

Germanium Phthalocyanine, GePc, and the Reduced Complexes SiPc(pyridine)₂ and GePc(pyridine)₂ Containing Antiaromatic π -Electron Circuits

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The reaction of GeCl₂(dioxane) with K₂Pc(DMF)₄ yields germanium phthalocyanine, GePc. GePc dissolves in pyridine to form GePc(py)₂. The ¹H NMR spectrum of GePc(py)₂ and nucleus-independent chemical shift (NICS) calculations on GePc(NMe₃)₂ both show the presence of a strong paratropic ring current. That ring current, along with the bond-length alternation in the crystal structure of GePc(BuPy)₂, indicates the presence of an antiaromatic π -electron circuit in GePc(py)₂. SiPc(py)₂ was synthesized, and its electronic structure is similar to that of GePc(py)₂.

We have reported the synthesis and characterization of Si(TPP)(THF)₂ (TPP = tetraphenylporphyrin), a complex in which the oxidation state of silicon is Si(IV) and the porphyrin ring system has an oxidation state of 4⁻.¹ In normal, aromatic porphyrin complexes, the ring system has an oxidation state of 2⁻ and the aromaticity is generally considered to be due to an 18 π -electron circuit in the ring system. The doubly reduced Si(TPP)(THF)₂ has a 20 π -electron circuit in its ring system and is antiaromatic, as indicated by C–C bond-length alternation along the 20-carbon periphery of the porphine ring system and NMR chemical shifts that indicate a strong paratropic² ring current. Si(TPP)(THF)₂ was the first antiaromatic porphyrin complex to be isolated.

More recently, we reported the synthesis of Ge(TPP) by the reaction of GeCl₂(dioxane) and Li₂(TPP)(ether)₂.³ In Ge(TPP), the oxidation state of germanium is Ge(II) and the complex is aromatic. Ge(TPP) undergoes a reversible reaction with pyridine, forming Ge^{IV}(TPP)(py)₂, wherein a formal transfer of two electrons from the germanium center to the

porphyrin ring system has occurred to yield a Ge(IV) complex with an antiaromatic porphyrin ring system.

There is one previous report of the synthesis of germanium phthalocyanine, GePc, accomplished by the reduction of GePcCl₂ with NaBH₄,⁴ but that compound was later shown to be instead germanium triazatetrabenzocorrole hydroxide, Ge(TBC)OH.⁵ We found that it is possible to synthesize blue-purple GePc by the reaction of GeCl₂(dioxane) with K₂Pc(DMF)₄ in THF for 12 h at 22 °C. The composition of the product isolated by filtration was GePc·0.2THF·2KCl. Because of the very low solubility of GePc in all non-coordinating solvents, it was not possible to separate it from the KCl byproduct. As with Ge(TPP),³ it appears that THF is not a strong enough ligand to coordinate to GePc to form GePc(THF)₂, and the THF in the product is merely occluded solvent that was not removed under vacuum.

Characterization of GePc was complicated by its very low solubility in solvents that do not form complexes of the type GePc(L)₂, where L is the solvent acting as a dative ligand to germanium. Efforts at single-crystal growth of GePc for X-ray diffraction were thwarted by its low solubility, and sublimation did not yield single crystals. NMR spectroscopy of GePc was not possible. Attempts to obtain the UV–vis spectrum of GePc yielded spectra identical to that of Ge(TBC)OH (see Supporting Information).⁵ It seems there are traces of Ge(TBC)OH in our sample of GePc·0.2THF·2KCl. GePc has extremely low solubility in organic solvents, while the solubility of Ge(TBC)OH is higher,⁵ so when a sample of our product is placed in a solvent such as THF, the small amount of Ge(TBC)OH in the sample dissolves while the GePc remains as a solid. Treatment of our GePc with benzoyl peroxide leads to a compound with a UV–vis spectrum consistent with the normal phthalocyanine GePc(OBz)₂. In contrast, Ge(TBC)OH does not react with oxidizing agents such as Br₂⁴ and could not be converted to GePc(OBz)₂ by

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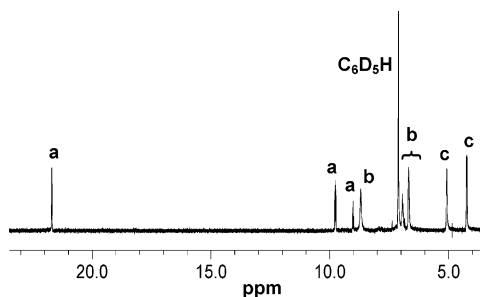


Figure 1. ^1H NMR spectrum of $\text{GePc}(\text{py})_2$ in C_6D_6 . Resonances labeled “a” are due to coordinated pyridine, “b” are free pyridine, and “c” are phthalocyanine ring resonances.

benzoyl peroxide, so it appears that the bulk of our product is GePc . Further evidence for the identity of our product is provided by its conversion to $\text{GePc}(\text{L})_2$ complexes and the characterization of those compounds (see below). The small amount of $\text{Ge}(\text{TBC})\text{OH}$ probably originates from traces of water in the reaction of $\text{GeCl}_2(\text{dioxane})$ and $\text{K}_2\text{Pc}(\text{DMF})_4$.

GePc dissolved in pyridine over the course of several hours to form a bright purple solution of $\text{GePc}(\text{pyridine})_2$. Precipitation with hexane yielded brown-purple $\text{GePc}(\text{py})_2 \cdot 2.7\text{KCl}$ (the KCl remains from the $\text{GePc} \cdot 0.2\text{THF} \cdot 2\text{KCl}$ starting material, and it appears that the KCl was more completely precipitated than $\text{GePc}(\text{py})_2$ was in this preparation). The UV–vis spectrum of $\text{GePc}(\text{py})_2$ is given in the Supporting Information.

$\text{GePc}(\text{py})_2$ has some solubility in benzene; its ^1H NMR spectrum in C_6D_6 is shown in Figure 1. The resonances of the coordinated pyridine, at 21.7, 9.8, and 9.0 ppm for the 2-, 3-, and 4-hydrogens, respectively, indicate the presence of a strong paratropic ring current, characteristic of an antiaromatic compound.² The Pc ring proton resonances occur at 5.1 and 4.3 ppm, upfield from the typical resonances for a normal phthalocyanine complex, which occur at about 9.6 and 8.3 ppm.⁶ (There are actually four types of chemically inequivalent Pc protons in $\text{GePc}(\text{py})_2$, as explained below, but they are interconverting quickly on the NMR time scale.) The Pc ring resonances of $\text{GePc}(\text{py})_2$ are in the range expected for nonaromatic alkene protons. Overall, the ^1H NMR data from $\text{GePc}(\text{py})_2$ indicate that there is an antiaromatic π -electron circuit in the central part of the phthalocyanine ring system and the peripheral benzo groups have lost some of their aromaticity relative to a normal phthalocyanine complex. The electronic structure is discussed further below.

Crystals of $\text{GePc}(\text{tBuPy})_2$ ($\text{tBuPy} = 4\text{-tert-butylpyridine}$) suitable for single-crystal X-ray diffraction were grown by slowly cooling a solution of GePc in hot 4-*tert*-butylpyridine. The structure is shown in Figure 2. In contrast to the porphyrin complexes $\text{Si}(\text{TPP})(\text{THF})_2^1$ and $\text{Ge}(\text{TPP})(\text{py})_2^3$, there is no ruffling in $\text{GePc}(\text{tBuPy})_2$ and the ring system is nearly planar. However, there is a distinct bond-length alternation in $\text{GePc}(\text{tBuPy})_2$, as in $\text{Si}(\text{TPP})(\text{THF})_2$ and $\text{Ge}(\text{TPP})(\text{py})_2$. The bond lengths are given in Figure 3, along with the calculated (Gaussian03,⁷ B3LYP/6-31G*(C,H,N),6-

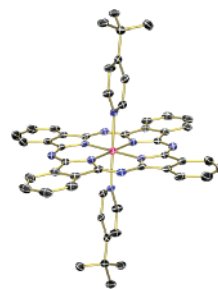


Figure 2. X-ray crystal structure of $\text{GePc}(\text{tBuPy})_2$.

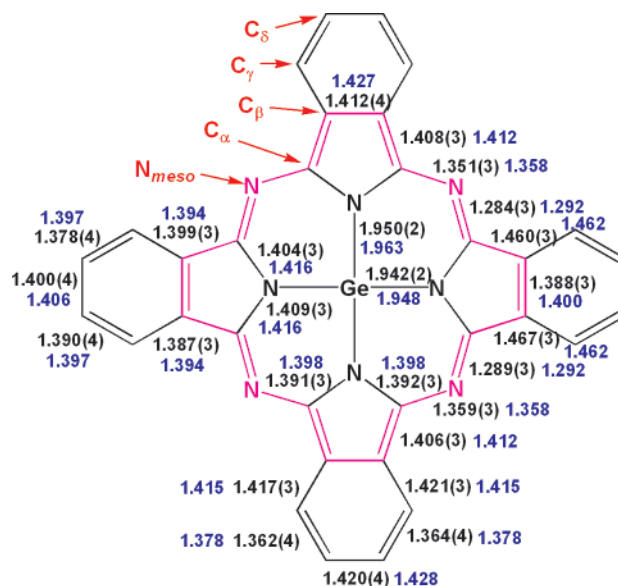


Figure 3. Valence-bond structure of $\text{GePc}(\text{tBuPy})_2$ with bond distances (Å) from the crystal structure of $\text{GePc}(\text{tBuPy})_2$ (black) and calculated (B3LYP/6-31G*(C,H,N),6-311G*(Ge)) for $\text{GePc}(\text{py})_2$ (blue). C–C and C– N_{meso} distances are given outside the ring, while Ge–N and C– $\text{N}_{\text{isoidole}}$ distances are given inside the ring. The germanium atom is on a crystallographic inversion center, and symmetry-equivalent distances are not shown.

311G*(Ge)) bond lengths for $\text{GePc}(\text{py})_2$. The valence-bond structure of Figure 3, with four covalent bonds to Ge and the single- and double-bond pattern throughout the rest of the ring system that those four covalent Ge–N bonds require, appears to be a reasonable representation of the electronic structure of the molecule. If the aromaticity of a normal-valent phthalocyanine ring system is considered to be due to an 18 π -electron circuit (although the situation is really more complex for this polycyclic system), then the doubly reduced $\text{GePc}(\text{py})_2$ should contain an antiaromatic 20 π -electron circuit. That circuit is highlighted in purple in Figure 3. Because the molecule is antiaromatic, the structure with the double and single bonds of the purple 20-atom circuit interconverted is not in resonance with the one shown, but instead the alternating-bond structure is the ground state, as in cyclobutadiene. The difference in bond length between the formal single and double $\text{C}_\alpha\text{--N}_{\text{meso}}$ bonds is 0.069 Å, $\text{C}_\alpha\text{--C}_\beta$ is 0.057 Å, and $\text{C}_\beta\text{--C}_\beta$ is 0.024 Å. The bond-length differences for $\text{C}_\alpha\text{--N}_{\text{meso}}$ and $\text{C}_\alpha\text{--C}_\beta$ are very similar to those observed for $\text{Si}(\text{TPP})(\text{THF})_2$, while the $\text{C}_\beta\text{--C}_\beta$ bond-length

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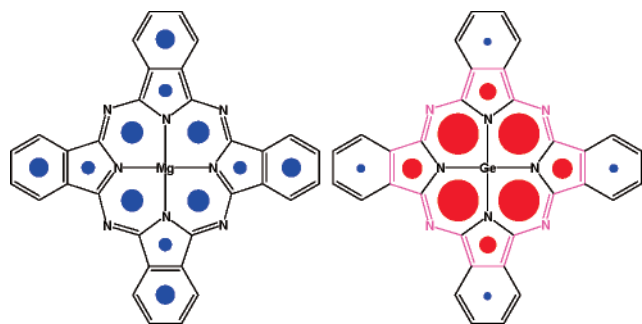


Figure 4. NICS(1) values for MgPc and GePc(NMe₃)₂. Blue circles represent negative NICS(1), and red circles represent positive NICS(1). The area of each circle is proportional to the absolute value of the NICS(1) at that point.

difference in GePc(^tBuPy)₂ is about half as large as that in Si(TPP)(THF)₂. That is presumably due to the fact that the C_β–C_β bonds in GePc(^tBuPy)₂ are also part of the fused benzo groups. The four benzo groups are not all equivalent in GePc(^tBuPy)₂. The benzo groups to the left and right in Figure 3 show only very little, if any, bond-length alternation, and are not significantly different from the benzo groups in a normal-valent phthalocyanine.⁸ That is consistent with the valence-bond picture of Figure 3, where the left and right benzo groups have a benzenoid aromatic sextet.⁹ The top and bottom benzo groups, on the other hand, exhibit significant bond-length alternation. The average difference between the C_β–C_γ and C_γ–C_δ bonds is 0.056 Å. That implies that those benzo groups have lost some of their aromaticity, consistent with the ¹H NMR data and the nucleus-independent chemical shift (NICS) calculations below.

NICS¹⁰ reveals the presence of diatropic or paratropic ring currents. In a conjugated, monocyclic π-system, a diatropic ring current is indicative of aromaticity and a paratropic ring current is indicative of antiaromaticity.² The question of aromaticity and antiaromaticity becomes somewhat more complicated for polycyclic systems such as phthalocyanines and porphyrins, but NICS calculations at several points within the molecule will give an overall picture of the ring currents present. NICS(1) calculations, performed 1 Å out of the plane of the ring system in question, have been shown to be a better gauge of ring currents than NICS(0) calculations, which are performed in the plane of the ring system.¹¹ Figure 4 shows the results of NICS(1) calculations on MgPc and GePc(NMe₃)₂. Calculations were done at the B3LYP/6-31G* level, with the 6-311G* basis set used for the germanium atom. Trimethylamine ligands were used in place of pyridine to avoid effects from the pyridine ring current. In Figure 4, the blue circles represent a negative NICS(1) value and a diatropic ring current while the red circles

represent a positive NICS(1) value and a paratropic ring current. The area of each circle is proportional to the absolute value of its calculated NICS(1) (all NICS(1) values are given in the Supporting Information). As expected for MgPc, at all locations there are negative NICS(1) and the entire system is aromatic. For GePc(NMe₃)₂, there are large, positive NICS(1) in the inner ring system and clearly a strong paratropic ring current. The largest value is +55.2, calculated 1 Å above the midpoint of the two isoindole C–N bonds. The smaller positive NICS(1) values at the centroids of the pyrrole rings indicate that the paratropic ring current of the 20 π-electron antiaromatic circuit (highlighted in purple) splits between the inner and outer paths through the pyrrole rings. The small, negative NICS(1) values for the benzo groups are consistent with their decreased aromaticity. It is somewhat surprising that the calculated NICS(1) are not significantly different for the top/bottom and left/right benzo groups, while the calculated geometry does correctly predict the bond-length alternation in the top/bottom benzo groups and the lack of bond-length alternation in the left/right benzo groups.

Treatment of silicon phthalocyanine dichloride, SiPcCl₂, with 2 equiv of Na/Hg in THF at 22 °C for 12 h gave dark gray-purple SiPc(THF)₂. Dissolution of SiPc(THF)₂ in pyridine and precipitation of the product with hexanes yielded dark purple SiPc(py)₂. The ¹H NMR spectrum of SiPc(py)₂ in C₆D₆ has resonances for coordinated pyridine at 19.9, 9.5, and 8.8 ppm for the 2-, 3-, and 4-hydrogens, respectively, and Pc ring resonances at 5.3 and 4.6 ppm. Those chemical shifts indicate a slightly smaller paratropic ring current in SiPc(py)₂ than in GePc(py)₂, although the overall electronic structures of SiPc(py)₂ and GePc(py)₂ appear to be quite similar. The NICS(1) calculated for SiPc(NMe₃)₂ are similar to those for GePc(NMe₃)₂. We made many attempts at growing crystals of SiPc(L)₂ (with L = THF, pyridine, 4-*tert*-butylpyridine, DMF, or anisole) suitable for single-crystal X-ray diffraction, but none were successful. The calculated structure of SiPc(py)₂ (B3LYP/6-31G*) has bond-length alternation similar to that in the calculated structure of GePc(py)₂.

In conclusion, we have synthesized, isolated, and characterized the first phthalocyanine complexes containing antiaromatic π-electron circuits. The crystal structure of GePc(^tBuPy)₂ shows that the antiaromaticity results in an alternating single- and double-bond structure that has not been previously observed in phthalocyanine complexes.

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Supporting Information Available: Synthetic details, spectra, table of NICS(1), calculated structure of SiPc(NMe₃)₂, complete ref 7, and crystallographic details, including a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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