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Reversible Oxidation State Change in Germanium(tetraphenylporphyrin) Induced by a Dative Ligand: Aromatic Ge^{II}(TPP) and Antiaromatic Ge^{IV}(TPP)(pyridine)$_2$

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Abstract: Treatment of $GeCl_2$(dioxane) with $Li_2(TPP)(OEt_2)_2$ (TPP = tetraphenylporphyrin) in THF yields Ge(TPP), the first free Ge(II) porphyrin complex. In pyridine Ge(TPP) is converted to Ge(TPP)(py)$_2$, an antiaromatic Ge(IV) complex, whereas in benzene the reaction is reversed, and pyridine dissociates from Ge(TPP)(py)$_2$ to form Ge(TPP). That reversible reaction represents an unusual, if not unique, example of an oxidation-state change in a metal induced by coordination of a dative ligand. UV−vis and ^{1}H NMR spectroscopy show that Ge(TPP) is an aromatic Ge(II) porphyrin complex, while the ^{1}H NMR spectrum of Ge(TPP)(py)$_2$ clearly indicates the presence of a strong paratropic ring current, characteristic of an antiaromatic compound. Both Ge(TPP) and Ge(TPP)(py)$_2$ have been crystallographically characterized, and the antiaromaticity of Ge(TPP)(py)$_2$ leads to alternating short and long C−C bonds along the 20-carbon periphery of its porphine ring system. Coordination of pyridine to Ge(TPP) greatly increases its reducing ability: the Ge(TPP)$^{0/2+}$ redox potential is about +0.2 V, while the Ge(TPP)(py)$_2$$^{0/+}$ redox potential is −1.24 V (both vs. ferrocene). The equilibrium constant of the reaction Ge(TPP) + 2 py = Ge(TPP)(py)$_2$ in C_6D_6 is 22 M^{-2}. The germanium complex of the more electron-withdrawing tetrakis[3,5-bis(trifluoromethyl)-phenyl]porphyrin, Ge(TAr^{F}P), and its pyridine adduct Ge(TAr^{F}P)(py)$_2$ were synthesized. The equilibrium constant of the reaction Ge(TAr^{F}P) + 2 py = Ge(TAr^{F}P)(py)$_2$ in C_6F_6/C_6D_6 is 2.3×10^4 M^{-2}. Density functional theory calculations are consistent with the experimental observation that M(TPP)(py)$_2$ formation from M(TPP) and pyridine is most favorable for M = Si, borderline for Ge, and unfavorable for Sn.

Introduction

Many porphyrin complexes of group 14 elements have been prepared, and the oxidation states of the group 14 atoms within the known compounds follow a trend that is consistent with the fact that the inert-pair effect[1−3] becomes more important lower in the periodic table: silicon and germanium are always present as Si(IV) and Ge(IV) (with one type of exception for germanium), tin is found as both Sn(IV) and Sn(II), and almost all known lead porphyrins contain Pb(II). A normal porphyrin ring system (excluding the central atom) has an oxidation state of 2−, so the oxidation state of silicon is Si(IV) in a complex of the type Si(porph)X_2, where "porph" is a porphyrin ring system and X is a substituent covalently bound to silicon. Examples of X in known Si(porph)X_2 complexes include chloride, fluoride, triflate, and alkyl groups.[4−7] Similarly, many germanium(IV) porphyrin complexes of the type Ge(porph)X_2 are known.[8−15] The one known type of germanium porphyrin in which the germanium is best considered Ge(II) is (porph)-GeFe(CO)$_4$, wherein the germanium acts as a carbene-like two-electron donor to the iron center.[16,17] Some complexes of the type Sn(porph), containing Sn(II), have been characterized,[18,19] and a large number of Sn(IV) complexes, Sn(porph)X_2, are known.[20] Several Pb(porph) complexes have been structurally

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characterized,[21,22] while $Pb(OEP)Cl_2$[23] (OEP = octaethylporphyrin) is the only Pb(IV) porphyrin complex that has been isolated and a few other Pb(IV) porphyrins have been studied in solution.[24,25]

We recently reported that the reduction of silicon tetraphenylporphyrin dichloride, $Si(TPP)Cl_2$, with two equivalents of Na/Hg in THF yields the complex $Si(TPP)(THF)_2$, which can be converted to $Si(TPP)(pyridine)_2$.[26] In the complexes $Si(TPP)(L)_2$, where L is a dative ligand, silicon does not adopt the Si(II) oxidation state, but instead remains Si(IV), and the porphyrin ring system therefore has an oxidation state of 4−. The aromaticity of a normal-valent porphyrin is generally attributed to its 18 π-electron system; as a result, in the doubly reduced ring system of $Si(TPP)(L)_2$ one would expect an antiaromatic, 20 π-electron system. Exactly such a 20 π-electron circuit of alternating double and single carbon−carbon bonds is present along the periphery of the porphine ring of $Si(TPP)(THF)_2$, as observed in the crystal structure. The antiaromaticity of the $Si(TPP)(L)_2$ compounds is also manifested in their NMR spectra, which have highly shifted resonances due to a strong paratropic ring current.[27] These $Si(TPP)(L)_2$ complexes were the first antiaromatic porphyrins to be isolated.

Our original motivation for the synthesis of the highly reduced $Si(TPP)(L)_2$ molecules was to utilize them as n-dopants for other porphyrin molecular semiconductors. The highly ruffled structure of $Si(TPP)(THF)_2$ (and presumably of other $Si(TPP)(L)_2$) made it unsuitable for that purpose. The ruffling of $Si(TPP)(THF)_2$ is caused, at least in part, by the small covalent radius of silicon and the short Si−N bonds in the porphyrin complex. We therefore decided to investigate $Ge(TPP)(L)_2$, where we anticipated that the larger covalent radius of germanium would lead to a more nearly planar porphyrin ring. The synthesis and characterization of Ge(TPP) and $Ge(TPP)(py)_2$ are described below, in addition to the synthesis of the germanium complex of the more electron-withdrawing tetrakis[3,5-bis(trifluoromethyl)phenyl]porphyrin, $Ge(TAr^FP)$, and its pyridine adduct $Ge(TAr^FP)(py)_2$.

Experimental Section

General Procedures and Materials. All manipulations were carried out using Schlenk line or glove box techniques unless otherwise noted. Reagents were purchased from commercial suppliers and used as received unless their purification is noted as follows. Ethereal solvents were distilled from a purple sodium benzophenone solution, and hydrocarbon solvents were distilled from purple sodium benzophenone solutions with added tetraglyme. Pyridine was distilled from potassium hydroxide and stored over activated 3 Å molecular sieves. C_6F_6 was dried over activated 3 Å molecular sieves. $Li_2(TPP)(Et_2O)_2$[28] and $[NEt_4][B(C_6F_5)_4]$[29,30] were prepared by published procedures.

Ge(TPP). $Li_2(TPP)(Et_2O)_2$ (410 mg, 0.529 mmol) and $GeCl_2$(dioxane) (124 mg, 0.535 mmol) were stirred in 25 mL of THF at 22 °C for 12 h. Soon after warming to 22 °C the solution turned from the vibrant dark blue-green color of $Li_2TPP(Et_2O)_2$ to olive green. Eventually, a green microcrystalline precipitate formed. The solution was reduced under vacuum to about 8 mL and then filtered, and the product was held under vacuum for 1 h. Yield of green Ge(TPP): 235 mg, 65%. ^1H NMR (C_6D_6): δ 9.00 (s, 8 H), 8.08 (dd, 8H), 7.44 (m, 12H). UV−vis (toluene, nm): 395, 442, 495, 702. IR (Nujol, cm^{-1}): 1826 (w), 1595, 1529 (w), 1506 (w), 1330 (m), 1200 (m), 1173 (s), 1069 (m), 1010 (w), 1000 (m), 982 (s), 914 (w), 876 (w), 802 (s), 749 (s), 717 (w), 702 (m), 661 (w). Anal. Calcd (found) for $C_{44}H_{28}N_4Ge$: C, 77.11 (77.25); H, 4.12 (4.06); N, 8.18 (8.08).

$Ge(TPP)(pyridine)_2$·Pyridine. A suspension of Ge(TPP) (204 mg, 0.298 mmol) in 15 mL of pyridine was stirred at 22 °C for 48 h. The solid slowly dissolved over the course of 24−36 h to form a bright-red solution. The pyridine was almost completely removed, and a microcrystalline material began to precipitate. Hexane was added to precipitate more of the product. The product was isolated by filtration and held under vacuum for 1 h. Yield of red-purple $Ge(TPP)(pyridine)_2$·pyridine: 192 mg, 70%. UV−vis (pyridine, nm): 426, 482, 522, 563, very broad 770. ^1H NMR (pyridine-d_5): δ 6.58 (m, 12 H), 5.86 (dd, 8H), 0.59 (br s, 8H). IR (Nujol, cm^{-1}): 1610 (m), 1596 (m), 1573 (w), 1519 (w), 1358 (w), 1318 (w), 1241 (m), 1210 (m), 1192 (m), 1156 (m), 1067 (s), 1044 (s), 1015 (s), 988 (s), 917 (w), 761 (m), 746 (s), 690 (s), 661 (w), 644 (m).

$H_2(TAr^FP)$ was synthesized by the Lindsey method[31] under the specific conditions used previously for the synthesis of tetrakis(pentafluorophenyl)porphyrin.[32] Pyrrole (0.90 mL, 12.7 mmol), 3,5-bis(trifluoromethyl)benzaldehyde (2.1 mL, 12.7 mmol), and 750 mL of CH_2Cl_2 were combined and degassed. $BF_3(OEt_2)$ (0.45 mL, 3.5 mmol) was added under N_2 counterflow. The solution was stirred under N_2 at 22 °C for 20 h. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone, DDQ, (2.89 g, 12.7 mmol) was added, and the mixture was heated to reflux for 2 h. Volatiles were evaporated, and the product was purified by chromatography on neutral alumina with 7:3 chloroform/hexanes, and recrystallized from CH_2Cl_2/CH_3OH. Yield of pale brownish-pink $H_2(TAr^FP)$: 1.24 g, 34%. ^1H NMR ($CDCl_3$): δ 8.82 (s, 8 H), 8.70 (s, 8H), 8.39 (s, 4H), −2.87 (s, 2H). UV−vis (CH_2Cl_2, nm): 417, 512, 545, 587. IR (cm^{-1}): 3316 (w), 1830 (w), 1619 (w), 1561(w), 1464 (m), 1316 (w), 1276 (s), 1253 (m), 1199 (s), 1164 (s), 1133 (s), 1107 (m), 1078 (w), 1054 (w), 1028 (w), 1014 (w), 979 (w), 920 (w), 904 (m), 847 (m), 807 (m), 794 (m), 726 (m), 708 (w), 692 (m), 680 (m).

$Ge(TAr^FP)$. $Li_2(Ar^FP)(OEt_2)_2$ was synthesized by deprotonation of $H_2(TAr^FP)$ with $LiN(SiMe_3)_2$ in ether.[28] The synthesis of $Ge(TAr^FP)$ was analogous to that of Ge(TPP), except that the product was precipitated from THF using heptane. Yield of dark green-brown $Ge(TAr^FP)$: 218 mg, 65%. ^1H NMR (C_6F_6 with small amt of C_6D_6): δ 9.20 (s, 8 H), 9.00 (s, 8H), 8.58 (s, 4H). UV−vis (α,α,α-trifluorotoluene, nm): 394, 442, 497, 720. IR (Nujol, cm^{-1}): 1617 (w), 1462 (s), 1278 (vs), 1184 (vs), 1132 (vs), 1078 (m), 1037 (m), 941 (w), 923 (w), 902 (s), 848 (m), 832 (w), 787 (m), 709 (w), 694 (s), 681 (s).

$Ge(TAr^FP)(pyridine)_2$·Pyridine. $Ge(TAr^FP)$ (101 mg, 0.0822 mmol) was dissolved in 5 mL of pyridine. The red-brown solution was allowed to stir for 15 min, the pyridine was almost completely removed, and hexanes was added to precipitate the product. The product was isolated by filtration and held under vacuum for 1 h. Yield of red-gray $Ge(TAr^FP)(pyridine)_2$·pyridine: 102 mg, 85%. ^1H NMR (C_6F_6 with small amt of C_6D_6): δ 21.7 (pyridine, d, 4 H, $J = 5.5$ Hz), 11.71 (pyridine, t, 4H, $J = 7.1$ Hz), 11.19 (pyridine, t, 2H, $J = 7.1$ Hz), 7.25 (s, 4H), 6.33 (s, 8H), 0.22 (s, 8H). ^1H NMR (pyridine-d_5): δ 7.34 (s, 4 H),

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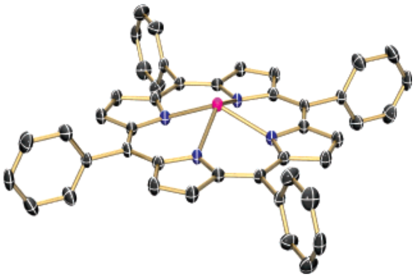

Figure 1. Solid-state structure of Ge(TPP). Important independent bond lengths (see Figure 4 for atom-type labels): Ge−N, 2.194(3) Å; N−C$_\alpha$, 1.373(5), 1.376(5) Å; C$_\alpha$−C$_\beta$, 1.435(6), 1.433(6) Å; C$_\beta$−C$_\beta$ 1.366(6) Å; C$_\alpha$−C$_{meso}$ 1.394(6), 1.401(6) Å.

6.52 (s, 8H), 0.58 (bs, 8H). UV−vis (pyridine, partly unresolved): 427 nm. IR (Nujol, cm^{-1}): 3081 (vw), 3059 (vw), 3046 (vw), 1613 (m), 1596 (m), 1582 (w), 1572 (w), 1529 (w), 1488 (m), 1452 (s), 1340 (s), 1280(vs), 1234 (s), 1177 (vs), 1131 (vs), 1069 (s), 1038 (m), 1006 (m), 927 (m), 899 (s), 847 (m), 837 (m), 768 (s), 753 (s), 702 (s), 693 (s), 680 (s), 644 (w), 626 (m), 604 (m).

Results and Discussion

Synthesis and Characterization of Ge(TPP). Reduction of Ge(TPP)Cl$_2$ with 2 equiv of Na/Hg in THF (the conditions used to produce Si(TPP)(THF)$_2$) did not give a tractable product. However, treatment of GeCl$_2$(dioxane) with Li$_2$(TPP)(OEt$_2$)$_2$ in THF at 22 °C for 12 h gave green, microcrystalline, air-sensitive Ge(TPP) in 65% yield. The behavior of the product in THF contrasts with that of the analogous silicon porphyrin, which forms Si(TPP)(THF)$_2$; we were unable to isolate free Si(TPP).[26]

Single crystals of Ge(TPP) suitable for X-ray diffraction were grown by slowly cooling a hot solution in THF. The crystal structure is shown in Figure 1. In the refined structure the porphine core of the ring system (i.e., the ring system excluding the phenyl groups) appears planar, while the germanium atom is 0.872 Å above the porphine plane. However, in the crystals the Ge(TPP) molecules are disordered, with half of the germanium atoms “above” the porphyrin plane and half “below”. If the molecules are domed, with the nitrogens all slightly out of the mean plane in the direction of the germanium atom and the rest of the ring system domed appropriately, then in the refined structure the porphine core would appear exactly planar. An examination of the atomic displacement ellipsoids in the refined structure reveals that the outermost carbons of the phenyl rings have a large component of their ellipsoids along the vertical direction, as would be expected for domed Ge(TPP) with 1:1 “up” and “down” disorder. In addition, the calculated structure of Ge(porphine) (Gaussian03,[33] B3LYP/6-311G**) is slightly domed, with an angle between the least-squares planes of opposite pyrrole rings of about 5°. Overall it seems most likely that Ge(TPP) is at least slightly domed.

There is crystallographic four-fold rotational symmetry for each molecule of Ge(TPP). There is no evidence of the type of bond-length alternation that is present in antiaromatic Si(TPP)(THF)$_2$,[26] but even if the bond-length alternation were present in Ge(TPP), it would be averaged out by the crystallographic four-fold rotational symmetry. Nevertheless, the absolute magnitudes of the bond lengths provide evidence that the compound is aromatic Ge^{II}(TPP) and not antiaromatic Ge^{IV}(TPP), in that they are similar to the average bond lengths computed from hundreds of crystal structures of normal-valent, aromatic porphyrins[34] and do not correspond to the averaged bond lengths of an antiaromatic germanium porphyrin, Ge^{IV}(TPP)(pyridine)$_2$ (see below). Additional evidence that Ge(TPP) contains Ge(II) comes from the large deviation of the germanium atom from the porphyrin plane. The covalent radius of germanium, 1.22 Å,[35] is not too large to be accommodated in the porphyrin plane; thus, the size of the germanium atom is not the cause of its deviation from the plane. Rather, it is the presence of a stereochemically active lone pair on Ge(II). In the computed structure of Ge(porphine) (B3LYP/6-311G**), the germanium atom is 0.868 Å above the N$_4$ plane, and the computed HOMO has a large component where the germanium lone pair would be expected (see Supporting Information for a picture of the HOMO). This view of the electronic structure of Ge(TPP) is consistent with the known (porphyrin)GeFe(CO)$_4$ complexes, wherein Ge(II) acts as a carbene-like donor to iron.[16,17]

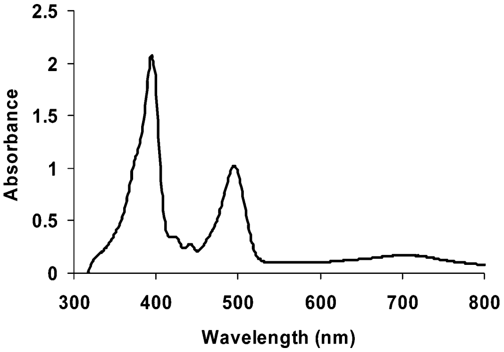

Figure 2. UV−vis spectrum of Ge(TPP) in toluene with maxima at 395, 442, 495, and 702 nm. The small absorption at 420 nm is due to a small amount of oxidized species.

Further evidence that Ge(TPP) contains Ge(II) comes from its spectroscopy. In the ^{1}H NMR spectrum, the resonance for the protons bound to C$_\beta$ comes at 9.0 ppm, a typical value for an aromatic porphyrin. In contrast, the resonance for the C$_\beta$ protons of Si^{IV}(TPP)(pyridine)$_2$ are shifted far upfield to 1.3 ppm. The UV−vis spectrum of Ge(TPP) in benzene, shown in Figure 2, is very similar to the reported spectrum of Sn(TPP).[19] There is a Soret band at 495 nm and a broad Q band at 702 nm. The absorption at 395 nm is due to a charge-transfer transition from the Ge 4p lone pair to the porphyrin e$_g$ (π*) orbital.[36]

Preparation and Characterization of Ge(TPP)(pyridine)$_2$. When green Ge(TPP) is placed in pyridine, it slowly dissolves over the course of 1−2 days, forming a bright-red solution of Ge(TPP)(py)$_2$. Single crystals of Ge(TPP)(py)$_2$·py were grown by slow diffusion of hexane into a concentrated solution of Ge(TPP)(py)$_2$ in pyridine. The crystal structure is shown in Figure 3. As in Si(TPP)(THF)$_2$, the structure is highly ruffled, with the four nitrogen atoms of the porphyrin ring coplanar and nearly perfect octahedral coordination around germanium. The meso carbons, C$_{meso}$, are above and below the porphyrin N$_4$ plane by an average of 0.825 Å, nearly as large as the deviation of 1.00 Å observed in Si(TPP)(THF)$_2$. We had expected that the larger

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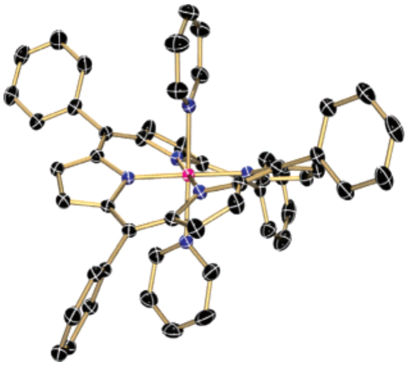

Figure 3. Solid-state structure of Ge(TPP)(pyridine)$_2$ in crystals of Ge(TPP)(pyridine)$_2$·pyridine.

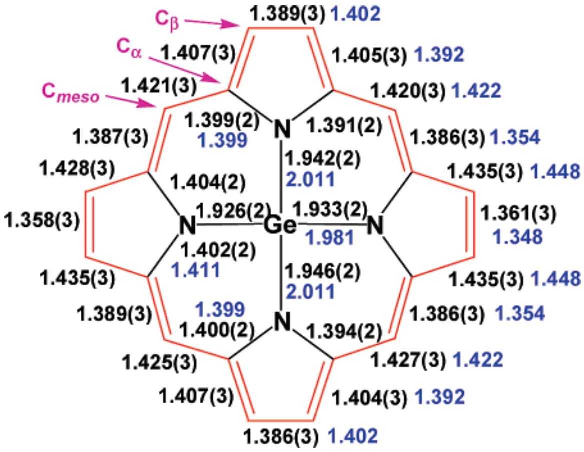

Figure 4. Valence-bond structure of Ge(TPP)(pyridine)$_2$ with selected bond distances (Å) from the crystal structure of Ge(TPP)(py)$_2$·py (black) and calculated (B3LYP/6-311G**) for Ge(porphine)(py)$_2$ (blue). C−C distances are outside the ring, and C−N and Ge−N distances are inside the ring. The Ge−N (pyridine) distances are 2.089(2) and 2.122(2) Å. The 20 π-electron circuit is highlighted in red.

covalent radius of germanium would lead to a more nearly planar structure, and in fact, in the reported crystal structures of Ge(IV) porphyrin complexes of the type Ge(porph)X$_2$, the structures range from moderately ruffled[12,13] to nearly planar.[14,15] One difference between Ge(TPP)(py)$_2$ and those other Ge(IV) porphyrins is that Ge(TPP)(py)$_2$ has four covalent Ge−N(pyrrole) bonds (see Figure 4), whereas the Ge(porph)X$_2$ complexes have the usual two covalent and two dative Ge−N bonds. That leads to shorter Ge−N bonds in Ge(TPP)(py)$_2$ and a more ruffled structure. It is also possible that the antiaromaticity of Ge(TPP)(py)$_2$ is actively contributing to the ruffling of the ring system.

The most unusual structural feature in Ge(TPP)(py)$_2$ is the alternating lengthened and shortened C−C bonds around the periphery of the porphine core (see Figure 4 for bond lengths). This type of structural distortion has been observed previously in only two porphyrin complexes, Si(TPP)(THF)$_2$[26] and Al(TPP)(THF)$_2$,[37] both reduced porphyrins like Ge(TPP)(py)$_2$. The valence-bond structure given in Figure 4, different from valence-bond structure of a normal-valent porphyrin, accounts for the structural distortion. The oxidation state of 4+ for germanium means that the oxidation state of the porphyrin ring system is 4−, rather than the usual 2− of an aromatic porphyrin ring system. The aromaticity of a normal-valent porphyrin is generally ascribed to its system of 18 π-electrons, therefore the π-system of Ge(TPP)(py)$_2$ should contain 20 π-electrons and be antiaromatic. The 20-carbon periphery of the porphine core of Ge(TPP)(py)$_2$ (highlighted in red in Figure 4) is the 20-π-electron system. It is antiaromatic and is therefore not in resonance with the structure with the double and single C−C bonds interconverted, but instead has the alternating-bond structure as its ground state. In Ge(TPP)(py)$_2$ the average difference in bond length between the formal single and double bonds for C$_\beta$−C$_\beta$ is 0.028 Å, C$_\alpha$−C$_\beta$ is 0.027 Å, and C$_{\text{meso}}$−C$_\alpha$ is 0.036 Å. Those distortions are about half the size of those observed in Si(TPP)(THF)$_2$[26] and also about half the size of those calculated (B3LYP/6-311G**) for Ge(porphine)(py)$_2$ (calculated bond lengths are shown in blue in Figure 4). It is not clear why the bond-length alternation is lower in Ge(TPP)(py)$_2$. Spectroscopy, detailed below, clearly shows that the complex exists in one of two distinct electronic states, either Ge$^{\text{II}}$(TPP) or Ge$^{\text{IV}}$(TPP)(py)$_2$, and not a hybrid of the two. It is possible that the Ge(TPP)(py)$_2$ molecules in crystals of Ge(TPP)(py)$_2$·py are not perfectly ordered with respect to the formal single and double bonds in the structure and are instead statically or dynamically disordered with a 3:1 population of the two orientations. That situation would give an apparent bond-length alternation of half of the actual magnitude in a given molecule.

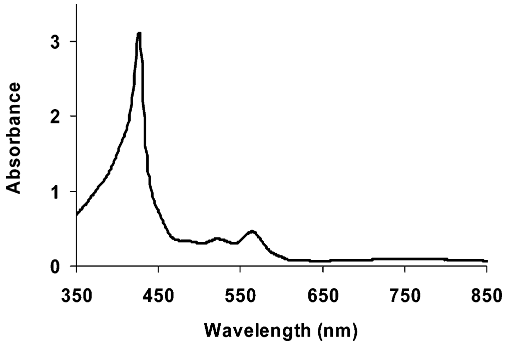

Figure 5. UV−vis spectrum of Ge(TPP)(py)$_2$ in pyridine with maxima at 426, 482, 522, 563, and 770 nm.

In the ^{1}H NMR spectrum of Ge(TPP)(pyridine)$_2$ in pyridine-d_5, the chemical shift of the C$_\beta$ protons is 0.6 ppm, far upfield of the usual chemical shift of about 9 ppm for the C$_\beta$ protons of an aromatic porphyrin, and slightly upfield of the chemical shift of 1.3 ppm for the C$_\beta$ protons of Si(TPP)(pyridine)$_2$. Those upfield chemical shifts are due to a strong paratropic ring current in Ge(TPP)(pyridine)$_2$ and Si(TPP)(pyridine)$_2$, which circulates in the opposite direction as the diatropic ring current of aromatic compounds and is characteristic of an antiaromatic compound.[27] A ^{1}H NMR spectrum of Ge(TPP)(pyridine)$_2$ can be obtained in C$_6$D$_6$, although pyridine slowly dissociates from the complex. The chemical shift of the ortho protons on pyridine of Ge(TPP)(pyridine)$_2$ in C$_6$D$_6$ is 21.6 ppm, and that large downfield shift for protons near the center of the porphyrin ring is also indicative of a paratropic ring current in the porphyrin ring system.

The UV−vis spectrum of Ge(TPP)(pyridine)$_2$ in pyridine is shown in Figure 5. It is similar to the spectrum of Si(TPP)(pyridine)$_2$, which has been analyzed in detail.[38]

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Table 1. Selected Redox Potentials of Ge(TPP), Ge(TPP)(py)$_2$, Sn(TTP), and Sn(TTP)(py)$_2$

	potential (V vs Fc)	
	0/–	–/2–
In THF		
Sn(TTP)	−1.64	−2.06
Ge(TPP)	−1.65	−2.09
	2+/+	+/0
In Pyridine		
Sn(TTP)(py)$_2$	−0.76	−1.20
Ge(TPP)(py)$_2$	−0.77	−1.24

A mixture of Ge(TPP) and pyridine in C_6D_6 was allowed to come to equilibrium for 7 days at 22 °C. Integration of the ^{1}H NMR spectrum showed that the equilibrium constant of the reaction Ge(TPP) + 2 pyridine = Ge(TPP)(py)$_2$ is 22 M^{-2}. If the standard state of a species in solution is taken to be 1 M and because the temperature of the experiment was near the standard temperature of 25 °C, the standard free energy of the reaction is very close to zero.

Electrochemistry. In a THF solution of Ge(TPP), the only porphyrin species that we expect to be present is Ge^{II}(TPP) with no axial ligands. In contrast, the equilibrium constant given above indicates that in pyridine solution, Ge(TPP) will be present almost exclusively as Ge^{IV}(TPP)(pyridine)$_2$. One would expect the difference in electronic structures between those two molecules to have a profound influence on their electrochemical behavior, and we found that to be true, as discussed below. The results are in very good agreement with a previous study of the cyclic voltammetry of Sn(TTP) (TTP = tetratolylporphyrin) in THF and pyridine,[39] with the only difference being the relative stabilities of the M(porph) and M(porph)(pyridine)$_2$ complexes for the two metals.

The redox potentials determined by cyclic voltammetry are given in Table 1, along with those from the previous study on Sn(TTP). In THF, Ge(TPP) undergoes two single-electron reductions to the monoanion and dianion at −1.65 and −2.09 V vs ferrocene$^{0/+}$ (see Figure 6). Those values are close to those reported for Sn(TTP) in THF of −1.64 and −2.06 V vs ferrocene$^{0/+}$ (with ferrocene$^{0/+}$ in THF taken to be +0.56 V vs SCE[40]), and they are at reasonable potentials for two single-electron reductions of a porphyrin ring system.[41] For Ge(TPP)(py)$_2$ in pyridine, two new reversible waves were observed at −0.77 and −1.24 V (see Figure 6), which are ascribed to the Ge(TPP)(py)$_2^{2+/+}$ and Ge(TPP)(py)$_2^{+/0}$ couples, respectively (the irreversible wave at ca. −0.3 V is of unknown origin). Again, the potentials correspond closely to those previously reported for Sn(TTP)(py)$_2^{2+/+}$ and Sn(TTP)(py)$_2^{+/0}$ in pyridine at −0.76 and −1.20 V.[39] For Sn(TTP), however, those waves were observable only when the potential was first swept in the positive direction, oxidizing Sn(TTP) to Sn(TTP)$^{2+}$, which formed Sn(TTP)(py)$_2^{2+}$, and the potential was then swept in the negative direction at the relatively fast rate of 10 V/s to form transiently stable Sn(TTP)(py)$_2^+$ and Sn(TTP)(py)$_2$. In contrast, neutral Ge(TPP)(py)$_2$ is present in pyridine solution under normal conditions, and potential sweeps in either direction show the Ge(TPP)(py)$_2^{2+/+}$ and Ge(TPP)(py)$_2^{+/0}$ waves. The relative instability of Sn(TTP)(py)$_2$ is in agreement with DFT calculations described at the end of the Results and Discussion section.

The irreversible (on the electrochemical time scale) oxidation of Sn(TTP) occurs at about +0.1 V vs ferrocene$^{0/+}$, and, similarly, the irreversible oxidation of Ge(TPP) in CH_3CN/benzene occurs at about +0.2 V (we were unable to observe the oxidation in THF). Thus, Ge(TPP)(py)$_2$ is much more easily oxidized than Ge(TPP) is, at −1.24 V instead of +0.2 V. When Ge(TPP) is oxidized, two electrons are removed from Ge, converting it from Ge(II) to Ge(IV). In contrast, in Ge(TPP)(py)$_2$ the germanium is already present as Ge(IV), and the two extra electrons are in the porphyrin ring system, which has an oxidation state best described as 4−. An electron is easily removed from that reduced, antiaromatic porphyrin ring system, and the potential for oxidation of Ge(TPP)(py)$_2$ is therefore quite negative. In other words, Ge(TPP)(py)$_2$ is a relatively good reducing agent, which was our original purpose in its synthesis.

Ge(TAr^{F}P) and Ge(TAr^{F}P)(pyridine)$_2$. If the equilibrium Ge^{II}(porph) + 2 pyridine = Ge^{IV}(porph)(py)$_2$ is considered to be a transfer of two electrons from Ge(II) to the porphyrin ring system, then one would expect a complex with a more electron-withdrawing porphyrin to have an equilibrium that lies further toward the product. We synthesized tetrakis[3,5-bis(trifluoromethyl)phenyl]porphyrin, H$_2$(TAr^{F}P), by the Lindsey method. Cyclic voltammetry in THF with 0.10 M [NBu$_4$][PF$_6$] showed that H$_2$(TAr^{F}P) was reversibly reduced at −1.34 and −1.72 V (vs ferrocene$^{+/0}$) and H$_2$(TPP) was reduced at −1.65 and −2.04 V under the same conditions. Both reductions of H$_2$(TAr^{F}P) occur at potentials about 0.32 V positive of H$_2$(TPP), a value close to that predicted by a published correlation between the redox potentials of the free-base form of several tetra(4-X-phenyl)porphyrins and the Hammett parameters of the X substituents,[42] using a Hammett parameter of 0.46 for a meta CF$_3$ group.[43] Treatment of H$_2$(TAr^{F}P) with 2 equiv of LiN(SiMe$_3$)$_2$ in ether gave Li$_2$(TAr^{F}P)(ether)$_2$, and the reaction of Li$_2$(TAr^{F}P)(ether)$_2$ and GeCl$_2$(dioxane) in THF for 12 h at 22 °C gave Ge(TAr^{F}P). Green-brown Ge(TAr^{F}P) dissolves quickly in pyridine to form red Ge(TAr^{F}P)(pyridine)$_2$.

Single crystals of Ge(TAr^{F}P)(pyridine)$_2$·pyridine were grown by slowly cooling a hot solution in pyridine/hexane. The crystal structure of Ge(TAr^{F}P)(pyridine)$_2$ is shown in Figure 7, and its valence-bond structure and bond lengths are shown in Figure 8. For this compound the bond-length difference between the formal single and double bonds for $C_\beta-C_\beta$ is 0.050 Å, for $C_\alpha-C_\beta$ is 0.052 Å, and for $C_{meso}-C_\alpha$ is 0.067 Å, close to the calculated values for Ge(porphine)(py)$_2$ of 0.054, 0.056, and 0.068 Å, respectively.

All the spectra of Ge(TAr^{F}P) and Ge(TAr^{F}P)(pyridine)$_2$ are consistent with aromatic Ge^{II}(TAr^{F}P) and antiaromatic Ge^{IV}(TAr^{F}P)(pyridine)$_2$, respectively. A ^{1}H NMR spectrum in C_6F_6/C_6D_6 of a mixture containing both Ge(TAr^{F}P) and Ge(TAr^{F}P)(pyridine)$_2$ is shown in Figure 9. The equilibrium constant of the reaction Ge(TAr^{F}P) + 2 pyridine = Ge(TAr^{F}P)(py)$_2$ in C_6F_6/C_6D_6 at 22 °C was found to be 2.3×10^4 M^{-2}, favoring the product more than in the case of Ge(TPP), as expected for the more electron-withdrawing TAr^{F}P.

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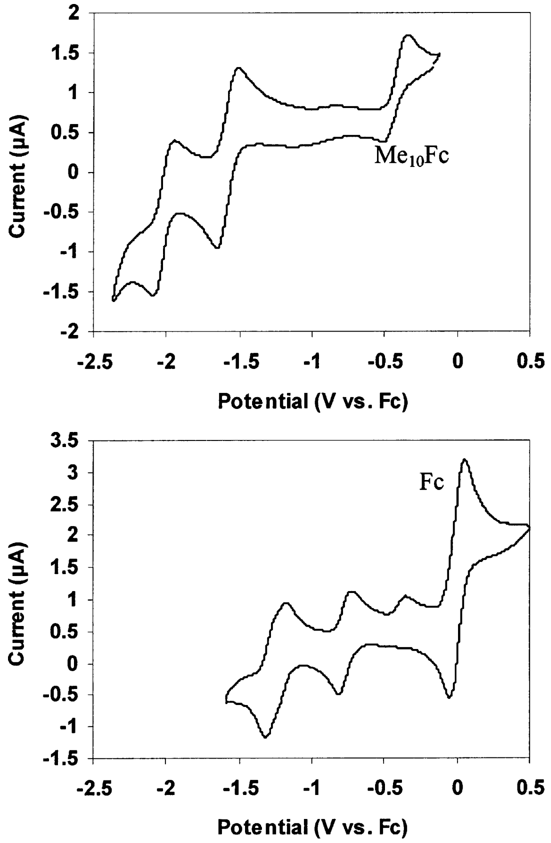

Figure 6. Cyclic voltammograms of Ge(TPP) in THF (top, 0.10 M [NEt$_4$][B(C$_6$F$_5$)$_4$], decamethylferrocene standard, 100 mV/s) and Ge(TPP)(py)$_2$ in pyridine (bottom, 0.10 M [NEt$_4$][B(C$_6$F$_5$)$_4$], ferrocene reference, 100 mV/s).

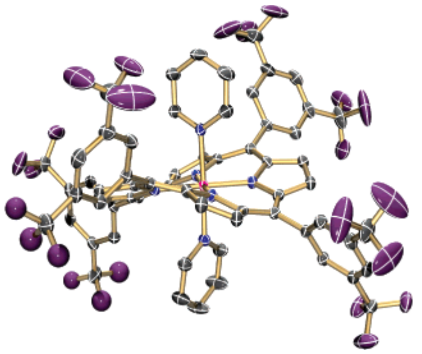

Figure 7. Solid-state structure of Ge(TAr^{F}P)(pyridine)$_2$ in crystals of Ge(TAr^{F}P)(pyridine)$_2$·pyridine. The $-$CF$_3$ groups with spherical fluorines were refined as disordered over two conformations; only one is shown.

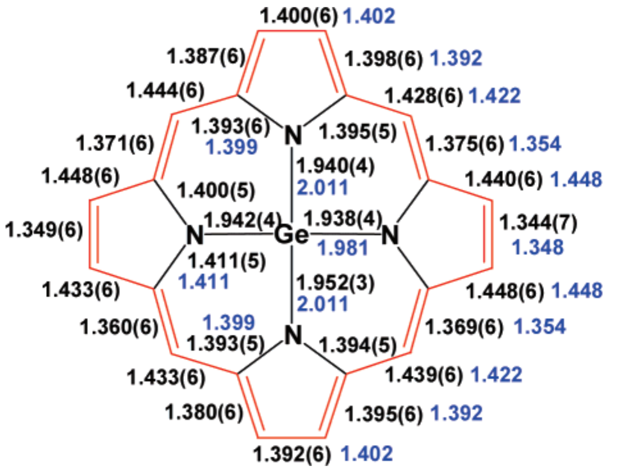

Figure 8. Valence-bond structure of Ge(TAr^{F}P)(py)$_2$ with selected bond distances (Å) from the crystal structure of Ge(TAr^{F}P)(py)$_2$·py (black) and calculated (B3LYP/6-311G**) for Ge(porphine)(py)$_2$ (blue). C$-$C distances are outside the ring, and C$-$N and Ge$-$N distances are inside the ring. The Ge$-$N (pyridine) distances are 2.087(4) and 2.096(4) Å.

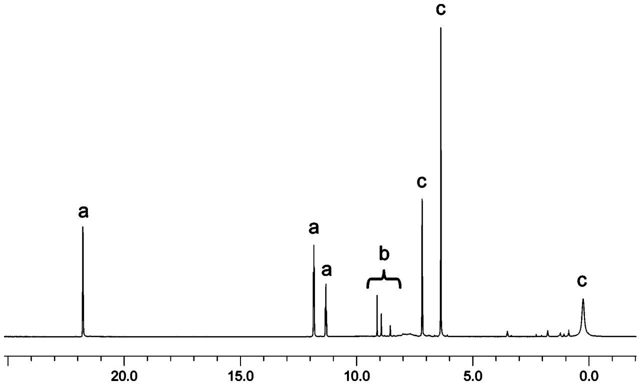

Figure 9. ^{1}H NMR spectrum of Ge(TAr^{F}P)(py)$_2$ and Ge(TAr^{F}P) in C$_6$F$_6$/C$_6$D$_6$. Resonances are marked as follows: *a* for pyridine in Ge(TAr^{F}P)(py)$_2$, *b* for uncomplexed Ge(TAr^{F}P) resonances, and *c* for porphyrin resonances of Ge(TAr^{F}P)(py)$_2$.

M^{II}(porph) + 2 py = M^{IV}(porph)(py)$_2$ for M = Si, Ge, or Sn. There is a clear trend in the propensity of porphyrin complexes of group 14 elements, M^{II}(porph), to undergo a reaction with a dative ligand L to form M^{IV}(porph)(L)$_2$. Si(TPP) has thus far been isolated only as a complex with donor ligands, in Si(TPP)(THF)$_2$ and Si(TPP)(py)$_2$. Ge(TPP) does not form an adduct with THF but in the presence of the stronger ligand pyridine forms Ge(TPP)(py)$_2$. Finally, no Sn(TPP)(L)$_2$ complexes have been isolated. The trend is rooted in the difference in oxidation state of the metal in M^{II}(porph) versus that in M^{IV}(porph)(L)$_2$. In M^{IV}(porph)(L)$_2$ the porphyrin ring system is antiaromatic, which is energetically unfavorable, whereas in M^{II}(porph) the metal has an oxidation state of 2+, which is unfavorable for elements near the top of group 14. For silicon, the antiaromatic complex Si^{IV}(TPP)(L)$_2$ is favored over one containing Si(II), while for tin the antiaromatic Sn^{IV}(TPP)(py)$_2$ is only transiently stable. Germanium porphyrins can be isolated in either state.

The energy of the reaction of eq 1 can be estimated by calculating the energy of each of the three molecules individually.

$$\mathrm{M^{II}(porphine)} + 2\ \mathrm{pyridine} \rightleftharpoons \mathrm{M^{IV}(porphine)(pyridine)_2} \tag{1}$$

Calculations were performed for M = Si, Ge, and Sn with the B3LYP functional and 6-311G** basis set, except for the Sn atom, which required an effective core potential, and cc-pVDZ-PP was used. Using just the electronic energy, the calculated energy of the reaction for M = Si was -54.4 kcal/mol; that for Ge was $+2.5$ kcal/mol, and that for Sn was $+24.5$ kcal/mol. Similar values were obtained with B3LYP and a different basis set, cc-pVDZ (and cc-pVDZ-PP for Sn): Si, -49.4 kcal/mol; Ge, $+3.8$ kcal/mol; Sn, $+23.9$ kcal/mol. Single-point energy calculations were done at the MP2/6-311G** level using the B3LYP/6-311G** geometries, and the energy of the reaction was calculated to be -93.0 kcal/mol for Si and -32.0 kcal/mol for Ge. Therefore, it appears to be coincidental that the

B3LYP-calculated energy of reaction for M = Ge is so close to zero, but the trend in energies of the reaction moving down the periodic table is correct for both the B3LYP and MP2 calculations. In addition, a full vibrational analysis was performed (B3LYP/6-311G**) to calculate the actual free energy of the reaction; the ΔG_{rxn} for Si was −15.4 kcal/mol, and that for Ge was +34.9 kcal/mol. There is probably inaccuracy in those values because of the presence of very low-energy torsional modes in M(porphine)(py)$_2$ and ruffling modes in M(porphine), but again the trend is correct, moving from Si to Ge.

Conclusions

The first free Ge(II) porphyrin complex, Ge(TPP), has been isolated and characterized. The oxidation state of germanium in Ge(TPP) is Ge(II), and the complex is aromatic. In the presence of pyridine Ge(TPP) undergoes a remarkable transformation, forming the antiaromatic Ge(IV) porphyrin complex Ge(TPP)(py)$_2$. That reaction, in which a dative ligand induces an oxidation-state change in a metal center, is, as far as we know, without precedent. A similar molecule with a more electron-withdrawing porphyrin ring, Ge(TAr^{F}P), behaves similarly, but its reversible reaction with pyridine favors the antiaromatic product, Ge(TAr^{F}P)(py)$_2$. The propensity of group 14 porphyrin complexes to form their antiaromatic adducts with pyridine follows the trend predicted by the inert pair effect.

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Supporting Information Available: Crystal structure data in CIF format, crystallographic details, picture of Ge(porphine) HOMO, and the complete version of ref 33. This material is available free of charge via the Internet at http://pubs.acs.org.

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