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Electrochemistry of Germanium Porphyrins in Nonaqueous Media. Reactions of Water and Hydroxide Ligands Associated with (P)Ge(ClO₄)₂ and (P)Ge(OH)₂, Where P Is the Dianion of Tetraphenylporphyrin (TPP) or Octaethylporphyrin (OEP)

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The electrochemistry of four germanium porphyrins was investigated in nonaqueous media. These compounds are represented as (P)Ge(X)₂ where P is the dianion of tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP) and X is OH⁻ or ClO₄⁻. The first one-electron oxidation of (P)Ge(ClO₄)₂ involves the porphyrin π ring system while for (P)Ge(OH)₂ the abstraction of one electron occurs from a bound OH⁻ ligand and generates (P)Ge(ClO₄)(OH) as the porphyrin electrooxidation product. The addition of one or two electrons to (P)Ge(ClO₄)₂ results in an initial anion radical or dianion, but this species reacts with associated water that is in solution or is bound to the Ge(IV) complex, and this leads to the ultimate formation of (P)Ge(ClO₄)(OH) and (P)Ge(OH)₂ as electroreduction products. Coulometric data as well as electrochemical, spectroelectrochemical, and ESR results are all self-consistent and are in good agreement with the proposed mechanism.

Introduction

Transition-metal metalloporphyrins complexed with hydroxide ions can undergo a ligand-centered oxidation, which occurs in nonaqueous media at potentials between -0.22 and +1.29 V vs SCE.² The exact oxidation potential depends on the occupancy of the d subshells of the transition-metal center, and the initial product of this one-electron transfer is postulated to be an OH radical, which can then react with a second OH⁻ anion in solution to give H₂O and coordinated O⁻. This reaction has only been demonstrated to occur for metalloporphyrins that have metals with unpaired d electrons.² However, it has also been pointed out that σ -bonded germanium porphyrins of the form (P)Ge(R)(OH) (where P is the dianion of octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP) and R = CH₃, CH₂C₆H₅, or C₆H₅) can be converted to (P)Ge(R)(ClO₄) upon electrooxidation while the electrochemical reduction of (P)Ge(R)(ClO₄) in the presence of trace H₂O leads to (P)Ge(R)(OH).³ This present paper examines in detail this type of OH⁻/H₂O conversion with respect to (P)Ge(OH)₂ and (P)Ge(ClO₄)₂.

Experimental Section

Instrumentation. Cyclic voltammograms were obtained with an EG&G Model 174A polarographic analyzer coupled to a Model 175 universal programmer, an IBM Instruments Model EC 225 voltammetric analyzer, or a BAS 100 electrochemical analyzer. Current-voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder. The Pt rotating-disk electrode was home-built and was coupled with an IBM Instruments Model EC1219 rotating-disk-electrode controller. A three-electrode system was used. This consisted of a Pt-button working electrode, a Pt-wire counter electrode, and a saturated calomel electrode (SCE) as reference. The reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with the solution and supporting electrolyte. The solution was deaerated with nitrogen for at least 10 min before introduction of the compound, and a nitrogen blanket was maintained over the solution during the experiment.

A home-built platinum thin-layer electrode was used to perform spectroelectrochemical measurements.⁴ The potential of the working electrode was controlled by an IBM Instruments Model EC 225 voltammetric analyzer. Typical scan rates were 0.003 V/s for thin-layer electrochemistry, and the concentration of supporting electrolyte was typically 0.3 M. A Tracor Northern Model 1710 holographic optical spectrometer multichannel analyzer was used for obtaining time-resolved and potential-resolved spectra. Electronic absorption spectra were also obtained on IBM Model 9430 or Perkin-Elmer Model 559 UV-visible spectrophotometers. ESR experiments were run on an IBM Model ER 100D spectrometer.

¹H NMR spectra were recorded on an IBM AF-80 spectrometer. Spectra were measured on 5-mg solutions in CDCl₃ with nondeuteriated CHCl₃ as internal reference. IR spectra were obtained on a Perkin-Elmer 580B instrument. Samples were prepared as 1% dispersions in CsI pellets.

Materials. Benzonitrile (PhCN) was distilled from P₂O₅ under an inert atmosphere at reduced pressure. Dichloromethane (CH₂Cl₂) was distilled from CaH₂ under argon. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was purchased from Aldrich Co., twice recrystallized from ethanol, and dried and stored in vacuo at 40 °C. Tetra-*n*-butylammonium hydroxide ((TBA)OH), which was a 1.0 M solution in methanol, was purchased from Aldrich Co. and used without further purification.

All syntheses were carried out in an open-air atmosphere. (OEP)Ge(OH)₂ and (TPP)Ge(OH)₂ were synthesized according to literature methods⁵⁻⁷ while (P)Ge(ClO₄)₂ was prepared by the general procedure described below.

(P)Ge(ClO₄)₂. A 50.0-mL portion of aqueous perchloric acid (0.3 mol) was added to 0.7 mmol of (P)Ge(Cl)₂ dissolved in 200 mL of dichloromethane. The mixture was stirred for 1 h and the reaction progress monitored by UV-visible spectroscopy. The organic layer was dried over MgSO₄, heptane added to the CH₂Cl₂ solution, and the solvent evaporated at room temperature to give (P)Ge(ClO₄)₂. The solid crystallized before dryness, and the final yields of (OEP)Ge(ClO₄)₂ and (TPP)Ge(ClO₄)₂ were 63% and 90%, respectively.

Results and Discussion

Spectroscopic Characterization of (P)Ge(OH)₂ and (P)Ge(ClO₄)₂. Infrared spectral data and UV-visible spectral properties of (P)Ge(OH)₂ and (P)Ge(ClO₄)₂ are listed in Table I. The infrared spectra are characterized by Ge-X vibration frequencies for X = ClO₄⁻ at 283 cm⁻¹ (P = TPP) and 315 cm⁻¹ (P = OEP) and X = OH⁻ at 655 cm⁻¹ (P = TPP) and 634 cm⁻¹ (P = OEP).

The four porphyrins belong to the "normal" class.⁸ Each complex has a Soret band between 404 and 426 nm (band B(0,0)) and two major Q bands (bands Q(1,0) and Q(0,0)) between 534 and 596 nm. The Soret bands of (OEP)Ge(ClO₄)₂ and (TPP)Ge(ClO₄)₂ are blue-shifted by 2-3 nm with respect to the Soret bands of (OEP)Ge(OH)₂ and (TPP)Ge(OH)₂, and this is consistent with the more ionic character of the Ge-ClO₄ bond, which decreases the electron density on the macrocycle.

This difference in electron density between the two sets of complexes is also reflected by the ¹H NMR spectra of (P)Ge(OH)₂ and (P)Ge(ClO₄)₂. The resonances of the meso protons of (OEP)Ge(ClO₄)₂ and (OEP)Ge(OH)₂ appear at 10.39 and 10.33 ppm while resonances of the pyrrole protons of (TPP)Ge(ClO₄)₂ and (TPP)Ge(OH)₂ are observed at 9.10 and 9.03 ppm, respec-

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Table I. IR^a and UV-Visible Spectral Data^b of (P)Ge(OH)₂ and (P)Ge(ClO₄)₂

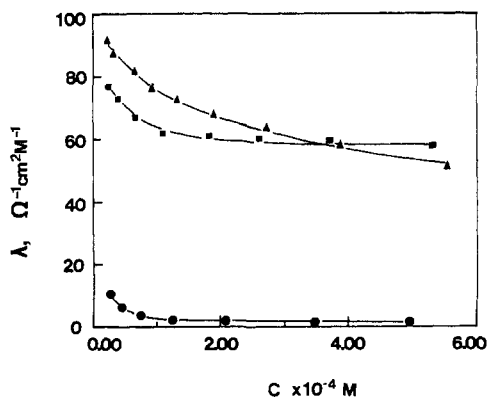
porphyrin ring, P	anion, X	$\nu(\text{Ge-X})$, cm ⁻¹	λ , nm ($10^{-4}\epsilon$, M ⁻¹ cm ⁻¹)				
			B(1,0)	B(0,0)	Q(2,0)	Q(1,0)	Q(0,0)
OEP	OH ⁻	634	387 (4.82)	407 (32.00)	496 (0.19)	534 (1.40)	570 (1.44)
	ClO ₄ ⁻	315	384 (4.67)	404 (37.02)	500 (0.23)	534 (1.44)	571 (1.54)
TPP	OH ⁻	655	404 (4.47)	426 (39.76)	517 (0.38)	556 (1.35)	596 (1.02)
	ClO ₄ ⁻	283	403 (3.86)	424 (44.25)	516 (0.30)	554 (1.72)	595 (0.69)

^a CsI pellet. ^b Solvent PhCN.**Table II.** ¹H NMR Data^a of (P)Ge(X)₂ (X = OH⁻, ClO₄⁻) in CDCl₃

porphyrin ring, P	anion, X	meso or pyr H		phenyl H		CH ₂		CH ₃	
		mult/i	δ	mult/i	δ	mult/i	δ	mult/i	δ
OEP	OH ⁻	s/4	10.33			q/16	4.16	t/24	1.99
	ClO ₄ ⁻	s/4	10.39			q/16	4.17	t/24	1.93
TPP	OH ⁻	s/8	9.03	m/12	7.75				
				m/8	8.03				
	ClO ₄ ⁻	s/8	9.10	m/12	7.79				
				m/8	8.28				

^a Legend: mult = multiplicity; s = singlet; t = triplet; q = quartet; m = multiplet; i = intensity.**Table III.** Half-Wave Potentials (V vs SCE) for the Reversible Oxidation and Reduction of (P)Ge(OH)₂ and (P)Ge(ClO₄)₂ in PhCN (0.1 M TBAP)

porphyrin ring, P	anion, X	oxidn		redn	
		1st	2nd	1st	2nd
TPP	OH ⁻	1.15	1.46 ^a	-1.09	-1.56
	ClO ₄ ⁻	1.48		-0.69	-1.08
OEP	OH ⁻	1.01	1.42 ^a	-1.37	-1.84
	ClO ₄ ⁻	1.33		-0.85	-1.20

^a E_{pa} of reaction 8 measured at 0.1 V/s (see Figure 2).**Figure 1.** Concentration dependence of the molar conductance of TBAP (■), (TPP)Ge(ClO₄)₂ (▲), and (TPP)Ge(OH)₂ (●) in PhCN.

tively (see Table II). No signal is detected for protons of the hydroxyl ligands.

The (P)Ge(OH)₂ complexes are nonelectrolytes in PhCN, but this is not the case for (P)Ge(ClO₄)₂, which dissociates to give [(P)Ge(ClO₄)₂]⁺ and ClO₄⁻. This dissociation is shown by the conductivity data in Figure 1. As seen in this figure, (TPP)Ge(ClO₄)₂ (represented by ▲) exhibits approximately the same molar conductance as TBAP (represented by ■) while (TPP)Ge(OH)₂ (shown as ●) shows virtually no conductivity. This implies that both TBAP and (TPP)Ge(ClO₄)₂ are 1:1 electrolytes in benzonitrile while (TPP)Ge(OH)₂ is undissociated in this solvent.

Electroreduction of (P)Ge(OH)₂. The reduction of (OEP)Ge(OH)₂ in DMSO has been reported to occur via a single one-electron-transfer step at E_{1/2} = -1.31 V vs SCE.⁹ (TPP)Ge(OH)₂ and (OEP)Ge(OH)₂ exhibit two reversible reductions between -1.09 and -1.84 V in PhCN (see Figure 2 and Table III). Plots of i_p vs. v^{1/2} are linear for the two reductions of (P)Ge(OH)₂,

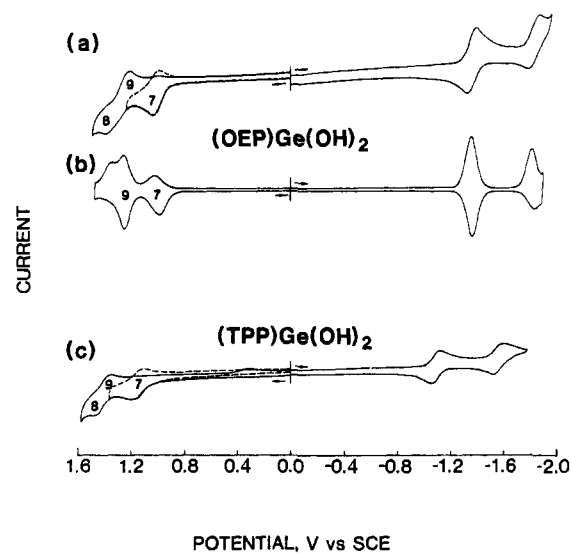
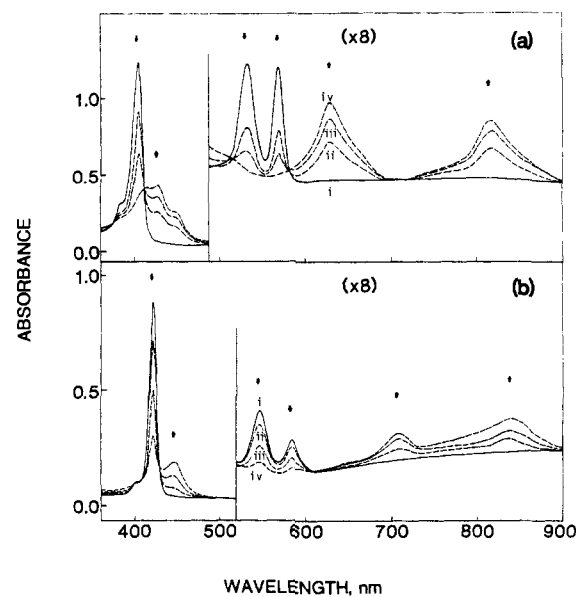
**Figure 2.** (a) Cyclic voltammogram and (b) differential pulse voltammogram of 1 × 10⁻³ M (OEP)Ge(OH)₂ and (c) cyclic voltammogram of 1 × 10⁻³ M (TPP)Ge(OH)₂ in PhCN, 0.1 M TBAP.**Figure 3.** Time-resolved electronic absorption spectra during the first reduction of (a) (OEP)Ge(OH)₂ at (i) 0, (ii) 30, (iii) 50, and (iv) 120 s and (b) (TPP)Ge(OH)₂ at (i) 0, (ii) 10, (iii) 40, and (iv) 120 s in PhCN, 0.3 M TBAP.(9) Fuhrhop, J.-H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* 1973, 95, 5140.

Table IV. Maximum Absorbance Wavelengths (λ_{\max}) and Corresponding Molar Absorptivities (ϵ) of Neutral, Oxidized, and Reduced (P)Ge(OH)₂ and (P)Ge(ClO₄)₂ Complexes in PhCN, 0.3 M TBAP

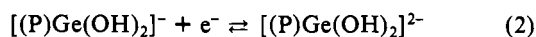
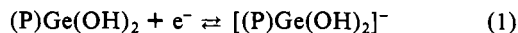
compd	electrode reacr	λ_{\max} , nm ($10^{-4}\epsilon$, M ⁻¹ cm ⁻¹)						
(OEP)Ge(OH) ₂	none	387 (4.82)	407 (32.00)	496 (0.19)	534 (1.40)	570 (1.44)		
	1e redn		434 (10.55)		633 (0.97)	821 (0.74)		
	1e oxidn		403 (30.21)		530 (1.06)	570 (1.42)		
(OEP)Ge(ClO ₄) ₂	none	384 (4.67)	404 (37.02)	500 (0.23)	534 (1.44)	571 (1.54)		
	1e oxidn		403 (17.01)	445 (1.01)		645 (0.91)		
	none	404 (4.47)	426 (39.76)	517 (0.38)	556 (1.35)	596 (1.02)		
(TPP)Ge(OH) ₂	1e redn		453 (7.28)		724 (1.43)	859 (2.24)		
	1e oxidn		422 (39.24)	464 (5.64)	552 (1.90)	592 (1.19)	667 (0.76)	806 (0.89)
	none	403 (3.86)	424 (44.25)	516 (0.30)	554 (1.72)	595 (0.69)		
(TPP)Ge(ClO ₄) ₂	1e oxidn		425 (11.04)	453 (3.07)				

indicating a reversible diffusion-controlled process.

A 470-mV separation between the two reductions of (P)Ge(OH)₂ suggests π -ring-centered reactions,¹⁰ and this is also indicated by time-resolved electronic absorption spectra taken during electroreduction. Examples of these time-resolved spectra are shown in Figure 3a for reduction of (OEP)Ge(OH)₂. The neutral (OEP)Ge(OH)₂ complex has an intense Soret peak at 407 nm and two major Q bands at 534 and 570 nm (see Table IV). After reduction by one electron the Soret band decreases in intensity and shifts to 434 nm. At the same time, the two peaks in the visible region disappear while broad peaks characteristic of an anion radical appear at 633 and 821 nm. These spectral changes are totally reversible, and the spectrum of the starting species could be regenerated by applying a more positive potential.

Similar reversible spectral changes occurred upon reduction of (TPP)Ge(OH)₂. The time-resolved spectra are shown in Figure 3b, and the peak maxima and molar absorptivities of each reduced complex are summarized in Table IV.

The reduction of (TPP)Ge(OH)₂ and (OEP)Ge(OH)₂ in PhCN was also monitored by ESR spectroscopy. A singlet ESR signal at $g = 2.003$ with $\Delta H_{pp} = 10$ G was detected for reduced (OEP)Ge(OH)₂. Exhaustive controlled-potential electrolysis of (TPP)Ge(OH)₂ at -1.30 V gave a signal at $g = 2.003$ with $\Delta H_{pp} = 6.7$ G. Thus, the spectroscopic and electrochemical data are self-consistent and indicate the successive formation of a porphyrin π anion radical and a dianion as shown by eq 1 and 2.



Reduction of (P)Ge(ClO₄)₂ in CH₂Cl₂. Figure 4 shows cyclic voltammograms of (TPP)Ge(ClO₄)₂ at various scan rates in CH₂Cl₂ containing 0.1 M TBAP. At 0.1 V/s there are six cathodic waves, which are labelled as processes 1–6. Processes 4–6 seem to be coupled to anodic peaks. This is not the case for processes 1 and 3 at low scan rates, but as the scan rate increases, these two processes become reversible as the other processes become irreversible or disappear. This is illustrated by the voltammogram at 50 V/s. At this scan rate the $E_{1/2}$ values for reduction are located at -0.69 and -1.08 V.

Reductive coulometry of (TPP)Ge(ClO₄)₂ at -0.80 V results in the addition of one electron and the disappearance of reduction process 1 while (TPP)Ge(OH)(ClO₄) or (TPP)Ge(OH)₂ spectrally appears as a final product. This is demonstrated by the thin-layer spectra shown in Figure 5. Unreduced (TPP)Ge(ClO₄)₂ has major peaks at 424, 554, and 595 nm (see Table IV). When a potential of -0.80 V is applied, the Soret band at 424 nm red-shifts by 2 nm while Q-band peaks shift from 554 to 557 and from 595 to 597 nm. The final spectrum after complete reduction of (TPP)Ge(ClO₄)₂ is shown in Figure 5a and resembles that of neutral (TPP)Ge(OH)₂. Furthermore, when a potential of -1.20 V is applied, the final spectrum resembles that of [(TPP)Ge(OH)₂]⁻. Similar types of spectral changes are observed during the first and second reduction of (OEP)Ge(ClO₄)₂, and the final spectral product after the addition of one electron to (OEP)Ge(ClO₄)₂ resembles (OEP)Ge(OH)₂. These spectral changes are

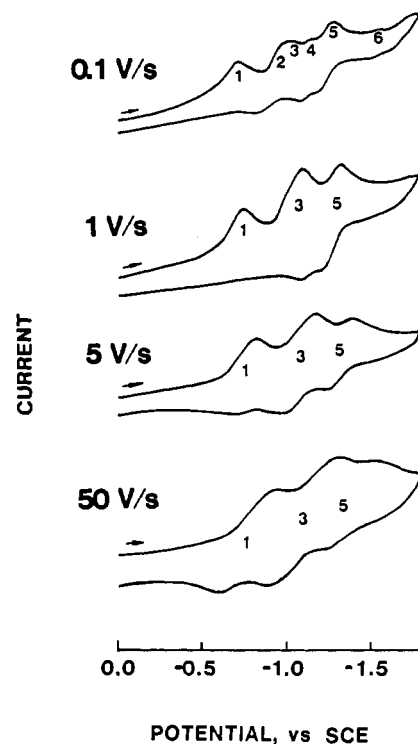


Figure 4. Cyclic voltammograms of (TPP)Ge(ClO₄)₂ at various scan rates in CH₂Cl₂, 0.1 M TBAP.

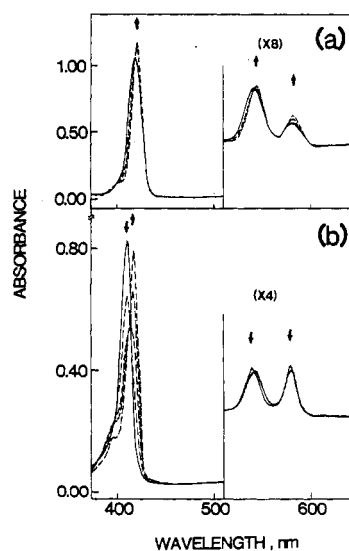


Figure 5. Spectra monitored during the first electroreduction of (a) (TPP)Ge(ClO₄)₂ at -0.80 V and (b) (OEP)Ge(ClO₄)₂ at -0.88 V in PhCN, 0.2 M TBAP.

shown in Figure 5b for the first electroreduction process.

Thin-layer and bulk controlled-potential coulometry were carried out at potentials corresponding to each reduction process

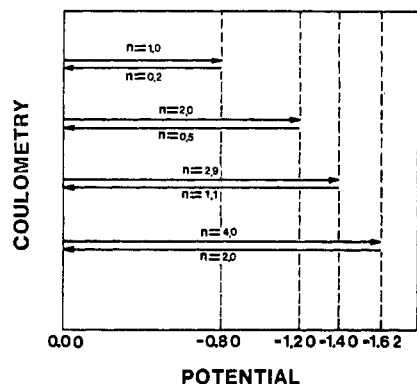
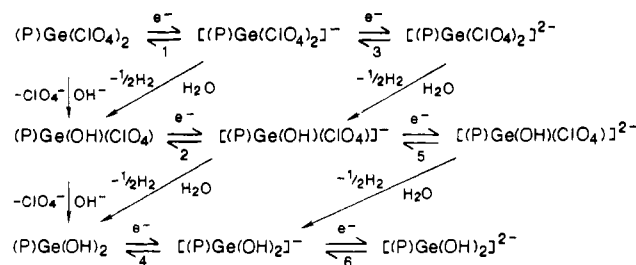


Figure 6. Coulometric n values obtained during thin-layer reduction and reoxidation of $(\text{TPP})\text{Ge}(\text{ClO}_4)_2$ in CH_2Cl_2 , 0.2 M TBAP.

Scheme I.



of $(\text{P})\text{Ge}(\text{ClO}_4)_2$, and the results are graphically illustrated in Figure 6 for the thin-layer reduction of $(\text{TPP})\text{Ge}(\text{ClO}_4)_2$. One electron is consumed by the complex when the potential is stepped from 0.00 to -0.80 V while 2.0 electrons are added upon going from an applied potential of 0.00 to -1.20 V. Both controlled-potential reductions are irreversible, and only 0.2 and 0.5 electron are abstracted upon resetting the potential at 0.00 V.

The number of electrons added is 2.9 when the initial potential of a fresh $(\text{TPP})\text{Ge}(\text{ClO}_4)_2$ solution is stepped from 0.00 to -1.40 V while 4.0 electrons are added to the complex upon going from 0.00 to -1.62 V. In this case, reoxidation of the reduced species requires 1.1 and 2.0 electrons, respectively.

Similar coulometric results were obtained by bulk controlled-potential electrolysis and suggest that either coordinated or free H_2O in the CH_2Cl_2 solution is reduced to OH^- . Under these conditions the overall scheme for reduction of $(\text{P})\text{Ge}(\text{ClO}_4)_2$ can be given as shown in Scheme I.

The reduction of $(\text{P})\text{Ge}(\text{ClO}_4)_2$ was also monitored in the presence of added $(\text{TBA})\text{OH}$. Addition of 1.0 equiv of $(\text{TBA})\text{OH}$ to $(\text{P})\text{Ge}(\text{ClO}_4)_2$ in CH_2Cl_2 generates $(\text{P})\text{Ge}(\text{ClO}_4)(\text{OH})$. A cyclic voltammogram of this solution shows that reactions 1 and 3 (Scheme I) have disappeared. In contrast, currents for reactions 4 and 6 are increased and have the same $E_{1/2}$ values as the first and second reductions of $(\text{TPP})\text{Ge}(\text{OH})_2$ (i.e., -1.09 and -1.56 V vs SCE). Thus these data indicate that the first one-electron reduction product of $(\text{P})\text{Ge}(\text{ClO}_4)_2$ apparently reduces water, which may be bound to the $[(\text{P})\text{Ge}(\text{ClO}_4)]^+$ complex as an axial ligand.

Electrooxidation of $(\text{P})\text{Ge}(\text{OH})_2$ in PhCN. Figure 2 illustrates the electrooxidation of $(\text{OEP})\text{Ge}(\text{OH})_2$ and $(\text{TPP})\text{Ge}(\text{OH})_2$ by cyclic voltammetry and differential pulse polarography in PhCN containing 0.1 M TBAP. Conventional voltammetric analysis of the current-voltage curves shows that the first oxidations (dashed lines, Figure 2a,c) are diffusion-controlled reversible one-electron transfers. However, when the potential scan is swept past 1.50 V (solid lines), a second oxidation process is observed. This oxidation occurs at $E_p = 1.42$ V for $(\text{OEP})\text{Ge}(\text{OH})_2$ and is labeled as process 8 in Figure 2a. Under these conditions there is also a cathodic peak at $E_p = 1.23$ V (peak 9) and no reverse peak associated with the oxidation peak 7.

The difference in anodic and cathodic peak potential between peaks 8 and 9 in Figure 2a is 190 mV, and this suggests that the peaks are not directly coupled by a reversible electron-transfer

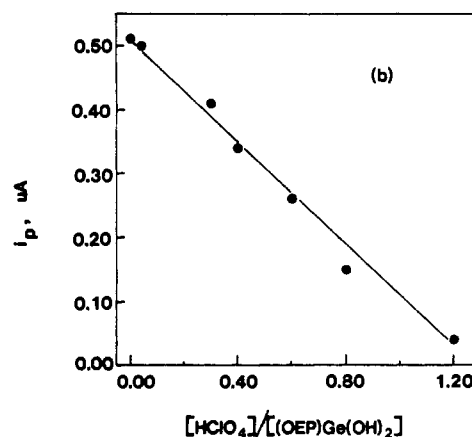
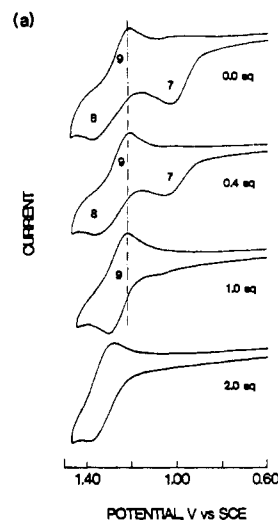


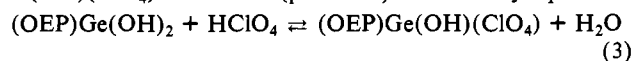
Figure 7. (a) Cyclic voltammograms of 6.5×10^{-4} M $(\text{OEP})\text{Ge}(\text{OH})_2$ in PhCN containing between 0.0 and 2.0 equiv of HClO_4 . (b) Plot of oxidation current for peak 7 as a function of HClO_4 concentration.

process. However, the value of $|E_p - E_{p/2}|$ is about 60 mV for all three peaks and this suggests an EC type mechanism in which the initial electrooxidation involves a diffusion-controlled one-electron abstraction.¹¹

Similar cyclic voltammograms are obtained for $(\text{TPP})\text{Ge}(\text{OH})_2$ in PhCN (Figure 2c). The first reversible oxidation occurs at $E_{1/2} = 1.15$ V (dashed line), but anodic and cathodic peaks are observed at $E_{pa} = 1.46$ V and $E_{pc} = 1.36$ V when the potential is scanned to 1.60 V. As will be shown in the following sections, the first oxidation of both $(\text{TPP})\text{Ge}(\text{OH})_2$ and $(\text{OEP})\text{Ge}(\text{OH})_2$ occurs at one of the two bound OH^- ligands.

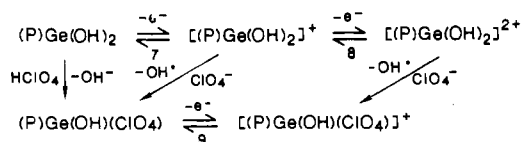
Electrochemically Monitored Titration of $(\text{OEP})\text{Ge}(\text{OH})_2$ with HClO_4 . Figure 7a shows cyclic voltammograms of $(\text{OEP})\text{Ge}(\text{OH})_2$ in PhCN containing increasing concentrations of HClO_4 . Current for the oxidation peak 7 decreases linearly with increasing HClO_4 concentration up to acid concentrations of 1.0 equiv (see Figure 7b). At the same time, the anodic peak 8 shifts negatively while the cathodic peak 9 remains unchanged.

A well-defined reversible oxidation is obtained in PhCN solutions containing 1.0 equiv of HClO_4 . This oxidation (process 9) has $|E_{pa} - E_{pc}| = 60$ mV and occurs at $E_{1/2} = 1.26$ V. The electrochemical data suggest that conversion of $(\text{OEP})\text{Ge}(\text{OH})_2$ to $(\text{OEP})\text{Ge}(\text{OH})(\text{ClO}_4)$ has occurred (eq 3) and that $(\text{OEP})\text{Ge}(\text{OH})(\text{ClO}_4)$ is oxidized (process 9) as shown by eq 4.

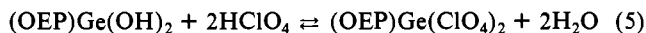


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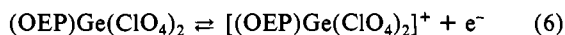
Scheme II



A well-defined reversible oxidation (i_p vs $v^{1/2}$ is linear) is also observed for (OEP)Ge(OH)₂ in solutions containing 2 equiv of HClO₄. This process occurs at $E_{1/2} = 1.33$ V, which is identical with the half-wave potential for the first oxidation of (OEP)Ge(ClO₄)₂ (see Table III). Furthermore, the UV-visible spectrum of the species in PhCN is identical with that of (OEP)Ge(ClO₄)₂. Thus, on the basis of the spectroscopic and electrochemical data, the overall reaction between (OEP)Ge(OH)₂ and 2 equiv of HClO₄ can be written as



The generated (OEP)Ge(ClO₄)₂ can then be oxidized as shown in eq 6.



The initial oxidation of (OEP)Ge(OH)₂ (peak 7, Figure 7) is proposed to occur at a bound OH⁻ ligand. The HOMO of (OEP)Ge(OH)₂ is $e_u(\text{O})$ from the OH group,¹² and this orbital is accessible to oxidation. Reversible oxidation and reduction potentials can be related to the energy of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), respectively.¹³ Therefore, the initial oxidation of (OEP)Ge(OH)₂ can be best rationalized in terms of abstracting an electron from the axial ligand site. Abstraction of an electron from the $e_u(\text{O})$ orbital would destabilize the Ge—OH bond so that the OH group could dissociate as a neutral species, i.e., a heterolytic cleavage of the Ge—OH bond. This would generate (OEP)Ge(OH)(ClO₄) in solution, and this is the species that is observed.

A similar electrochemical behavior is observed for (TPP)Ge(OH)₂ in PhCN, and the overall mechanism for oxidation of both (P)Ge(OH)₂ complexes in PhCN is proposed to occur as shown in Scheme II.

Scan-Rate Dependence of Oxidation. According to Scheme II, a cleavage of the Ge—OH bond occurs after the oxidation process responsible for peak 7. This cleavage is demonstrated by the differential pulse voltammogram of (OEP)Ge(OH)₂ in Figure 2b. The second oxidation peak 9 occurs at the same potential as for oxidation of the species obtained in solutions of (OEP)Ge(OH)₂ containing 1.0 equiv of HClO₄. The species in solution is assigned as (OEP)Ge(OH)(ClO₄). Reaction 8 is not observed on the oxidation cycle of the differential pulse voltammogram, and this suggests that the oxidation product associated with peak 7 has been converted to neutral (OEP)Ge(OH)(ClO₄) on the differential pulse voltammetric time scale. The peak at $E_p = 1.33$ V is associated with reduction of [(OEP)Ge(OH)(ClO₄)]⁺.

Significant currents are observed for reaction 8 of (OEP)Ge(OH)₂ on the conventional cyclic voltammetric time scale of 0.1 V/s. A cleavage of the Ge—OH bond occurs immediately after this oxidation, and the resulting [(OEP)Ge(OH)(ClO₄)]⁺ can be reduced at 1.23 V when the scan direction is changed. This is seen in the cyclic voltammogram of Figure 2a. Continuous cyclic scans for oxidation and reduction of this compound show that reactions 7 and 8 disappear on the second scan. These peaks are replaced by peak 9.

Figure 8 shows cyclic voltammograms of (OEP)Ge(OH)₂ at different scan rates in PhCN containing 0.1 M TBAP. Processes 7 and 8 become reversible at fast scan rates and can be assigned

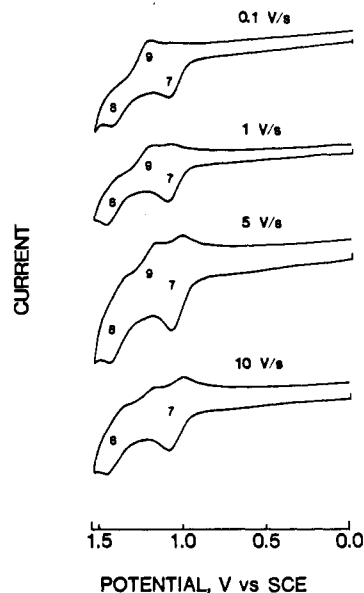


Figure 8. Cyclic voltammograms of (OEP)Ge(OH)₂ at various scan rates in PhCN, 0.1 M TBAP.

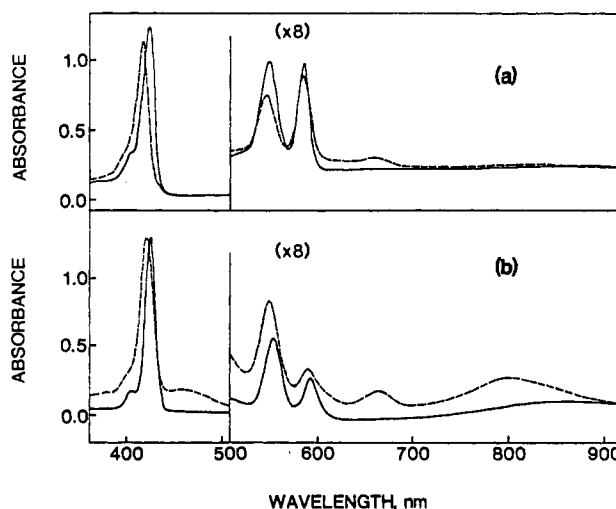
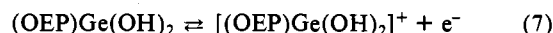


Figure 9. Electronic absorption spectra of (—) neutral and (---) singly oxidized (a) (OEP)Ge(OH)₂ and (b) (TPP)Ge(OH)₂ in PhCN, 0.3 M TBAP.

as due to the transient formation of [(OEP)Ge(OH)₂]⁺ and [(OEP)Ge(OH)₂]²⁺ as shown by eq 7 and 8.



(TPP)Ge(OH)₂ exhibits a similar behavior in PhCN. At a scan rate of 50 V/s the two oxidations approach reversibility, and the half-wave potentials of these processes are at $E_{1/2} = 1.15$ and 1.58 V.

Spectroelectrochemistry. The time-resolved electronic absorption spectra obtained during oxidation of (OEP)Ge(OH)₂ in PhCN are shown in Figure 9a. For clarity only the starting (solid line) and final spectra (dashed line) are shown. The final spectrum after oxidation by one electron is indicative of a neutral germanium(IV) porphyrin, and the absorption peaks have about the same intensity as in the original spectrum. This is not unexpected since it is the OH⁻ ligand that is oxidized to give (OEP)Ge(OH)(ClO₄) as a final product. However, two weak broad bands appear at 666 and 821 nm, and these may be due to formation of a transient π cation radical, [(OEP)Ge(OH)(ClO₄)]⁺ or [(OEP)Ge(OH)₂]⁺.

Time-resolved spectral changes monitored during the oxidation of (TPP)Ge(OH)₂ at 1.25 V are represented in Figure 9b. Again, only the starting and final spectra are shown for clarity. There

(12) Schaffer, A. M.; Gouterman, M. *Theor. Chim. Acta* 1970, 18, 1.

(13) Maccoll, A. *Nature (London)* 1949, 163, 178.

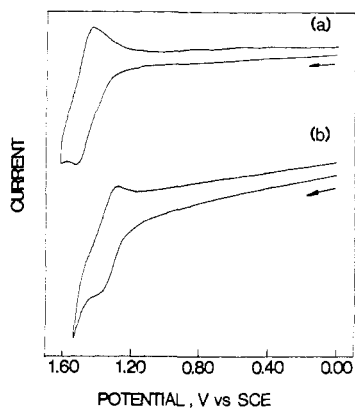


Figure 10. Cyclic voltammograms of (a) 10^{-3} M (TPP)Ge(ClO₄)₂ and (b) 10^{-3} M (OEP)Ge(ClO₄)₂ in PhCN, 0.1 M TBAP.

are no isobestic points in this process, consistent with a chemical reaction following electron transfer and the presence of several species in solution.

The intensities of both the Soret band and the Q bands of (TPP)Ge(OH)₂ first drop upon application of 1.25 V but then shift toward shorter wavelengths while the intensities again increase. The Soret band shifts from 426 to 422 nm while the two Q bands shift from 556 to 552 nm and from 596 to 592 nm. At the same time, three broad bands appear at 464, 667, and 806 nm. These bands are also indicative of a π cation radical, which can be either [(TPP)Ge(OH)(ClO₄)]⁺ or [(TPP)Ge(OH)₂]⁺.

Additional evidence for formation of a neutral Ge(IV) species is provided by ESR measurements of electrooxidized (OEP)Ge(OH)₂ in PhCN. The species generated in the first oxidation at 1.14 V is ESR-silent. However, the species generated at 1.30 V is ESR-active and has a low-temperature symmetrical singlet spectrum at $g = 2.004$. The peak width of this signal is 6.5 G, typical of a delocalized cation radical.

Oxidation of (OEP)Ge(ClO₄)₂ and (TPP)Ge(ClO₄)₂ in PhCN. Cyclic voltammograms of (OEP)Ge(ClO₄)₂ and (TPP)Ge(ClO₄)₂ are shown in Figure 10, and the half-wave potentials for these oxidations are given in Table III. Figure 11a illustrates the voltage-resolved spectra during the electrooxidation of (OEP)Ge(ClO₄)₂ in PhCN. The neutral complex has an intense Soret peak at 404 nm and two peaks at 534 and 571 nm. After abstraction of one electron from this complex, the Soret band decreases in intensity and the two bands in the visible region disappear while a new band at 645 nm appears.

Similar voltage-resolved spectra of oxidized (TPP)Ge(ClO₄)₂ are shown in Figure 11b. The original Soret band at 424 nm decreases in intensity as the two Q bands at 554 and 595 nm disappear. The final spectrum has only one broad Soret band at 425 nm. Three well-defined isobestic points are present at 390, 436, and 515 nm.

Solutions of (OEP)Ge(ClO₄)₂ were electrolyzed at 1.40 V and gave an ESR signal at $g = 2.001$ and with a peak width of 5.7 G. This is typical of what is expected for a delocalized π cation radical. Therefore, this oxidation can be assigned as due to a π -ring-centered oxidation.

Summary. The electrochemical, spectroelectrochemical, and ESR results are self-consistent and are in good agreement with the proposed mechanisms. The first one-electron oxidation of germanium(IV) porphyrins with weakly basic ligands such as

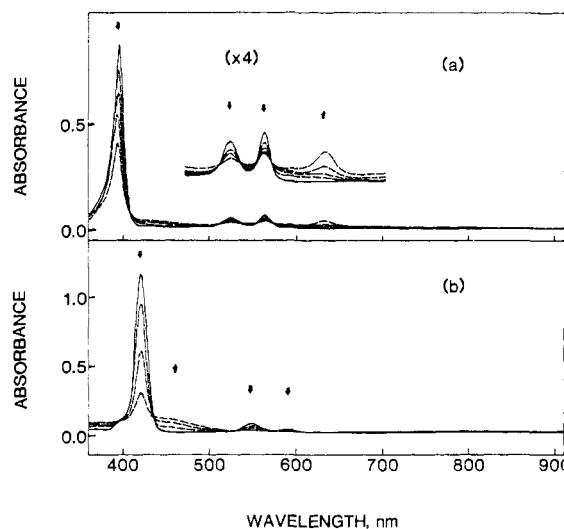


Figure 11. Voltage-resolved electronic absorption spectra of (a) (OEP)Ge(ClO₄)₂ at 0.96, 1.32, 1.36, 1.44, and 1.56 V and (b) (TPP)Ge(ClO₄)₂ at 1.20, 1.44, 1.52, and 1.62 V in PhCN, 0.3 M TBAP.

perchlorate is porphyrin-ring-centered and results in formation of a germanium(IV) porphyrin π cation radical. However, for complexes with strongly basic oxoanions such as OH⁻, the first electrochemical one-electron oxidation is axial-ligand-centered. This ligand dissociates after oxidation and is replaced by ClO₄⁻ from the supporting electrolyte. Under these conditions the final product of the one-electron oxidation is still a neutral germanium(IV) porphyrin. This work also demonstrates that the electroreduction of germanium(IV) porphyrins depends upon the specific bound anion. Complexes with ClO₄⁻ are initially reduced at the π ring system but generate a reactive species that reduces water to give OH⁻.

The OH⁻/H₂O conversion suggests that bound OH⁻ ligands are not always innocent anions when bound to metalloporphyrins. The preferential oxidation of OH⁻ was predicted for (P)Ge(OH)₂,¹² but had never been experimentally demonstrated. Our study also shows that uncomplicated porphyrin π anion radicals (such as those found in [(P)Ge(ClO₄)₂]⁻) are not always as unreactive as one might assume and that the homogenous reduction of trace H₂O (or H⁺) in solution or H₂O bound to the complex should be considered when evaluating irreversible redox reactions of metalloporphyrins in nonaqueous media.

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Registry No. (OEP)Ge(OH)₂, 50936-73-7; [(OEP)Ge(OH)₂]⁺, 111847-42-8; [(OEP)Ge(OH)₂]²⁺, 111847-43-9; [(OEP)Ge(OH)₂]⁻, 111847-38-2; [(OEP)Ge(OH)₂]²⁻, 111847-39-3; (OEP)Ge(ClO₄)₂, 111847-32-6; [(OEP)Ge(ClO₄)₂]⁺, 111847-45-1; [(OEP)Ge(ClO₄)₂]⁻, 111847-46-2; [(OEP)Ge(ClO₄)₂]²⁻, 111847-48-4; (TPP)Ge(OH)₂, 41150-80-5; [(TPP)Ge(OH)₂]⁺, 111847-40-6; [(TPP)Ge(OH)₂]²⁺, 111847-41-7; [(TPP)Ge(OH)₂]⁻, 111847-36-0; [(TPP)Ge(OH)₂]²⁻, 111847-37-1; (TPP)Ge(ClO₄)₂, 111847-33-7; [(TPP)Ge(ClO₄)₂]⁺, 111847-44-0; [(TPP)Ge(ClO₄)₂]⁻, 111847-49-5; [(TPP)Ge(ClO₄)₂]²⁻, 111847-47-3; (TPP)Ge(OH)(ClO₄), 111847-34-8; (OEP)Ge(OH)(ClO₄), 111847-35-9; (TBA)OH, 2052-49-5; TBAP, 1923-70-2; H₂O, 7732-18-5.