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Cofacial Assembly of Partially Oxidized Metallomacrocycles as an Approach to Controlling Lattice Architecture in Low-Dimensional Molecular Solids. Synthesis and Properties of Cofacially Joined Silicon and Germanium Hemiporphyrazine Polymers

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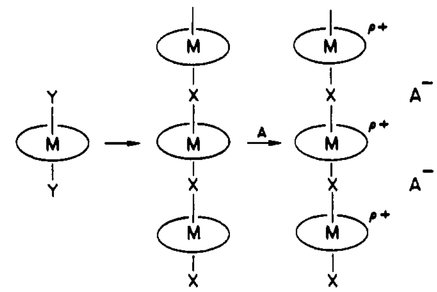
This contribution reports an integrated chemical, spectroscopic, X-ray diffractometric, and charge transport investigation of the cofacially linked metallomacrocyclic polymers $[M(hp)O]_n$, where M = Si and Ge and hp = hemiporphyrazinato. The synthesis of the new M = Si compound (from $Si(hp)Cl_2$ and $Si(hp)(OH)_2$) and modified syntheses of the M = Ge analogue are reported. Optical spectra are discussed as a function of M and X for the various $M(hp)X_2$ derivatives. Radiotracer studies of the degree of polymerization using $M(hp)(O^3H)_2$ precursors yield $\bar{n}$ values for typical $[M(hp)O]_n$ samples of 20 (M = Si) and 50 (M = Ge). On the basis of data for monomeric $M(hp)X_2$ derivatives, both vibrational and high-resolution solid-state ^{13}C NMR spectra of the $[M(hp)O]_n$ polymers can be assigned in terms of a cofacially linked polymer architecture. X-ray diffraction data suggest that the $[M(hp)O]_n$ polymers are crystalline and structurally similar; however, the crystal structures are not similar to that of $[Fe(hp)O]_n$ nor to those of the analogous $[M(Pc)O]_n$ polymers, Pc = phthalocyaninato. Doping of the $[M(hp)O]_n$ polymers with iodine using several procedures results in iodine uptake but no significant increase in electrical conductivity. It appears that iodination is accompanied by destruction of the polymer M-O-M framework.

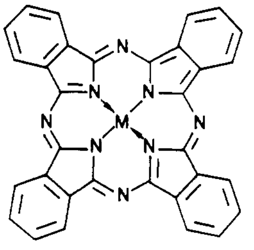
Introduction

A major problem in the rational design and synthesis of low-dimensional molecular materials[1] is control of crystallization architecture. We have recently demonstrated that the cofacial assembly strategy (eq 1) represents an efficacious



(1)

approach to enforcing stacking and lattice structure in low-dimensional materials composed of metallomacrocycles.[2-4] For systems where the metallomacrocycle is a phthalocyanine (M(Pc), A) we have shown that doping with a wide range of electron acceptors (e.g., halogens,[2,3] quinones,[3d,5] nitrosyl salts[5b,c,6]) affords structurally well-defined, conductive polymers[7] having high air and thermal stability and varying in transport characteristics from "molecular metals" to wide-gap semiconductors. Moreover, the stringent structural control exerted by the covalent -M-O-M- backbones allows a detailed investigation of collective properties (magnetic, optical, charge transport) as a function of interplanar spacing, and a probing of the donor-acceptor interactions without fear of disrupted stacking.



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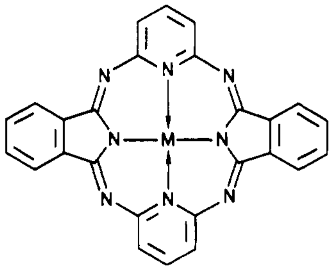
It would clearly be of interest to extend investigations of the aforementioned type to polymers composed of non-phthalocyanine macrocycles. Hemiporphyrazine complexes[8] of group 4A (M(hp), B) differ in a number of interesting ways



B

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from group 4A phthalocyanines in both electronic and molecular structure.[9,10] Preliminary studies indicate that Ni(hp) can be oxidized with iodine but that the product is an insulator.[11] This result raises the fascinating question of whether the problem is structural and whether *forcing* M(hp) units into a cofacial array with close interplanar spacings as in an $[Si(hp)O]_n$ macromolecule might afford a low-dimensional electrical conductor. In the present contribution, we report on the synthesis and physicochemical characterization as regards macromolecular structure and response to halogen doping of the above new, cofacially joined hemiporphyrazine polymer. Furthermore, we provide parallel structural information (new and/or more extensive) and dopant response observations on the related germanium polymer, $[Ge(hp)O]_n$, which was first reported by Esposito et al. in 1967.[9a-c]

Experimental Section

Reagents. Commercial solvents and reagents were either used as received or purified as specified in the experimental details. All gaseous nitrogen used was Matheson Prepurified. The germanium complexes $Ge(hp)Cl_2$ and $Ge(hp)(OH)_2$ were prepared by the literature procedure.[9a]

Apparatus and Analytical Measurements. The tube furnace used for polymerizations was a Lindberg Hevi-Duty, Model 54031A. It was calibrated to ±5 °C with a mercury thermometer and a chromel–alumel thermocouple. The temperature was stabilized for 30–60 min prior to use.

Infrared spectra were recorded on Perkin-Elmer 283, 267, 599b (dispersive) or Nicolet 7199 (FT) instruments. Samples were examined as Nujol mulls between KBr plates and were referenced to polystyrene unless otherwise indicated. Some KBr-disk spectra were also recorded. Electronic spectra were recorded on a Cary 17D or Perkin-Elmer 330 spectrophotometer in quartz cuvettes.

Solid-state NMR spectra were recorded on a JEOL FX-60Q fitted with a magic-angle spinner and cross-polarization instrumentation. Spectra were externally referenced to HMB (hexamethylbenzene) at 132.3 ppm. Spectra were acquired with use of 4096 data points over 8000 Hz with a filter of 4000 Hz. The Hartmann–Hahn contact time was set at 3–5 ms, and the pulse delay was usually 4–10 s. Acquisition times of 64 ms were used. Normally 6000–15 000 acquisitions were made per spectrum. To prevent computer overflow, acquisitions were made in groups of 100 or 1000, transformed, and then averaged.

Raman spectra were recorded on a locally constructed apparatus consisting of a Spex 1401 double monochromator fitted with a cooled photomultiplier detector and interfaced to a Nova computer. Laser irradiation was provided by a Spectra-Physics Ar^+ laser operating on the 5145-Å line with a power output of 100–200 mW at the sample after passing through the standard heavy metal plasma filter. The 180° back-scattering geometry was used, with samples being spun in 5-mm Pyrex tubes.

Mass spectral data were recorded on a HP 5985 GC/MS at 70 eV ionizing voltage. We thank Dr. Doris Hung for technical assistance.

X-ray powder diffraction data were recorded on a Rigaku-Geigerflex automated powder diffractometer. Nickel-filtered Cu Kα radiation was employed for all X-ray measurements. The diffraction geometry was such that the incident beam and detector beam angles remained equal with respect to the sample. Samples consisted of powders pressed in pellets (1 mm thickness × 13 mm diameter) in a die under 8–10 tons of pressure. Densities were determined by the method of neutral buoyancy using aqueous solutions of $ZnCl_2$.

Elemental analyses were performed by H. Beck (Northwestern University), Micro-Tech, Inc. (Skokie, IL), or Galbraith, Inc. (Knoxville, TN). Tritium assays were performed by New England Nuclear, Inc. (Boston, MA).

Electrical conductivities were measured on a locally constructed apparatus[12a] using the four-probe Van der Pauw[12b,c] technique. Samples were pellets (6 mm × 1 mm × 1 mm) that were pressed from powder samples in a die under 8–10 tons of pressure. We thank Dr. J. W. Lyding for his advice and assistance.

Preparation of Hemiporphyrazine, hpH_2 (2,5:13,16-Diimino-7,11:18,22-dinitrilodibenzo[*c*,*n*][1,6,12,17]tetraazacyclodocosene). In a modification of the literature procedure,[8] sublimed 2,6-diaminopyridine (Aldrich; 15.00 g, 0.1375 mol) was dissolved with stirring and heating in 110 mL of 1-chloronaphthalene under a dry nitrogen atmosphere. The mixture was then cooled somewhat so that 17.61 g (0.1375 mol) of phthalonitrile (Eastman) could be added. The reaction was then gently refluxed for ca. 32 h under nitrogen. Upon cooling, filtering, washing with MeOH, and drying under vacuum (0.01 torr) for 12 h, 25.8 g (85%) of gold-orange crystals was obtained. MS (m/e): 440, hpH_2^+; 220, hpH_2^{2+}.

Preparation of Hemiporphyrazinatogermanoxane, $[Ge(hp)O]_n$. The polymerization procedures described below are modifications of those reported by Esposito et al.[9a]

Method A. $Ge(hp)(OH)_2$ (2.20 g, 4.04 mmol) was refluxed in 55 mL of 1-chloronaphthalene for 2.3 h. The brown powder was collected by filtration and washed with ether to give 1.68 g (79%) of $[Ge(hp)O]_n$. Anal. Calcd for $C_{26}H_{14}N_8GeO$: C, 59.25; N, 21.26; H, 2.68. Found: C, 58.15; N, 20.02; H, 2.65.

Method B. $Ge(hp)(OH)_2$ (2.1283 g, 3.905 mmol) was heated in a porcelain boat in an evacuated (dynamic, 0.01 torr) 25 mm i.d. pyrex tube at 300 °C for 6 h. The resulting brown $[Ge(hp)O]_n$ weighed 2.0429 g (99%). The infrared spectrum was identical with that from method A.

Due to the fact that no contaminants are introduced into the polymer, method B was the preferred procedure for further work. Anal. Calcd for $C_{26}H_{14}N_8GeO$: C, 59.25; N, 21.26; H, 2.68; Cl, 0.00. Found: C, 59.22; N, 21.32; H, 2.59; Cl, 0.17.

Preparation of (Hemiporphyrazinato)dichlorosilicon, $Si(hp)Cl_2$. In a dry nitrogen-purged reflux vessel, 7.00 g (0.0159 mol) of hpH_2 was dissolved with heating in 110 mL of dry (distilled from BaO) quinoline. The mixture was then cooled to ca. 40–60 °C, and 25 mL of freshly distilled $SiCl_4$ (Alfa) was added by syringe under a gentle nitrogen flush. The mixture was then brought to reflux and heated for 2.5 h, at which point the mixture contained a bright red crystalline substance, somewhat different in color from hpH_2. The excess $SiCl_4$ was next distilled off under atmospheric pressure until the quinoline itself could be brought to reflux. At this point, the red substance returned to solution and the mixture rapidly darkened to a brown color. Further reflux (ca. 0.8 h) darkened the mixture somewhat more. Heating was then ceased, and the reaction mixture was allowed to cool to 50–80 °C and then filtered hot through a Büchner funnel, to yield a dark blue, microcrystalline product. This product was washed with dry pyridine and dry ether to give 3.00 g (35%) of $Si(hp)Cl_2$. MS (m/e): 536–540 ($SiCl_2$ isotope pattern), $Si(hp)Cl_2^+$; 501–504 (SiCl isotope pattern), $Si(hp)Cl^+$; 251, $Si(hp)Cl^{2+}$; 63–65, $SiCl^+$.

Preparation of Hemiporphyrazinediyldihydroxysilane, $Si(hp)(OH)_2$. A mixture of $Si(hp)Cl_2$ (1.486 g, 0.00276 mol), 20 mL of H_2O, and 60 mL of pyridine was refluxed for 5.0 h to give 0.8274 g (60%) of $Si(hp)(OH)_2$ after filtering and washing with water.

Yields can be improved significantly (near-quantitative) by carrying the reaction out at or near room temperature for 8–15 h. Addition of 10–20 mL of 29% NH_4OH is necessary to facilitate reaction at room temperature.

The reaction can be judged successful by the change in reflected color of the suspended hemiporphyrazine from blue ($Si(hp)Cl_2$) to violet ($Si(hp)(OH)_2$).

Preparation of Hemiporphyrazinatosiloxane, $[Si(hp)O]_n$. The polymerization reaction was carried out in a manner analogous to that for the reaction for the corresponding germanoxane. $Si(hp)(OH)_2$ (0.524 g, 1.047 mmol) in a porcelain boat was heated in an evacuated

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(<0.01 torr, dynamic) tube furnace at 300 °C for 14 h. This yield 0.4950 g (98%) of $[Si(hp)O]_n$ as a brown microcrystalline powder.

Anal. Calcd for $C_{26}H_{14}N_8OSi$: C, 64.71; N, 23.22; H, 2.92; Si, 5.82; Cl, 0.00. Found: C, 64.03; N, 22.52; H, 3.32; Si, 6.02; Cl, 0.08.

Preparation of Iodinated $[M(hp)O]_n$ Polymers. Method A (M = Silicon). $[Si(hp)O]_n$ (0.3096 g, 0.6414 mequiv) and 0.9895 g (3.899 mmol) of I_2 were heated with stirring in 15 mL of chlorobenzene at 100–110 °C for 48 h, the mixture was centrifuged, the supernatant was decanted, and the dark brown solid product was washed with C_6H_6 until the supernatant was pale yellow. The product was then vacuum-dried at room temperature to yield a material that, on the basis of iodine analysis, contained 1.51 I/macrocycle.

Anal. Found: I, 28.39.

Method A (M = Germanium). $[Ge(hp)O]_n$ (0.3890 g, 0.7387 mequiv) and 0.3846 g (1.515 mmol) of I_2 were heated with stirring in chlorobenzene at 100–110 °C for 48 h and treated in the same way as for the siloxane.

The product contained 1.48 I/macrocycle.

Anal. Found: I, 26.31.

Method B (M = Silicon). $[Si(hp)O]_n$ (0.1974 g, 0.4091 mequiv) and 0.0528 g (0.208 mmol) of I_2 were stirred at room temperature in 15–20 mL of C_6H_6 for 7 days, the mixture was centrifuged, and the solid was washed with C_6H_6 to yield 0.2338 g of iodinated product. The product contained 0.57 I/macrocycle.

Anal. Found: I, 10.76. IR (cm^{-1}, Nujol mull): 3300 w, vbr, 3090 vw, 3045 vw, 1685 m, 1640 s, 1590 vs, 1554 m, 1437 s, 1322 m, 1293 w/m, 1264 w/m, 1210 m, 1155 m, 1105 s, 990 w/m, vbr, 908 vw, 812 m/s, 770 w/m, 709 m/s, 700 (sh) w/m, 679 w/m, 504 w/m, 483 vw.

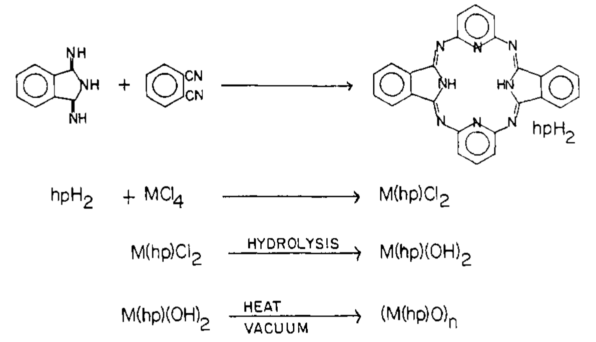
Method B (M = Germanium). $[Ge(hp)O]_n$ (0.2524 g, 0.4789 mequiv) and 0.0659 g (0.260 mmol) of I_2 were stirred at room temperature in 15–20 mL of C_6H_6 for 7 days to yield, after washing with C_6H_6 and centrifuging, 0.3123 g of iodinated product. The product contained 0.50 I/macrocycle.

Anal. Found: I, 8.90. IR (cm^{-1}, Nujol mull): 3300 m, vbr, 3105 vw, 3091 vw, 3040 vw, 1725 vw, 1675 m, 1630 s, 1610 m, 1588 s, 1553 m/s, 1436 s, 1319 m, 1292 w/m, 1257 m, 1209 m/s, 1190 w/m, 1160 w, 1140 vw, 1107 s, 1048 vw, 1030 vw, 1001 vw, 985 w, 902 (superposition of two peaks; one w/m, br, the other w/m sharp), 810 s, 772 m, 735 w, 700 s/vs, 579 m, 488 w/m.

Determination of Degree of Polymerization by Radiochemical End-Group Analysis.[3b] Preparation of $Si(hp)(OH^*)_2$ (Tritium-Labeled Species). $Si(hp)Cl_2$ (300 mg, 0.622 mmol) was loaded into a 20 cm long 24/40 male Schlenk tube. A small (10 × 3 mm) stirring bar was added. With use of extreme caution, 1.800 mL of T_2O/H_2O (170 μCi/mL) was carefully added by syringe. Next, 0.7 mL of dry (BaO distilled) pyridine was added by syringe. A female cap was then placed on the Schlenk tube, and a nitrogen bubbler was attached. A condenser was arranged by wrapping rubber tubing tightly around the upper portion of the Schlenk tube and passing cold water through it. The Schlenk tube was next lowered into a hot (115–120 °C) oil bath and the depth adjusted so that reflux was gentle. The mixture was allowed to reflux for 4 h and cooled, and 1.000 mL of 29% NH_4OH was added by syringe. Reflux was continued and allowed to proceed until all of the blue $Si(hp)Cl_2$ was converted into the violet $Si(hp)(OH^*)_2$ (14 h). Then, 2.000 mL of dry pyridine was used to wash the product into an 8-dram screw-cap vial. The cap was affixed and the vial centrifuged. The supernatant was removed by pipette and put into a tritium waste bottle. Then, 1.000 mL of T_2O/H_2O was added by syringe, the closed vial was thoroughly shaken and centrifuged, and the supernatant was discarded. This procedure was repeated once more. The residue was then dried under a flow of dry N_2 to give 303 mg (90%) of gray-violet microcrystals. A portion of this product (14 mg) was thoroughly mixed with 109.7 mg of unlabeled $Si(hp)(OH)_2$ and submitted for duplicate tritium activity analysis. The activity of this diluted sample of $Si(hp)(OH^*)_2$ was 772.8 (8) dpm/mg. This would yield a value of 6831 (7) dpm/mg for the undiluted $Si(hp)(OH^*)_2$. Quantities in parentheses in these and subsequent activity and degree of polymerization analyses represent the dispersion for duplicate determinations.

Conversion of $Si(hp)(OH^*)_2$ to $^*HO[Si(hp)O]_nH^*$. Polymerization was effected in the same way as for the unlabeled polymer (vide supra) (polymerization temperature 270 °C). Samples were removed at 1 h (3438.5 (25) dpm/mg), 4 h (616.5 (88)), 14 h (331.7 (16)), 58.5 h (303.5 (41)), and 107.25 h (284.5 (4)). Using the equation given in the text, one can determine the mean degree of polymerization $\bar{n}$ (time (h), $\bar{n}$): 1, 2.02 (11); 4, 11.5 (12); 14, 21.3 (1); 58.5, 23.3 (11); 107.25, 24.9 (4).

Scheme I



Preparation of $Ge(hp)(OH^*)_2$. $Ge(hp)(OH^*)_2$ (tritium labeled) was prepared in the same manner as $Si(hp)(OH^*)_2$. The $Ge(hp)Cl_2$ is more difficult to hydrolyze and consequently required a somewhat longer reaction time. The activity of undiluted $Ge(hp)(OH^*)_2$ was 6948.3 (33) dpm/mg. Polymerization of $Ge(hp)(OH^*)_2$ to $^*HO(Ge(hp)O)_nH^*$ was carried out at 300 °C in a manner identical with that for the unlabeled polymer. Heating time (h) (activity (dpm/mg)): 1 (1254 (40)), 5 (627 (35)), 29 (154.9 (20)), 71.5 (130.9 (21)), 94 (120.2 (7)). With use of the equation in the text, these activities yield the following mean degrees of polymerization (time (h), $\bar{n}$): 1, 5.7 (27); 5, 11.4 (47); 29, 46.4 (11); 71.5, 54.9 (13); 94, 59.75 (26).

Results and Discussion

Synthesis and Chemical Properties of $M(hp)Cl_2$, $M(hp)(OH)_2$, and $[M(hp)O]_n$ Compounds. Synthetic routes to the hemiporphyrazinato polysiloxane and polygermanoxane compounds are outlined in Scheme I. We find that the yield in the literature synthesis[8] of hpH_2 can be improved somewhat (from ca. 60% to as high as 85%) by ensuring that both reactants have completely dissolved at low temperature (about 100–150 °C) before bringing the reaction mixture to reflux temperature (261 °C). Formation of the dark blue $Ge(hp)Cl_2$ occurs smoothly and rapidly by reaction of hpH_2 with $GeCl_4$ in refluxing quinoline. Reaction is typically complete in 15–20 min. Several prior attempts to prepare silicon hemiporphyrazines by this procedure have apparently been unsuccessful,[13] and indeed, we find that refluxing hpH_2 and excess $SiCl_4$ in quinoline produces a red, extremely moisture-sensitive compound instead of $Si(hp)Cl_2$. However, distilling the excess $SiCl_4$ from the reaction mixtures results in a color change from red to brown as the quinoline reaches reflux. Further reflux (30–60 min) darkens the mixture considerably with formation of the product $Si(hp)Cl_2$ in 30–40% yield.

Conversion of both dichlorides to the corresponding dihydroxides by alkaline hydrolysis is straightforward. (Hemiporphyrazinato)dichlorosilicon reacts readily over 5 h (14 h at room temperature) and usually requires not more than aqueous pyridine to effect the conversion. Addition of 29% NH_4OH accelerates the hydrolysis, but unless care is taken, extensive decomposition may occur. (Hemiporphyrazinato)dichlorogermanium requires NH_4OH to effect complete reaction, although in this case decomposition is relatively minor. Thermal polymerization of the dihydroxides occurs slowly in the temperature range 270–300 °C and is accompanied by a color change from dark violet to dark brown. The degrees of polymerization obtained by this procedure have been measured by a radiochemical end-group analysis and will be discussed in a following section (vide infra).

The corresponding silicon and germanium hemiporphyrazines are similar in appearance. Both of the di-

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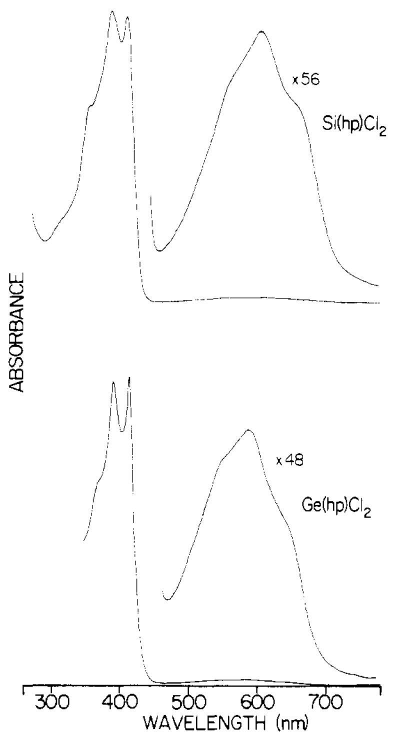

Figure 1. Solution optical spectra of $Si(hp)Cl_2$ (in C_6H_6) and $Ge(hp)Cl_2$ (in 1-chloronaphthalene).

chlorides are dark blue in polycrystalline form and in solution. The solid dihydroxides are gray-blue transmitting (green when ground to powders)/violet reflecting while, as noted above, the polymers are brown. Qualitatively, $Si(hp)Cl_2$ appears to be more soluble in coordinating solvents and more volatile than the germanium analogue. While $Ge(hp)Cl_2$ dissolves in hot (>200 °C) 1-chloronaphthalene with no apparent decomposition, $Si(hp)Cl_2$ decomposes rapidly under the same conditions to form a yellow solution. $Si(hp)Cl_2$ also hydrolyzes more readily than $Ge(hp)Cl_2$. Thus, it is possible to convert $Si(hp)Cl_2$ to $Si(hp)(OH)_2$ by reaction with aqueous base at room temperature, while the analogous reaction with $Ge(hp)Cl_2$ requires gentle refluxing. $Si(hp)Cl_2$ appears to degrade under the effects of atmospheric moisture over several days. Thus, a pressed-pellet X-ray powder diffraction sample gave patterns that evidenced substantial peak broadening after several days exposure to air. $Ge(hp)Cl_2$ was not observed to behave in this manner.

Solution Optical Spectra. As exemplified by $Si(hp)Cl_2$ and $Ge(hp)Cl_2$ in Figure 1, the solution optical spectra of metal hemiporphyrazines differ considerably from those of metal phthalocyanines.[3b,14,15] Data are set out in Table I. Although assignments will be discussed elsewhere,[10] it is worth noting here that, for both group 4A M(hp) and M(Pc) complexes, the intense absorption near 400 nm shifts to lower energy with decreasing electronegativity of M. However, the weaker M(hp) transition at 600 nm simultaneously shifts to higher energy, in contrast to the M(Pc) porphyrinic "Q band". In a comparison of hpH_2 and PcH_2, it is noted that the former lacks appreciable absorption in the 600-nm region, while the latter differs from the M(Pc) derivatives only in the multiplicity (reflecting lowered symmetry[14,15]) and exact energy of the intense transition in this region.

Table I. Solution Optical Spectral Data for Silicon and Germanium Hemiporphyrazines and the Free Ligand[a]

compd	solvent	λ_{max}, nm	log ε
$Si(hp)Cl_2$	C_6H_6	648 sh	2.70
		606	2.82
		582 sh	2.76
		410	4.59
		388	4.60
		360 sh	4.43
		323 sh	4.09
$Ge(hp)Cl_2$	C_6H_6	*b*	
		408	
		386	
		367 sh	
		329 sh	
$Ge(hp)Cl_2$	1-chloronaphthalene	626 sh	2.82
		596	2.97
		560 sh	2.93
		412	4.73
		389	4.73
		371	4.57
$Si(hp)(OH)_2$	pyridine	611 sh	2.85
		578	2.76
		551 sh	2.74
		417	4.52
		394	4.62
		383 sh	4.59
		362 sh	4.50
		314	4.19
$Ge(hp)(OH)_2$	pyridine	610 sh	2.89
		569	3.00
		542 sh	2.95
		414	4.53
		397	4.57
		387	4.62
		378	4.56
		357	4.48
		358	4.47
		322 sh	4.18
hpH_2	1-chloronaphthalene	419 sh	3.54
		379 sh	4.52
		367	4.60

[a] sh = shoulder. [b] Transitions at λ > 440 nm not located due to low solubility.

Table II. Average Degree of Polymerization ($\bar{n}$) of $[M(hp)O]_n$ Polymers (M = Si, Ge) from Tritium End-Group Analyses

	T, °C	time, h	$\bar{n}$[a]
$[Si(hp)O]_2$	270	1	2.02 (11)
		4	11.5 (12)
		14	21.3 (1)
		58.5	23.3 (11)
		107.25	24.9 (4)
$[Ge(hp)O]_n$	300	1	5.7 (27)
		5	11.4 (47)
		29	46.4 (11)
		71.5	54.9 (13)
		94	59.8 (26)

[a] Quantities in parentheses represent the dispersion from the mean in a duplicate measurement.

Polymer Molecular Weights by Tritium Labeling. The degree of polymerization of both the siloxane and germanoxane hemiporphyrazine polymers has been determined by radiochemical end-group analysis.[3b] The procedure involves preparing the tritium-labeled dihydroxygermanium and dihydroxysilicon hemiporphyrazines (eq 2) and then polymer-

$$M(hp)Cl_2 + 2OH^{*-} \rightarrow M(hp)(OH^*)_2 + 2Cl^- \quad (2)$$

izing a portion to the respective polymers. Comparison of tritium assay of polymers to that of monomers assays how many hydroxy end groups remain in the polymer. The tritium

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(15) (a) Schaffer, A. M.; Gouterman, M.; Davidson, E. R. *Theor. Chim. Acta* **1973**, *30*, 9–30. (b) Schaffer, A. M.; Gouterman, M. *Theor. Chim. Acta* **1972**, *25*, 62–70. (c) Edwards, L.; Gouterman, M. *J. Mol. Spectrosc.* **1970**, *33*, 292–310.

Table III. Infrared Spectral Data for Monomeric and Polymeric Group 4A Hemiporphyrazines

compd	ν, cm^{-1}
Si(hp)Cl_2^{b}	3090 vw, 3058 vw, 1990 vw, 1940 vw, 1794 vw, 1747 vw, 1685 s, 1633 vs, 1593 vs, 1548 vs, 1472 s, 1439 vs, 1376 s, 1348 w, 1320 s, 1299 m, 1263 s, 1210 s, 1194 s, 1174 vw, 1156 m, 1113 vs, 1011 vw, 997 w, 955 vw, 913 m, 898 m, 880 vw, 862 vw, 843 vw, 815 vs, 775 s, 752 w, 738 vw, 717 s, 693 s, 681 w, 676 w, 652 w, 580 vw, 552 vw, 496 vs, 448 s
Ge(hp)Cl_2^{b}	1720 w, 1688 s, 1647 vs, 1607 s, 1590 vs, 1550 vs, 1467 m, 1437 vs, 1392 vw, 1361 s, 1344 vw, 1315 s, 1292 w, 1263 s, 1207 vs, 1185 m, 1160 m, 1098 vs, 1083 m, 1007 vw, 990 vw, 904 w, 880 w, 825 m, 816 m/s, 772 m, 732 vw, 693 vs, 680 m, 661 vw, 486 w, 465 vw, 420 vw, 366 w, 347 s, 314 s
Si(hp)$(OH)_2$^{a}	3260 m, br, 1691 m, 1639 s, 1594 s, 1556 m/s, 1440 s, 1324 m, 1301 w/m, 1265 m, 1213 m, 1201 m, 1165 w, 1137 w, 1121 w/m, 1103 m/s, 1089 m, 1028 w/m, 991 w/m, 893 s, 872 m, 814 m/s, 775 m, 760 w/m, 745 w, 721 w/m, 711 s, 681 w/m, 506 w, 487 m
Ge(hp)$(OH)_2$^{a}	3410 br, m/s, 3085 vw, 3050 vw, 3025 vw, 1719 vw, 1671 s, 1625 vs, 1608 vs, 1586 vs, 1548 vs, 1468 s, 1431 vs, 1373 s, 1321 s, 1298 w, 1256 s, 1219 m, 1205 s, 1166 vw, 1157 w, 1103 vs, 1048 vw, 1001 vw, 986 w, 950 vvw, 902 w, 810 s, 772 vw, 766 w/m, 738 w, 701 s, 680 vs, 487 w/m
$[Si(hp)O]_n$^{a}	3092 vw, 3042 w, 1684 m, 1640 s, 1589 vs, 1553 m/s, 1437 s, 1323 m, 1293 m, 1264 m, 1209 m, 1170 w, 1160 w, 1152 w, 1105 s, 990 m–s (variable, br), 909 w, 811 vs, 771 m, 744 w, 710 vs, 703 vs, 681 m, 503 m, 485 m, 406 w/m
$[Ge(hp)O]_n$^{a}	3080 vw, 3040 vw, 1672 m, 1629 s, 1603 vs, 1582 vs, 1549 s, 1433 vs, 1318 s, 1290 w, 1256 m, 1206 m, 1190 vw, 1153 w, 1110 vs, 1004 vw, 900 (840–940, br) m, 808 vs, 768 w, 734 vw, 700 vs, 678 w, 485 vw, 472 vw

[a] Nujol mull. [b] KBr pellet.

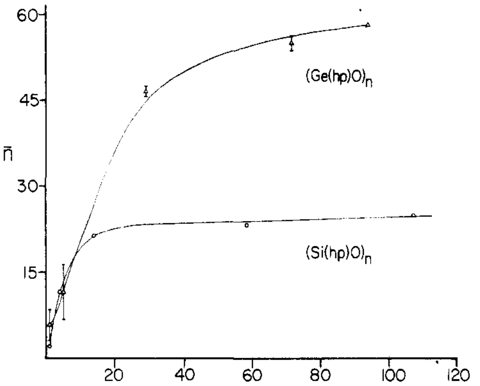

Figure 2. Average degree of polymerization $\bar{n}$ vs. heating time for $[Ge(hp)O]_n$ (300 °C) and $[Si(hp)O]_n$ (270 °C). Bars indicate dispersion about the mean for duplicate analyses (where resolvable on this plot).

activities of the monomer and polymer are analytically related to the average degree of polymerization ($\bar{n}$) by eq 3, assuming

$$\bar{n} = \frac{C_{OH}M_{OH} - 18.0152C_p}{M_pC_p} \tag{3}$$

$$n\text{M(hp)(OH*)}_2 \rightarrow \text{H*O[-M(hp)O-]}_n\text{H*} + (n-1)\text{H*}_2\text{O} \tag{4}$$

the process in eq 4. In eq 3 C_{OH} = activity of monomer (dpm/mg), C_p = activity of polymer (dpm/mg), M_{OH} = molecular weight of monomer, and M_p = molecular weight of polymer repeat unit (dpm = disintegrations per minute). Data are set out in Table II and Figure 2. It can be seen that, in either system for the temperature employed, $\bar{n}$ approaches an asymptotic limit with heating time: viz., $\bar{n} \rightarrow$ ca. 25, M = Si; $\bar{n} \rightarrow$ ca. 60, M = Ge. Similar observations were made in the $[M(Pc)O]_n$ systems.[3b] In the present case, detailed studies were not conducted at other temperatures.

Polymer Structure. Vibrational Spectra. A crucial issue in this study was to assess the degree to which the $[M(hp)O]_n$ structures correspond to the model of axially connected metal hemiporphyrazine units portrayed in eq 1; i.e., have the hp macrocycle and axial ligation remained intact? In discussing the vibrational spectra, we draw upon detailed comparisons that are now possible between the M = Si and Ge hemiporphyrazines, as well as the $[M(pc)O]_n$ results,[3b] which include ^{18}O labeling data.

Solid-state infrared spectra of the various M(hp)Cl_2, M(hp)$(OH)_2$, and $[M(hp)O]_n$ compounds are shown in Figures

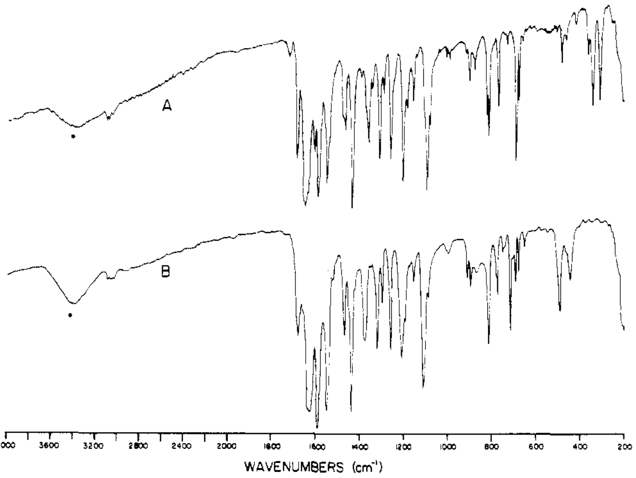

Figure 3. Infrared spectra (transmittance) of Ge(hp)Cl_2 (A) and Si(hp)Cl_2 (B) taken as KBr wafers. The asterisk (*) indicates moisture in the KBr.

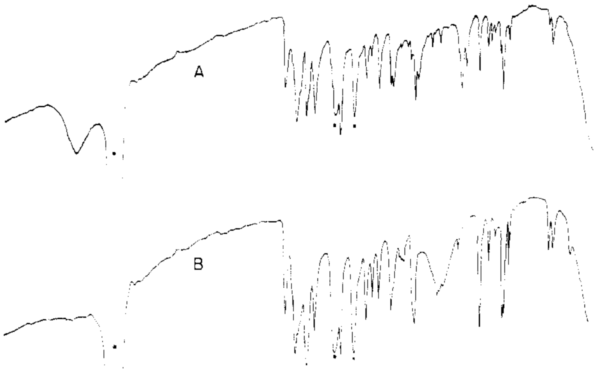

Figure 4. Infrared spectra (transmittance) of Si(hp)$(OH)_2$ (A) and $[Si(hp)O]_n$ (B) taken as Nujol mulls. The asterisk (*) indicates Nujol absorption.

3–5; data are compiled in Table III. These allow straightforward identification of the characteristic hp-centered internal coordinate changes. As can be seen in Figure 3, the spectra of Si(hp)Cl_2 and Ge(hp)Cl_2 are rather similar in the 1800–600-cm^{-1} "fingerprint" region. The antisymmetrically coupled Cl–Ge–Cl stretch has previously been assigned at 347 cm^{-1}.[9a] Under closer examination in the present study, two transitions at 347 and 317 cm^{-1} are actually observed; we find that both disappear upon hydrolysis of Ge(hp)Cl_2. Likewise, we assign

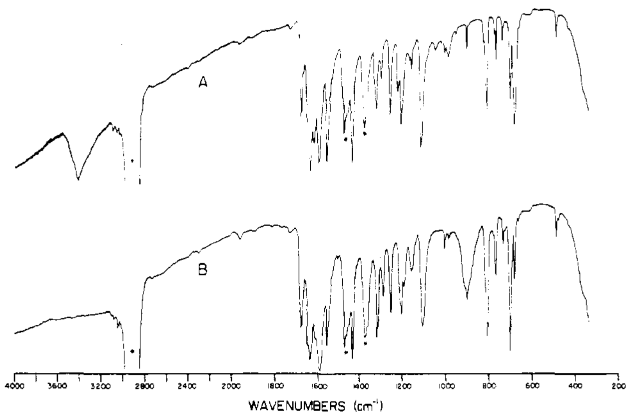

Figure 5. Infrared spectra (transmittance) of $Ge(hp)(OH)_2$ (A) and $[Ge(hp)O]_n$ (B) taken as Nujol mulls. The asterisk (*) indicates Nujol absorption.

two bands at 493 and 446 cm^{-1}, which are also discharged upon hydrolysis, to the Cl–Si–Cl stretching modes in $Si(hp)Cl_2$. The multiplicity of stretches in both $M(hp)Cl_2$ compounds is likely due to factor group or correlation field (solid-state) effects. In $Si(Pc)Cl_2$, the corresponding metal–halogen stretch is also a doublet, i.e., 462 and 424 cm^{-1}.[3b]

As in the dichlorides, infrared spectra (Nujol mull) of the dihydroxides (Figures 4 and 5) are comparable in the mid-IR region down to approximately 1000 cm^{-1}. The position of the OH stretch appears to be different (ν_{GeO-H} = 3403 cm^{-1};[9a] ν_{SiO-H} = 3260 cm^{-1}). The position is likely influenced by the extent of hydrogen bonding between hydroxy groups of adjacent molecules. Silanol stretches as low as 3125 cm^{-1} have been reported in the condensed phase,[16] while vapor-phase IR spectra of $(CH_3)_3SiOH$ reveal a ν_{SiO-H} as high as 3737 cm^{-1}.[17] In $Ge(hp)(OH)_2$, the transition at 676 cm^{-1} (overlapping with an hp-cenetered mode), which disappears upon polymerization, has been assigned to the antisymmetric O–Ge–O stretch;[9a] the analogous band in $Ge(Pc)(OH)_2$ occurs at 646 cm^{-1}.[3b] In $Si(hp)(OH)_2$, we assign the transitions at 898 and 871 cm^{-1} (presumably split for the same reason as in $Si(hp)Cl_2$) to O–Si–O stretching transitions. The corresponding mode in $Si(Pc)(OH)_2$, verified by ^{18}O substitution, occurs at 830 cm^{-1}.[3b] The present results reinforce the earlier assertion[9a] that $M(hp)X_2$ M–X stretching frequencies are invariably higher in energy than in the analogous $M(Pc)X_2$ derivatives.

The infrared spectra of the $[M(hp)O]_n$ polymers (Figures 4 and 5) are nearly identical throughout with the exception of the "M–O stretch". Formally, of course, such a transition should be described with reference to the optical branch of the $(-M-O-)_n$ dispersion relation.[18] The broad band at 903 cm^{-1} in $[Ge(hp)O]_n$, which appears upon polymerization, has been assigned to the "Ge–O stretch".[9a] On the basis of this result and the identification of the $[Si(Pc)O]_n$ "Si–O stretch" at 1000 cm^{-1} (verified by ^{18}O substitution), we assign the broad band at 990 cm^{-1} to the local "Si–O" stretch of $[Si(hp)O]_n$.

Polymer Structure. Solid-State NMR Spectra. Further verification of the integrity of the macrocyclic rings in the $[Ge(hp)O]_n$ polymer (and by inference, in $[Si(hp)O]_n$) is provided by high-resolution, solid-state ^{13}C CP MAS spectroscopy. As can be seen in Figure 6, chemical shift patterns in $Ge(hp)Cl_2$, $Ge(hp)(OH)_2$, and $[Ge(hp)O]_n$ are quite similar

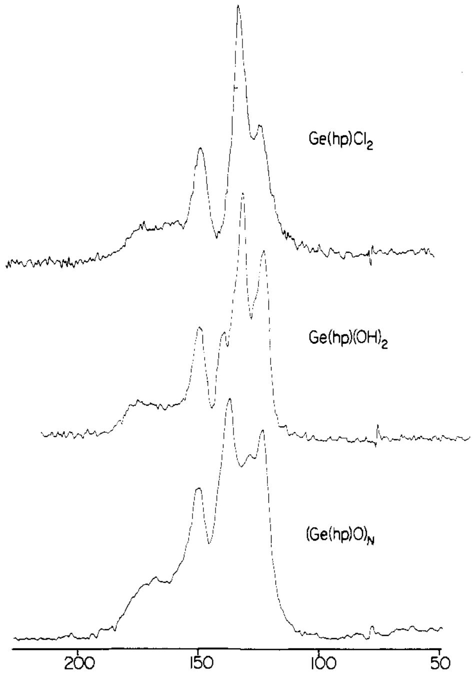

Figure 6. Solid-state ^{13}C NMR spectra of $Ge(hp)Cl_2$, $Ge(hp)(OH)_2$, and $[Ge(hp)O]_n$.

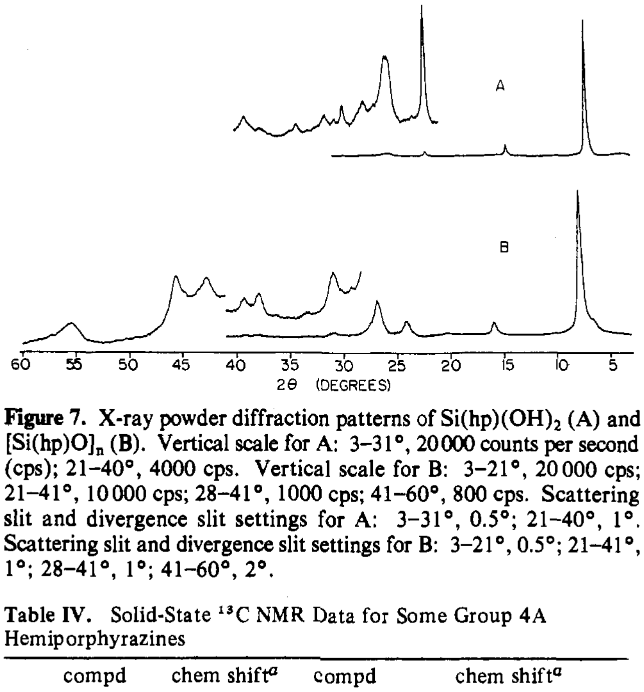

Figure 7. X-ray powder diffraction patterns of $Si(hp)(OH)_2$ (A) and $[Si(hp)O]_n$ (B). Vertical scale for A: 3–31°, 20000 counts per second (cps); 21–40°, 4000 cps. Vertical scale for B: 3–21°, 20000 cps; 21–41°, 10000 cps; 28–41°, 1000 cps; 41–60°, 800 cps. Scattering slit and divergence slit settings for A: 3–31°, 0.5°; 21–40°, 1°. Scattering slit and divergence slit settings for B: 3–21°, 0.5°; 21–41°, 1°; 28–41°, 1°; 41–60°, 2°.

Table IV. Solid-State ^{13}C NMR Data for Some Group 4A Hemiporphyrazines

compd	chem shift[a]	compd	chem shift[a]
$Si(hp)(OH)_2$	121.9	hpH_2	125.1
	131.3		133.1
	138.8 sh		142.2 sh
	150.2		153.4
	160.5 w		169.5 w
	171.3	$Si(hp)Cl_2$	124.1
$Ge(hp)(OH)_2$	123.2		132.7
	131.8		137.1 sh, vw
	139.6		151
	149.1		157.9–181.8 sh, br
	174.9	$Ge(hp)Cl_2$	124.3
$[Ge(hp)O]_n$	123.2		132.8
	128.5		149.6
	137.0		156.6–181.0 sh, br
	149.8		
	167.4		

[a] In ppm from Me_4Si.

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Table V. *d* Spacings, Densities, and 2θ Values for $M(hp)(OH)_2$ and $[M(hp)O]_n$ (M = Si, Ge)

$Si(hp)(OH)_2$[a]		$[Si(hp)O]_n$[c]		$Ge(hp)(OH)_2$[a]		$[Ge(hp)O]_n$[d]	
2θ, deg	*d*, Å	2θ, deg	*d*, Å	2θ, deg	*d*, Å	2θ, deg	*d*, Å
7.23 (3)	12.23 (5)	6.74 (5)	13.11 (10)	7.42 (3)	11.91 (5)	6.65 (5)	13.29 (10)
14.72 (3)	6.018 (12)	7.84 (3)	11.28 (4)	10.43 (3)	8.485 (24)	7.88 (3)	11.22 (4)
22.26 (4)	3.994 (7)	15.93 (3)	5.563 (10)	12.39 (3)	7.144 (16)	15.93 (5)	5.563 (17)
25.47	3.497	20.22 (3)	4.390 (6)	14.95 (3)	5.926 (12)	19.82 (4)	4.479 (9)
25.96[b]	3.432[b]	24.13 (3)	3.688 (5)	16.37 (4)	5.415 (13)	24.15 (10)	3.685 (15)
27.93 (6)	3.194 (7)	26.84 (5)	3.321 (6)	16.75 (4)	5.293 (13)	25.83 (5)	3.449 (6)
29.88 (6)	2.990 (6)	29.25 (10)	3.053 (10)	19.15 (4)	4.635 (10)	26.08 (4)	3.418 (6)
31.55 (7)	2.836 (6)	30.96 (7)	2.888 (6)	20.46 (4)	4.341 (8)		
34.20 (7)	2.662 (5)	33.46 (10)	2.678 (8)	20.79 (5)	4.272 (10)		
39.06 (7)	2.306 (4)	37.86 (7)	2.376 (4)	22.33 (5)	3.98 (9)		
		39.29 (7)	2.293 (4)	23.52 (5)	3.782 (8)		
		42.06 (7)	2.119 (3)	25.18 (5)	3.537 (7)		
		45.54 (7)	1.992 (3)	26.30 (7)	3.389 (9)		
		54.31 (7)	1.689 (2)	27.40 (4)	3.255 (5)		
				29.99 (5)	2.984 (5)		

[a] Only the most intense reflections are reported in the table. [b] Very broad reflection. [c] Density = 1.63 (2) g/cm³. [d] Density = 1.62 (1) g/cm³.

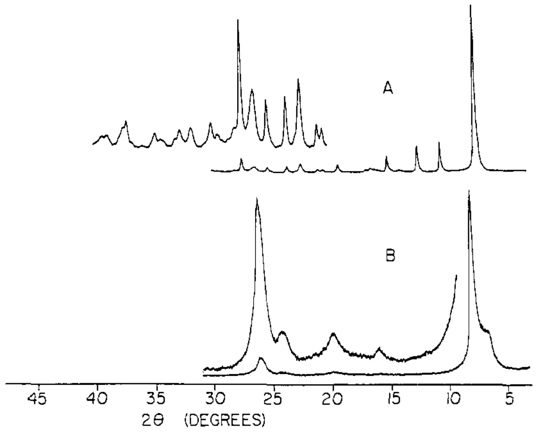

Figure 8. X-ray diffraction patterns of $Ge(hp)(OH)_2$ (A) and $[Ge(hp)O]_n$ (B). Vertical scale for A: 3–30°, 40 000 csp; 20–40°, 8000 cps. Vertical scale for B: 3–31°, 10 000 cps; 9–31°, 1000 cps. Scattering slit and divergence slit settings for A: 3–30°, 0.5°; 20–40°, 1°. Scattering slit and divergence slit settings for B: 3–21°, 0.5°; 9–21°, 0.5°.

and are in the region expected for aromatic carbon atoms in such a macrocycle.[19] The chemical shift dispersions are, however, considerably greater than in analogous phthalocyanine compounds.[3b,20] The rather broad, low-field resonances appear to be attributable to ^{14}N quadrupole-perturbed signals[21] from carbon atoms directly bonded to nitrogen.[19] Solid-state NMR data are set out in Table IV.

Polymer Architecture. X-ray Diffraction Analysis. X-ray powder diffraction spectra for corresponding $M(hp)(OH)_2$, $[M(hp)O]_n$ pair are shown in Figures 7 and 8. Data and measured densities are set out in Table V. It is immediately apparent that, qualitatively, the $[M(hp)O]_n$ polymers are highly crystalline and probably similar in structure. In the case of the highly crystalline $[M(Pc)O]_n$ and $\{[M(Pc)O]I_y\}_n$ polymers, useful structural information could be obtained by using computer techniques to simulate and evaluate various hypothetical crystal structures.[3a,b] Carefully chosen model compounds and considerations of packing interactions were employed to generate structures for testing. A similar analysis was attempted for $[Si(hp)O]_n$ and $[Ge(hp)O]_n$ using the same computational approaches[22] and metrical parameters from $Ge(hp)[C{\equiv}CC(CH_3)_3]_2$[9e] and $Ge(hp)(OCH_2CH_2OCH_2CH_3)_2$,[9d] which have planar hp rings, as starting points. The crystal structure of the face-to-face hemiporphyrazine polymer $[Fe(hp)O]_n$,[23] which has eclipsed arrays of saddle-shaped hp rings ($P2/n$, a = 16.149 Å, b = 3.992 Å, c = 16.143 Å), was also employed as a model. Despite an exhaustive consideration[24] of various simple and less simple trial structures, no satisfactory fit to the experimental data could be found. It is clear that the $[M(hp)O]_n$ polymers are not isostructural with the $[M(Pc)O]_n$ analogues[3a,b] nor with $[Fe(hp)O]_n$. It is noteworthy, however, that the strong $[Si(hp)O]_n$ reflection at 2θ = 26.84° corresponds to a lattice spacing of 3.32 Å. A similar reflection in $[Si(Pc)O]_n$ was assigned to the Pc–Pc interplanar spacing of 3.33 Å. The situation is less clear for $[Ge(hp)O]_n$.

Iodine Doping Experiments. In the case of the $[M(Pc)O]_n$ polymers, iodine doping increases the electrical conductivity of a pressed-pellet sample from 10^{-6} to 1 Ω^{-1} cm^{-1} (M = Si), and from 10^{-8} to 10^{-1} Ω^{-1} cm^{-1} (M = Ge), and produces a crystallographically tetragonal, mixed-valent material of composition $\{[M(Pc)O^{0.37+}](I_3^-)_{0.37}\}_n$. Partial oxidation of the $[M(hp)O]_n$ polymers was carried out with iodine, using several procedures (see Experimental Section for details), including that employed with the $[M(Pc)O]_n$ polymers. Although iodine uptake was evident in the elemental analyses, four-probe electrical conductivities of compressed polycrystalline samples were no higher than 10^{-10}–10^{-12} Ω^{-1} cm^{-1}. As a point of reference, the starting $[M(hp)O]_n$ materials have conductivities less than 10^{-11}–10^{-12} Ω^{-1} cm^{-1}. Some insight into the $[M(hp)O]_n$ iodination chemistry is provided by infrared spectroscopy. Rather than the development of electronic absorption as in the case of the $\{[M(Pc)O]I_y\}_n$ polymers,[3a] the hemiporphyrazine materials display diminution in the intensity of the M–O stretching transitions relative to hp-centered transitions (see Experimental Section for data). A similar observation was made in the case of $[Sn(Pc)O]_n$ iodination[3a] and

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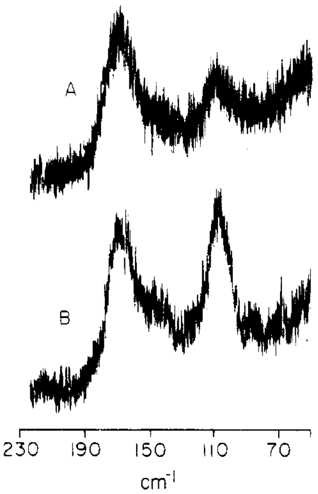

Figure 9. Resonance Raman spectra (ν_0 = 5145 Å) of $\{[Si(hp)O]I_{1.51}\}_n$ (A) and $\{[Ge(hp)O]I_{1.48}\}_n$ (B).

was attributed to destruction of the Sn–O–Sn backbone. X-ray powder diffraction studies of $[M(hp)O]_n$ doping reveal not only the appearance of several new reflections but also the presence of substantial quantities of the starting materials in even the most heavily iodinated materials. Resonance Raman spectra of typical $\{[M(hp)O]I_y\}_n$ samples (Figure 9) exhibit surprisingly weak scattering at 113 and 165 cm^{-1}. From past experience,[2] it appears qualitatively that the amount of polyiodides (I_3^-, I_5^-, $I_2 \cdot I_3^-$)[2] present is rather small.

Conclusions

This contribution extends significantly what is known about cofacially linked $[M(hp)O]_n$ hemiporphyrazinato polymers. The series now includes M = Si, and the vibrational and solid-state NMR data along with the X-ray diffraction results expand the existing structural information. The tritium-labeling experiments provide the first accurate data on the degrees of polymerization. Interestingly, however, straightforward partial oxidation procedures do not lead to electrically conductive arrays of cofacial π-radical cations but to insulating materials in which the polymeric M–O–M backbone is no longer intact.

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Registry No. hpH$_2$, 343-44-2; $[Ge(hp)O]_n$, 52757-66-1; Ge(hp)(OH)$_2$, 16918-34-6; Si(hp)Cl$_2$, 93134-16-8; Si(hp)(OH)$_2$, 93110-54-4; $[Si(hp)O]_n$, 93110-56-6; Ge(hp)Cl$_2$, 16918-33-5; 2,6-diaminopyridine, 141-86-6; phthalonitrile, 91-15-6.

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Kinetics of Reduction of Ferrichrome and Ferrichrome A by Chromium(II), Europium(II), Vanadium(II), and Dithionite

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Reduction of ferrichrome (Fc) by europium(II) and vanadium(II) follows the rate law $-d[Fc]/dt = k[Fc][M(II)]$ with $k = (8.64 \pm 0.06) \times 10^2$ M^{-1} s^{-1} at 25 °C, pH 4.1, and $\mu = 0.5$ for europium(II) and $k = 24.8 \pm 0.1$ M^{-1} s^{-1} at 25 °C, pH 4.0, and $\mu = 1.0$ for vanadium(II). The rates are nearly independent of pH between 2.6 and 4. For europium(II), $\Delta H^* = 2.7 \pm 0.5$ kcal mol^{-1} and $\Delta S^* = -36 \pm 1$ cal K^{-1} mol^{-1}; for vanadium(II), $\Delta H^* = 3.9 \pm 0.5$ kcal mol^{-1} and $\Delta S^* = -39 \pm 1$ cal K^{-1} mol^{-1}. Reduction of ferrichrome by chromium(II) is an inner-sphere process rate limited by dissociation of one hydroxamate from iron(III). Dissociation occurs by an acid-independent pathway (k_1) and an acid-dependent pathway (k_2). The rate of formation of intact ferrichrome from the dissociated, protonated bis complex is given by k_{-2}, and the rate of electron transfer is given by k_3. The rate law for reduction by chromium(II) is $-d[Fc]/dt = k_3[Cr(II)][Fc](k_1 + k_2[H^+])/(k_{-2} + k_3[Cr(II)])$, and $k_1 = 0.108 \pm 0.020$ s^{-1}, $k_2 = 296 \pm 15$ M^{-1} s^{-1}, and $k_3/k_{-2} = 188 \pm 26$ M^{-1} for pH 2.6–4.0, 25 °C, and $\mu = 0.5$. Reduction by dithionite occurs only by the SO_2^- radical according to rate constant k_0. The rate law is $-d[Fc]/dt = k_0K^{1/2}[Fc][S_2O_4^{2-}]^{1/2}$ where K is the equilibrium constant for dissociation of $S_2O_4^{2-}$. At 25 °C, pH 7.8, and $\mu = 0.5$, $k_0 = (2.12 \pm 0.03) \times 10^4$ M^{-1} s^{-1}. The value of k_0 is nearly independent of pH from 5.8 to 7.8. At pH 7.8, $\Delta H^* = 6.0 \pm 0.5$ kcal mol^{-1} and $\Delta S^* = -19 \pm 1$ cal K^{-1} mol^{-1}. Reduction of ferrichrome A (FcA) by chromium(II), europium(II), or vanadium(II) follows the rate law $-d[FcA]/dt = (k_4 + k_5K_a/[H^+])[FcA][M(II)]$ over the pH range 2–4. K_a is the acid-dissociation constant for loss of one proton from ferrichrome A. The parameters k_4 (M^{-1} s^{-1}) and k_5K_a (s^{-1}), respectively, at 25 °C are 11 ± 1 and $(15 \pm 1) \times 10^{-3}$ for chromium(II) ($\mu = 0.5$), 322 ± 5 and $(146 \pm 3) \times 10^{-3}$ for europium(II) ($\mu = 0.5$), and 31.1 ± 0.4 and $(12.7 \pm 0.2) \times 10^{-3}$ for vanadium(II) ($\mu = 1.0$). Values of ΔH_4^* (kcal mol^{-1}) and ΔS_4^* (cal K^{-1} mol^{-1}), respectively, for the rate constant k_4 are 21 ± 3 and -16 ± 8 for chromium(II), 3.7 ± 0.3 and -34 ± 1 for europium(II), and 2.6 ± 0.2 and -43 ± 1 for vanadium(II). Reduction by all three M(II) ions is outer sphere. Reduction of ferrichrome A by dithionite occurs only by the SO_2^- radical according to the same rate law found for ferrichrome. At 25 °C, pH 7.6, and $\mu = 0.5$, $k_0 = (8.6 \pm 0.6) \times 10^3$ M^{-1} s^{-1}. The rate is nearly independent of pH from 5.7 to 7.6. At pH 7.6, $\Delta H^* = 4 \pm 1$ kcal mol^{-1} and $\Delta S^* = -26 \pm 3$ cal K^{-1} mol^{-1}.

Introduction

Siderophores are powerful iron(III) chelators that are synthesized by a wide variety of microorganisms and excreted in response to low-iron stress. In the microbial medium exterior to the cell, the siderophore solubilizes and binds iron, and the iron is then delivered to the interior of the microorganism. These general features of iron(III) siderophore transport have been presented in more detail elsewhere,[4] and

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