90.4 (1)	89.6 (1)	90.0	90.0

commodated into the central core (approximate radius 2.01 Å)[20,22] and all show the same effect of increasing the symmetry of the macrocycle with a minimal perturbation of the system.

On the other hand, the size of the metal can severely affect the geometry of the core. Metals with large radii which are forced to remain in the plane of the macrocycle (i.e. octahedral geometry) cause large changes in the bond distances and angles of the macrocycle. This has been shown by the structures of $(Cl)_2Sn(TPP)^3$ and $(Cl)_2Sn(OEP).^4$ Due to the large Sn–N distance (~2.1 Å) the $\angle C_aNC_a$ is forced to increase by approximately 3°. This causes the C_b–C_b bond distance to increase by 0.02–0.03 Å in order to minimize the reduction of the already strained $\angle NC_aC_b$. Thus, the D_{4h} approximate symmetry is retained, but the pyrroles have been changed from their free-base geometry because of the inherent straining of the porphine macrocycle.

References and Notes

(1) A. R. Kane, R. G. Yalman, and M. E. Kenney, *Inorg. Chem.*, 7, 2588 (1968).
(2) J. E. Maskasky and M. E. Kenny, *J. Am. Chem. Soc.*, 95, 1443 (1973).
(3) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Am. Chem. Soc.*, 94, 6689 (1972).
(4) D. L. Cullen and E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, 29, 2507 (1973).
(5) A. N. Schaffer and M. Gouterman, *Theor. Chim. Acta*, 18, 1 (1970).
(6) M. Gouterman, F. P. Schwarz, P. D. Smith, and D. Dolphin, *J. Chem. Phys.*, 59, 676 (1973).
(7) I. Moustakali and A. Tulinsky, *J. Am. Chem. Soc.*, 95, 6811 (1973).
(8) B. M. L. Chen and A. Tulinsky, *J. Am. Chem. Soc.*, 94, 4144 (1972).
(9) P. W. Codding and A. Tulinsky, *J. Am. Chem. Soc.*, 94, 4151 (1972).
(10) R. L. Vandlen and A. Tulinsky, *Acta Crystallogr., Sect. B*, 27, 437 (1971).
(11) H. W. Wyckoff, M. Doscher, D. Tsernoglou, T. Inagami, L. N. Johnson, K. D. Hardman, N. M. Allewell, D. M. Kelly, and F. M. Richards, *J. Mol. Biol.*, 27, 563 (1967).
(12) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 24, 351 (1968).
(13) A. Tulinsky, N. V. Mani, C. N. Morimoto, and R. L. Vandlen, *Acta Crystallogr., Sect. B*, 29, 1309 (1973).
(14) R. E. Long, Ph.D. Thesis, University of California, Los Angeles, Calif., 1965.
(15) J. W. Lauher, and J. A. Ibers, *J. Am. Chem. Soc.*, 96, 4447 (1974).
(16) F. R. Hopf, T. P. O'Brien, W. R. Scheidt, and D. C. Whitten, *J. Am. Chem. Soc.*, 97, 277 (1975).
(17) Supplementary material; Table of $|F_o|$ and F_c.
(18) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972.
(19) H. J. Hecht and P. Luger, *Acta Crystallogr., Sect. B*, 30, 2843 (1974).
(20) J. L. Hoard, *Ann. N.Y. Acad. Sci.*, 206, 18 (1973).
(21) D. L. Cullen and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, 96, 2095 (1974).
(22) J. L. Hoard, *Science*, 174, 1295 (1971).