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Infrared and Nuclear Magnetic Resonance Studies of Some Germanium Phthalocyanines and Hemiporphyrazines¹

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Infrared and nmr studies have been carried out on a series of germanium hemiporphyrazines and phthalocyanines. The nmr studies have shown that the hemiporphyrazine ring, in contrast to the phthalocyanine ring, is not aromatic. The infrared studies have yielded a set of Ge-X and Ge-O frequencies.

Introduction

A few years ago 5,26:13,18-diimino-7,11:20,24-dinitrilodibenzo[*c,n*]-1,6,12,17-tetraazacyclodocosine² or metal-free hemiporphyrazine, hpH_2 ,³ Figure 1, was reported.^{4,5} Also reported were magnesium, copper, lead, and other metal derivatives of this phthalocyanine-like macrocycle. More recently it was found in this laboratory that hemiporphyrazine, like phthalocyanine, forms germanium derivatives.

This situation provided the basis for the present work, major objectives of which were the determination of the aromaticity of the hemiporphyrazine ligand and the determination of the frequencies of the Ge-X and Ge-O stretching modes in some halo, oxy, and hydroxy germanium hemiporphyrazines and germanium phthalocyanines.

Experimental Section

hpH_2 .—To prepare this compound a modification of Campbell's method was used.⁴ A mixture of 25.53 g of phthalonitrile, 22.11 g of 2,6-diaminopyridine, and 150 ml of 1-chloronaphthalene was refluxed for 19 hr, cooled, and filtered. This gave 24.85 g of red-orange product, a portion of which was purified by recrystallization from 1-chloronaphthalene. *Anal.* Calcd for $C_{26}H_{16}N_8$: C, 70.90; H, 3.66; N 25.44. Found: C, 71.06; H, 3.51, N, 25.30.

hpD_2 .—A 5.0-g sample of $hpNa_2$ ⁶ was refluxed with a solution of 14 ml of D_2O and 100 ml of dry pyridine for 24 hr and filtered. This gave 2.83 g of yellow hydrated hpD_2 . Vacuum sublimation of 479 mg of this at 300° yielded 308 mg of red-orange crystals. *Anal.* Calcd for $C_{26}H_{14}D_2N_8$: C, 70.58; N, 25.32. Found: C, 70.64; N, 25.40.

$hpGeCl_2$.—A small amount of quinoline was distilled from a mixture of 10.0 g of hpH_2 and 150 ml of quinoline, and then a mixture of 3 ml of germanium tetrachloride in 10 ml of quinoline was added. The resultant was refluxed for 15 min, partially cooled, filtered, further cooled, and refiltered. After being washed with methanol, acetone, and ether, the product weighed 6.04 g, a 46% yield based on hpH_2 . Recrystallization of the

chloride from 1-chloronaphthalene gave blue-black-reflecting, green-yellow-transmitting pleochroic crystals. *Anal.* Calcd for $C_{26}H_{14}N_8GeCl_2$: C, 53.66; H, 2.42; Ge, 12.47; Cl, 12.18. Found: C, 53.70; H, 2.48; Ge, 12.78; Cl, 12.18. Efforts to increase the yield by increasing the reaction time failed, giving, in fact, lower yields.

$hpGe(OH)_2$.—A mixture of 473 mg of recrystallized $hpGeCl_2$, 13 ml of pyridine, and 13 ml of water was refluxed for 3 hr. The product was washed, refluxed with 50 ml of water and 50 ml of concentrated ammonium hydroxide for 1.5 hr, and reworked. This gave 309 mg of blue-black-reflecting, green-yellow-transmitting crystals. *Anal.* Calcd for $C_{26}H_{16}N_8GeO_2$: C, 57.29; H, 2.96; Ge, 13.32. Found: C, 57.43; H, 3.36; Ge, 13.82.

$hpGe(OD)_2$.—A mixture of 135 mg of recrystallized $hpGeCl_2$, 10 ml of dry pyridine, and 2 ml of D_2O was refluxed for 2.5 hr. The resultant blue-black-reflecting, green-yellow-transmitting pleochroic crystals weighed, after washing, 98 mg. *Anal.* Calcd for $C_{26}H_{14}D_2N_8GeO_2$: C, 57.08; Ge, 13.27. Found: C, 56.94, 57.05; Ge, 13.18.

$hpGeF_2$.—To get $hpGeF_2$, 2.70 g of $hpGe(OH)_2$ was evaporated to dryness three times with mixtures of 3.5 ml of 48% hydrofluoric acid and 8 ml of pyridine (one treatment giving incomplete conversion).

α - $hpGeF_2$.—A mixture of 284 mg of $hpGeF_2$ twice recrystallized from 1-chloronaphthalene was refluxed with 7 ml of 1-chloronaphthalene and filtered. The resultant was diluted with 6 ml of 1-chloronaphthalene, refluxed for 20 min, and cooled very slowly. This gave 109 mg of large blue-black-reflecting, yellow-transmitting pleochroic crystals. *Anal.* Calcd for $C_{26}H_{14}N_8GeF_2$: C, 56.89; H, 2.57; Ge, 13.22; F, 6.92. Found: C, 57.16; H, 2.56; Ge, 12.93; F, 6.69.

β - $hpGeF_2$.—A sample of recrystallized $hpGeF_2$ was digested successively with 1,2,4-trimethylbenzene, chlorobenzene, and 1,2,4-trimethylbenzene. This gave blue-black opaque crystals. *Anal.* Found: C, 56.54; H, 2.29; Ge, 13.50; F, 6.84.

Infrared spectra showed that the conversion was complete after the first step. Other work showed that this polymorph could also be obtained from toluene or chlorobenzene extractions.

γ - $hpGeF_2$.—A mixture of 975 mg of $hpGeF_2$ and 35 ml of 1-chloronaphthalene was refluxed for 15 min, filtered, cooled under running water, and refiltered. The resultant blue-black crystals, somewhat contaminated with crystals of the α modification, weighed 740 mg. *Anal.* Found: C, 56.73; H, 2.66; Ge, 13.48; F, 6.70.

$hpGeBr_2$.—A mixture of 1.81 g of $hpGe(OH)_2$, 5.5 ml of bromotriethylsilane, and 35 ml of 1,2,4-trimethylbenzene was refluxed for 50 min, cooled, and filtered. This gave 2.11 g of product. Recrystallization from 1-chloronaphthalene gave blue-black-reflecting opaque needles. These were washed with 1-chloronaphthalene and ether and then with pyridine, benzene, and ether (to remove an impurity giving an infrared absorption at $\sim 3350\text{ cm}^{-1}$). *Anal.* Calcd for $C_{26}H_{14}N_8GeBr_2$: C, 46.55; H, 2.10; Ge, 10.82; Br, 23.82. Found: C, 46.88; H, 2.30; Ge, 10.90; Br, 23.65. The bromide was found to be unstable, the

(1) This work was supported in part by the National Science Foundation under Grant GP-1702 and the Office of Naval Research under Contract Nonr 1141(18). Additional support was provided by an NDEA fellowship.

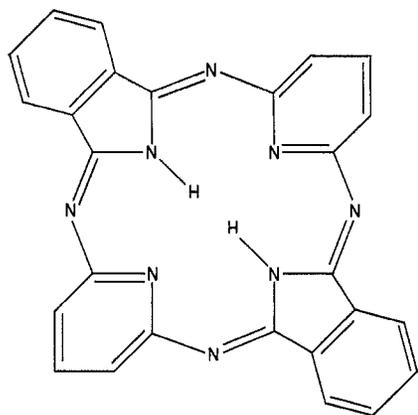
(2) A. M. Patterson, L. T. Capell, and D. F. Walker, Ed., "The Ring Index," 2nd ed, American Chemical Society, Washington, D. C., 1960, No. 7174, p 1100.

(3) The trivial name hemiporphyrazine and the symbol hpH_2 for this compound are used at the suggestion of Dr. Roy M. Adams of the Committee on Nomenclature, Inorganic Section, American Chemical Society, and Dr. Kurt Loening of Chemical Abstracts. Their suggestions stem from Campbell's patent.⁴

(4) J. B. Campbell, U. S. Patent 2,765,308 (1956).

(5) J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 5008 (1952).

(6) Synthesis to be reported elsewhere.

Figure 1.—Metal-free hemiporphyrzine, hpH_2 .

storage of a sample in a desiccator at room temperature for 1 month resulting in decomposition detectable by infrared spectra.

hpGeI₂.—A small amount of chlorobenzene was distilled from a 20-ml portion of this solvent, and then 0.20 ml of triethyliodosilane and 0.36 g of $hpGe(OH)_2$ were added. The resultant was refluxed for 3 min and filtered. This yielded 0.28 g of blue-black-reflecting, brown-transmitting pleochroic crystals. No satisfactory method of purifying this compound was found. Infrared spectra indicated that a sample of it stored for 1 month underwent considerable decomposition.

(hpGeO)₂.—A mixture of 225 mg of pure $hpGe(OH)_2$ and 5.8 ml of 1-chloronaphthalene was refluxed for 2 hr, cooled, and filtered. The resultant brown powder weighed 184 mg. *Anal.* Calcd for $C_{26}H_{14}N_8GeO$: C, 59.25; H, 2.68; Ge, 13.77. Found: C, 58.76; H, 3.08; Ge, 13.49. This compound was also prepared by the condensation of $hpGe(OH)_2$ at $>300^\circ$ in a vacuum.

Differential thermal analysis was applied to obtain further information about the formation of this compound. In this work, the range covered was 100–500°, the heating rate was 10°/min, the atmosphere was nitrogen, and the reference material was powdered quartz. The dta curve obtained had as its only important feature an endotherm beginning at about 310° and reaching a maximum at 365°. The curve obtained when $hpGe(OD)_2$ was substituted for $hpGe(OH)_2$ was the same except that the endotherm was slightly shifted, its maximum being at 373°. Infrared spectra showed that the product of both reactions was $(hpGeO)_2$.

On the basis of these results, assignment of the endotherms to the condensation reaction is unambiguous. The differences between the results for $hpGe(OH)_2$ and $hpGe(OD)_2$ indicate that cleavage of the O–H bond is an important step in the reaction.

hpGe(OCH₃)₂.—A mixture of 643 mg of $hpGe(OH)_2$ and 50 ml of methanol was refluxed for 1.5 hr, cooled, and filtered. This yielded 631 mg of the β polymorph.

α -hpGe(OCH₃)₂.—A mixture of 213 mg of the synthesis product, 5 ml of methanol, and 300 ml of benzene was refluxed for 10 min, cooled slightly, filtered, and kept at 5° for 6 hr. Refiltration yielded 34 mg of blue-black-reflecting opaque plates. *Anal.* Calcd for $C_{28}H_{20}N_8GeO_2$: C, 58.68; H, 3.52; Ge, 12.67. Found: C, 58.43; H, 3.27; Ge, 13.02.

β -hpGe(OCH₃)₂.—A mixture of 123 mg of $hpGe(OCH_3)_2$, which had been recrystallized from benzene, and 30 ml of toluene was refluxed for 1 hr and quickly cooled. This yielded 75 mg of blue-black-reflecting needles. *Anal.* Found: C, 59.23; H, 3.58; Ge, 12.86. The β form was also obtained by the recrystallization of $hpGe(OCH_3)_2$ from a solution of methanol in 1,2,4-trimethylbenzene.

hpGe(O-n-C₄H₉)₂.—A 1.66-g sample of $hpGe(OH)_2$ was refluxed with 50 ml of 1-butanol for 1 hr. Then 860 mg of the resultant partially converted product was refluxed with 10 ml of 1-butanol for 1 hr. Recrystallization of a portion of the product from 1,2,4-trimethylbenzene gave blue-black-reflecting, yellow-transmitting needles. *Anal.* Calcd for $C_{34}H_{32}N_8GeO_2$: C,

62.13; H, 4.91; Ge, 11.04. Found: C, 62.57; H, 4.95; Ge, 11.19.

hpGe(OC₆H₅)₂.—A mixture of 1.98 g of $hpGe(OH)_2$, 6.36 g of phenol, and 25 ml of benzene was refluxed for 3 hr and filtered. Evaporation of the filtrate gave 730 mg of product. Recrystallization of a portion of this from a solution of phenol in pyridine twice and from chlorobenzene once yielded blue-black-reflecting, green-yellow-transmitting pleochroic crystals. *Anal.* Calcd for $C_{38}H_{42}N_8GeO_2$: C, 65.46; H, 3.47; Ge, 10.41. Found: C, 64.94; H, 3.27; Ge, 10.32.

hpGe(OSi(C₂H₅)₃)₂.—A solution of 0.55 ml of triethylsilanol in 20 ml of chlorobenzene was added over an 8-hr period to a refluxing mixture of 1.0 g of $hpGe(OH)_2$ and 50 ml of chlorobenzene. The resultant mixture was refluxed 5 hr, filtered, and evaporated to dryness. This gave 1.30 g of product. Recrystallization of a portion of the product from cyclohexane twice gave blue-black-reflecting, green-yellow-transmitting crystals. *Anal.* Calcd for $C_{38}H_{44}N_8GeSi_2O_2$: C, 59.00; H, 5.73. Found: C, 58.76; H, 6.06.

PcGeF₂.—A 100-mg sample of $PcGe(OH)_2$ was evaporated to dryness on a steam bath with 20 ml of 48% hydrofluoric acid. This gave 98 mg of product. Extraction of a portion of this with chloronaphthalene gave red-reflecting, blue-transmitting crystals. *Anal.* Calcd for $C_{32}H_{16}N_8GeF_2$: C, 61.68; H, 2.59; Ge, 11.65; F, 6.10. Found: C, 61.44; H, 2.75; Ge, 12.21; F, 6.39.

PcGeBr₂.—A 100-mg sample of $PcGe(OH)_2$ was refluxed with a solution of 2 ml of triethylbromosilane in 20 ml of 1,2,4-trimethylbenzene for 1 hr. The resultant product weighed 102 mg. Recrystallization of this from 1-chloronaphthalene yielded red-reflecting, green-transmitting crystals. *Anal.* Calcd for $C_{32}H_{16}N_8GeBr_2$: C, 51.60; H, 2.17; Ge, 9.74; Br, 21.45. Found: C, 51.68; H, 2.20; Ge, 9.55; Br, 21.66.

PcGeI₂.—A 200-mg sample of $PcGe(OH)_2$ was refluxed with 0.5 ml of triethyliodosilane in 40 ml of 1,2,4-trimethylbenzene for 1 hr and filtered. This gave 239 mg of product. Extraction with 1-chloronaphthalene containing I₂, under a nitrogen atmosphere, gave red-reflecting, green-transmitting crystals. *Anal.* Calcd for $C_{32}H_{16}N_8GeI_2$: C, 45.81; H, 1.92; Ge, 8.65; I, 30.25. Found: C, 46.06; H, 2.04; Ge, 8.61; I, 29.93.

PcGe(OD)₂.—A mixture of 198 mg of recrystallized $PcGeCl_2$, 10 ml of dry pyridine, and 2 ml of D₂O was refluxed for 4.5 hr. This gave 181 mg of a blue powder. *Anal.* Calcd for $C_{32}H_{16}D_2N_8GeO_2$: C, 61.88; Ge, 11.69. Found: C, 62.10; Ge, 11.80.

(PcGeO)₂.—A 179-mg sample of pure $PcGe(OH)_2$ was heated under vacuum at 350° for 1.7 hr. The resultant was a dark blue powder. *Anal.* Calcd for $C_{32}H_{16}N_8GeO$: C, 63.94; H, 2.68; N, 18.64; Ge, 12.08. Found: C, 64.04; H, 2.92; N, 18.67; Ge, 12.03.

PcGe(OSi(C₂H₅)₃)₂.—A mixture of 1.00 g of $PcGe(OH)_2$, 0.5 ml of triethylsilanol, and 50 ml of chlorobenzene was refluxed for 2.5 hr and filtered. Evaporation of the filtrate yielded 1.21 g of product. Recrystallization from toluene twice gave red-reflecting, blue-transmitting crystals. *Anal.* Calcd for $C_{44}H_{46}N_8GeSi_2O_2$: C, 62.34; H, 5.47. Found: C, 62.17; H, 5.39.

X-Ray Powder Patterns.—The accompanying calculated d spacings and estimated intensities were obtained from Debye-Scherrer photographs which were taken with a 114.6-mm camera and vanadium-filtered Cr K α radiation. The samples were held in 0.3-mm glass capillaries. α - $hpGeF_2$: 9.54 s, 8.14 s, 7.04 vw, 6.04 vs, 4.76 w, 4.49 m, 4.10 m, 3.76 m, 3.55 w, 3.45 s, 3.33 w, 3.18 w, 3.10 w, 3.02 m, 2.96 m, 2.84 w, 2.72 vw, 2.62 m, 2.50 w, 2.38 vw, 2.29 w, 2.26 w, 2.20 m, 2.09 w, 2.06 vw, 2.00 w, 1.96 vw, 1.90 w, 1.88 vw, 1.85 vw, 1.79 vw, 1.73 w. β - $hpGeF_2$: 9.51 s, 9.11 s, 8.20 m, 7.06 vs, 6.65 w, 6.04 m, 5.15 w, 4.88 m, 4.53 w, 3.82 w, 3.34 s, 3.04 vw, 2.96 vw, 2.76 vw, 2.63 vw, 2.51 vw. γ - $hpGeF_2$: 9.53⁷ m, 8.97 s, 8.18⁷ m, 7.06 vs, 6.53 w, 6.05⁷ m, 5.15 w, 4.84 m, 4.51 w, 4.09 vw, 3.87 vw, 3.80 w, 3.48⁷ m, 3.34 s, 3.23 w, 3.04 w, 2.96 vw, 2.85 vw, 2.76 w, 2.63 vw, 2.50 vw, 2.48 vw, 2.29 vw, 2.20 vw, 2.18 vw. $hpGeCl_2$: 8.29 vs,

(7) Due in part or completely to the presence of α - $hpGeF_2$.

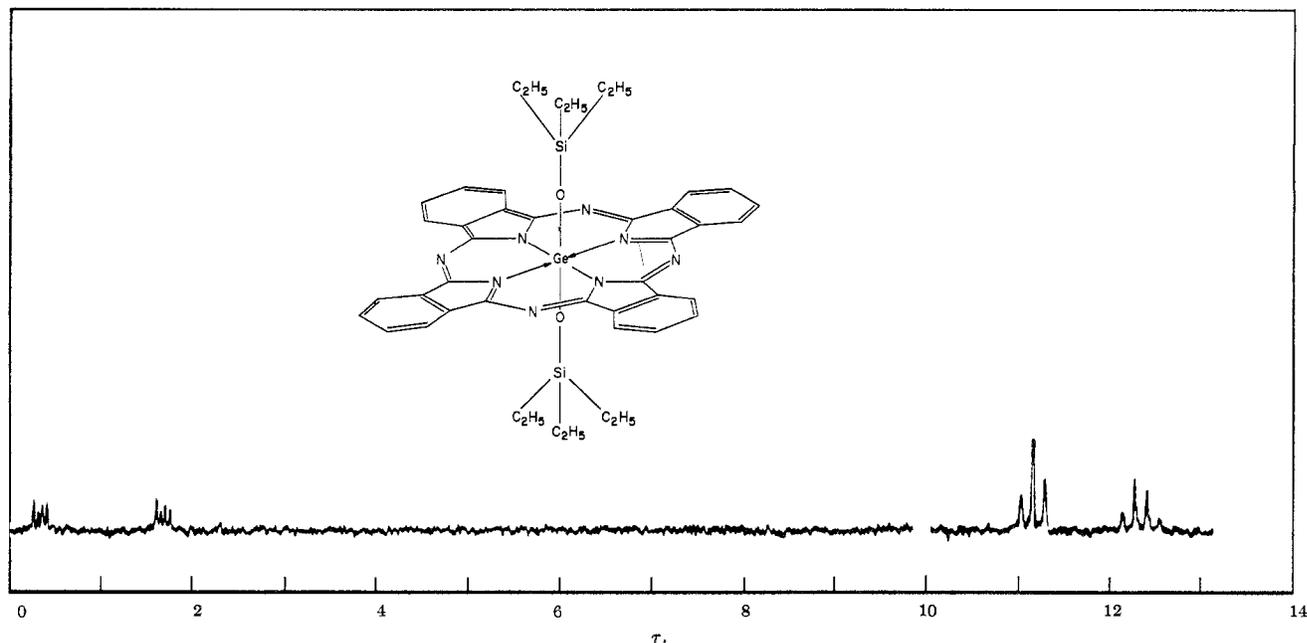


Figure 2.—The nmr spectrum of $\text{PcGe}[\text{OSi}(\text{C}_2\text{H}_5)_3]_2$.

7.49 s, 7.10 s, 6.60 w, 5.94 m, 5.15 s, 4.09 m, 3.76 w, 3.67 w, 3.50 vs, 3.37 w, 3.22 w, 3.06 m, 2.75 vw, 2.68 vw, 2.56 m, 2.35 vw, 2.27 w, 2.20 vw, 2.11 m, 2.05 w, 1.97 w. hpGeBr_2 : 8.36 vs, 7.57 m, 7.21 m, 6.66 w, 6.07 vw, 5.19 s, 4.13 w, 3.93 vw, 3.69 vw, 3.54 vs, 3.26 w, 3.08 w, 2.78 vw, 2.73 vw, 2.58 vw, 2.36 m, 2.30 vw, 2.23 vw, 2.14 w, 2.04 w, 1.95 vw. $\alpha\text{-hpGe}(\text{OCH}_3)_2$: 12.00 m, 9.43 w, 8.52 vs, 7.23 m, 6.65 w, 6.28 w, 5.95 w, 5.42 w, 4.68 m, 4.34 w, 4.02 w, 3.81 w, 3.42 w, 3.29 s, 3.06 vw, 2.81 vw, 2.63 vw. $\beta\text{-hpGe}(\text{OCH}_3)_2$: 8.45 vs, 7.85 w, 6.28 m, 5.93 w, 5.34 w, 4.92 w, 4.66 w, 4.33 w, 4.01 s, 3.81 w, 3.68 w, 3.50 w, 3.41 vw, 3.33 vw, 3.14 vw, 3.04 vw, 2.95 vw, 2.80 m, 2.60 vw, 2.49 vw, 2.41 vw, 2.33 vw, 2.14 w, 2.01 w, 1.83 vw, 1.76 vw.

Infrared Spectra.—Infrared spectra were obtained from mineral oil mulls with the aid of Beckman IR8, IR5A-CsBr, and IR-11 infrared spectrophotometers. Polystyrene, 1,2,4-trichlorobenzene, and water vapor were used for calibration.

Nmr Spectra.—A Varian A-60A spectrometer was used to obtain nmr spectra. Tetramethylsilane was used as an internal standard. A magnet temperature of 39° was used for the spectra from which the line positions were taken. A higher temperature, 55° , was used for the spectrum shown in Figure 2 (in order to get a more concentrated solution).

Discussion

Nmr Spectra.—In the spectrum of $\text{PcGe}(\text{OSi}(\text{C}_2\text{H}_5)_3)_2$, Figure 2, the multiplets are centered at τ 0.30, 1.62, 11.24, and 12.42. For the lines in the two high-field multiplets, the separation is 7.6 cps. On the basis of previous work,⁸ the low-field multiplets can be assigned to the 3,6 and 4,5 ring protons. The remaining triplet and quartet can then be assigned to the methyl and methylene protons of the triethylsiloxy group. These assignments lead directly to values for J and δ for the ethyl group of 7.6 cps and -1.18 ppm, respectively (the minus sign indicating that the methylene protons appear at higher field than the methyl protons).

In the strikingly different spectrum of the structurally similar compound, $\text{hpGe}(\text{OSi}(\text{C}_2\text{H}_5)_3)_2$, Figure 3, general assignment of the low-field lines to the ring protons

and the high-field lines to the ethyl protons is reasonable. To make more detailed assignments for the low-field lines is difficult except for the association of the pair of lines at $\tau \sim 3.1$ with the pyridine ring *meta* protons. Analysis of the lines associated with the ethyl group can be carried out by a fitting procedure,⁹ J being assumed as 7.6 cps, and also with the aid of the equations of Rogers,¹⁰ J again being assumed as 7.6 cps. Both approaches give a value for δ of -0.33 ppm.

On the basis of this and previous nmr work,^{8,11} it is clear that the phthalocyanine ring has a large ring current and, using ring current as a criterion of aromaticity, is highly aromatic. It is also clear that the hemiporphyrane ring has little ring current and thus has little aromaticity associated with it. This conclusion is in direct agreement with that reached by Knox and Richards¹² from considerations of the bond lengths and the nonplanarity of the ring in $\alpha\text{-hpGeF}_2$. As expected, the available bond length data on the phthalocyanines are in line with the aromaticity of this ligand.¹³⁻¹⁶

Besides providing data with regard to the aromaticity of the two macrocycles, the nmr spectra on $\text{PcGe}(\text{OSi}(\text{C}_2\text{H}_5)_3)_2$ and $\text{hpGe}(\text{OSi}(\text{C}_2\text{H}_5)_3)_2$ also serve to illustrate nicely a point made earlier, namely, that the inhomogeneous magnetic field furnished by a phthalocyanine ring can considerably ease the problem of inter-

(9) The program for carrying out this spectrum fitting procedure was prepared by Dr. Donald Whitman, and the authors are indebted to him for its use.

(10) P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 5983 (1960).

(11) J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *Inorg. Chem.*, **5**, 1979 (1966).

(12) K. Knox and R. R. Richards, private communication.

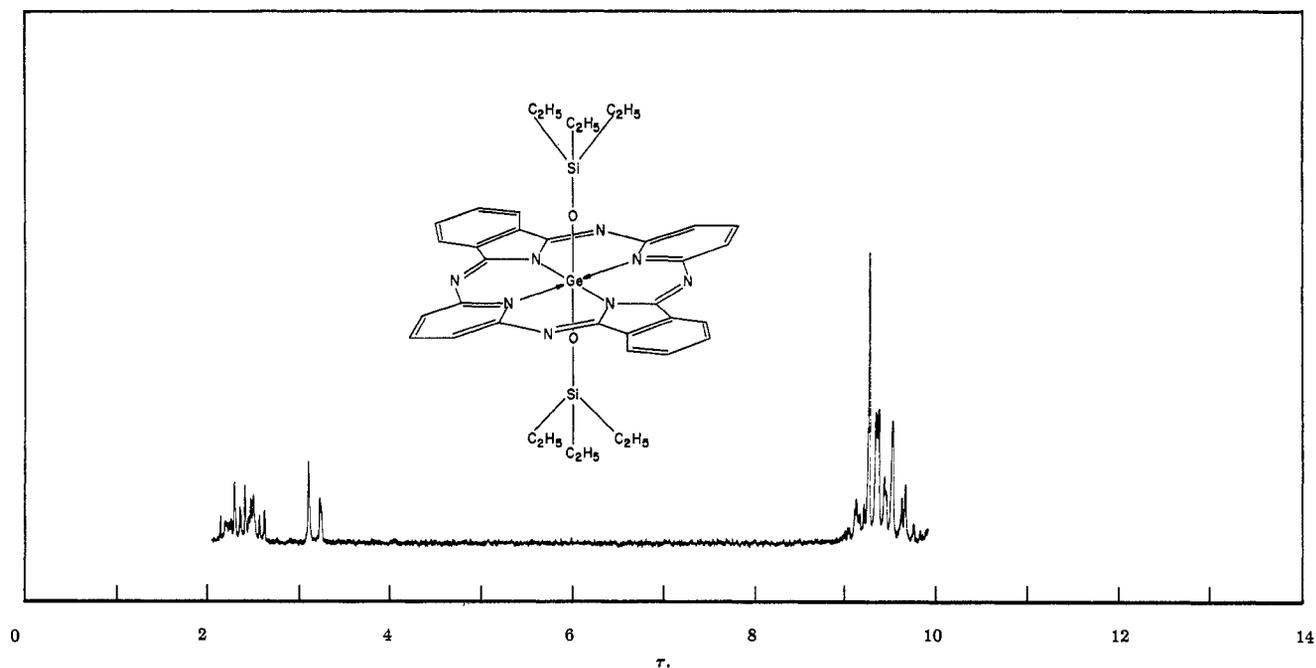
(13) J. M. Robertson, *J. Chem. Soc.*, 1195 (1936).

(14) J. M. Robertson and I. Woodward, *ibid.*, 219 (1937).

(15) J. M. Robertson and I. Woodward, *ibid.*, 36 (1940).

(16) L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Science*, **151**, 596 (1966).

(8) J. A. Elvidge, A. B. P. Lever, and M. P. Sammes, as quoted by A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, **7**, 82 (1965).

Figure 3.—The nmr spectrum of $\text{hpGe}[\text{OSi}(\text{C}_2\text{H}_5)_3]_2$.

preting the spectrum of a group in the proper circumstances.¹¹

Infrared Spectra of Germanium Complexes.—In the series of germanium phthalocyanines and hemiporphyrans listed in Table I, the two nonmacrocyclic ligands must be *trans* to each other and, as a consequence, the interpretation of these spectra is not complicated by stereochemical uncertainties. Partially absent also is another difficulty often common to the interpretation of the spectra of complexes, *i.e.*, uncertainty as to the importance of solid-state effects. This comes about because, according to powder data, $\text{hpGe}(\text{OH})_2$ and $\text{hpGe}(\text{OD})_2$ and $\text{PcGe}(\text{OH})_2$ and $\text{PcGe}(\text{OD})_2$ are isostructural, and hpGeCl_2 and hpGeBr_2 are probably isostructural.

TABLE I
ASSIGNMENTS FOR THE Ge-O AND Ge-X VIBRATIONS (cm^{-1})

Mode	Pc	hp
Ge-OH asym str	644	676
Ge-OD asym str	633	666
Ge-OH bend	305	292
Ge-OD bend	302	285
Ge-F asym str	606	625 (α) 629 (β) 635 (γ) ^a
Ge-Cl asym str	312	347
Ge-Br asym str	226	256
Ge-I asym str	185	221

^a This value is only approximate since the samples of the γ form studied contained considerable quantities of the α form and overlapping of the Ge-F bands occurred.

This situation and the relative simplicity and consistency of the two sets of spectra permit the assignments for the germanium-halogen and germanium-oxygen vibrations shown in Table I to be made with considerable confidence.¹⁷ Further support of these

(17) The spectra discussed in this section are shown in the theses of J. N. Esposito, University Microfilms No. 66-14,287, and L. E. Sutton.

assignments is found in their internal consistency, their general agreement with such assignments as are in the literature for octahedral germanium complexes,^{18,19} and, for the Ge-O assignments, the shifts which occur on deuteration of the hydroxyl group.

In Table II are shown assignments for the O-H and O-D stretching and bending modes for the hydroxy and deuterioxy compounds. Little question is attached to these assignments, the shifts in the spectra being quite clear.

TABLE II
ASSIGNMENTS FOR THE OH AND OD VIBRATIONS (cm^{-1})

Mode	Pc	hp
O-H str	3493	3403
O-D str	2585	2524
O-H bend	988	1050
O-D bend	742	779

While the spectra of the compounds just discussed are constant, this is not true of the spectrum of $(\text{Pc-GeO})_x$, the position of the broad, strong Ge-O-Ge asymmetric stretching band varying over a range of at least 864–899 cm^{-1} .²⁰ It is thus not surprising that the position of the Ge-O-Ge band in $(\text{hpGeO})_x$ also varies. Here the range found so far is from 878 to 911 cm^{-1} , the low value being for a sample prepared by the condensation of $\text{hpGe}(\text{OH})_2$ in a nitrogen atmosphere (the product of a dta experiment), and the high value being for a sample prepared by the condensation of $\text{hpGe}(\text{OH})_2$ in 1-chloronaphthalene and stored for 16 months. As in the case of $(\text{PcGeO})_x$, these variations can quite reasonably be interpreted in terms of ordering of the polymer.

(18) J. Griffiths and D. Irish, *Inorg. Chem.*, **3**, 1134 (1964).

(19) I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J. Chem. Soc.*, 1514 (1963).

(20) W. J. Kroenke, L. E. Sutton, R. D. Joyner, and M. E. Kenney, *Inorg. Chem.*, **2**, 1064 (1963).

The Ge–O–Ge band in (hpGeO)_x is, like its counterpart in (PcGeO)_x, both broad and relatively strong. The breadth of the band in both compounds can be attributed to the coupling of vibrations and provides further evidence for the polymeric nature of (hpGeO)_x and (PcGeO)_x.

Examination of the data in this paper on the frequencies of the germanium–halogen and –oxygen vibrations reveals an interesting fact, namely, that for comparable bands the hemiporphyrzine band consistently occurs at a higher frequency. This suggests that in the hemiporphyrzines the *trans* groups are bound more tightly. Supporting this conclusion are the relative positions of the O–H and O–D stretching bands of hpGe(OH)₂, hpGe(OD)₂, PcGe(OH)₂, and PcGe(OD)₂ (strengthening of the Ge–O bond should weaken the O–H bond and *vice versa*).

Also supporting this conclusion are the powder pattern data for the polymers (PcGeO)_x and (hpGeO)_x. Previously the 3.50-Å line in the pattern of (PcGeO)_x has been interpreted in terms of a Ge–O bond length of 1.75 Å.²⁰ A similar interpretation of the 3.40-Å line in the pattern of (hpGeO)_x yields a Ge–O bond length of 1.70 Å and this somewhat shorter bond length again suggests that the *trans* groups are held more tightly in the hemiporphyrzines.

Just why the *trans* group bonds in the hemiporphyrzines are stronger than those in the phthalocyanines is not completely clear. However, the data with regard to the aromaticity of the two macrocycles developed in this paper and the data on bond lengths and molecular shapes developed by Knox, Speakman, Templeton, and Robertson^{12–16,21} and their co-workers provide some basis for an answer. It seems reasonable to suggest that, while the four central nitrogen atoms in the phtha-

locyanine ring are bound strongly and uniformly to the germanium atom, this is not the case in the hemiporphyrzines. Here it appears likely that the pyridine rings retain much of their original character and that their nitrogen atoms are relatively weakly bound to the germanium atom. If so, this would naturally lead to stronger *trans* group bonds.

Infrared Spectrum of Metal-Free Hemiporphyrzine.

—Some controversy has existed in the past concerning the assignment of the N–H stretching vibration in the infrared spectrum of metal-free phthalocyanine.^{22,23} Because of this, the spectra of hpH₂ and hpD₂ are of interest. Little difficulty attaches to the assignment of the N–H vibrations in these compounds, since hpH₂ shows a sharp band at 3452 cm⁻¹ and a broad, strong band at 574 cm⁻¹ while hpD₂ shows what are quite apparently the counterparts of these bands at 2569 and 417 cm⁻¹. Assignment of the high-frequency bands to N–H and N–D stretching modes and the low-frequency bands to the corresponding bending modes is thus unambiguous.

Reaction Chemistry.—Enough germanium hemiporphyrzines have now been made so that it is clear that the chemistry of this series of compounds is quite similar to that of the germanium phthalocyanines^{24,25} (and the silicon and tin phthalocyanines for that matter). However, the parallel is not complete, the hemiporphyrzine ring being considerably more subject to chemical attack than the phthalocyanine ring.

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A Mössbauer-Effect Study of Some Iron–Phthalocyanine Derivatives

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The ⁵⁷Fe Mössbauer spectra of phthalocyanineiron(II) and several of its derivatives have been measured at temperatures between 77 and 423°K. Diamagnetic adducts of phthalocyanineiron(II) with several organic bases show quadrupole split spectra, and the peak separation varies with base strength. The electric field gradient arises from anisotropic covalent bonding. The spectra observed from phthalocyanineiron(II) and phthalocyaninechloroiron(III) are discussed in terms of their possible electronic structures.

Introduction

Phthalocyanine and its metal derivatives are of considerable interest both because of their novel geometry

and because of their structural similarity to the biologically important porphyrins. Iron-containing compounds are of particular importance in the latter respect and their structures may be investigated by Mössbauer spectroscopy. Several such studies of haemo-

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