

delocalization from central metal ion to ligands.³⁰ The hyperfine interaction decreases as electrons are delocalized to ligand orbitals, a feature found particularly useful in interpretation of Cu(II)-protein spectra.³¹ ENDOR spectra of bound ⁵⁷Fe may be comparably valuable in characterizing and understanding high-spin rhombic Fe(III)-protein complexes.

Summary

The feasibility of using ENDOR spectroscopy to study ⁵⁷Fe hyperfine interactions in rhombic high-spin Fe(III) complexes has

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been demonstrated. The sensitivity of the ⁵⁷Fe ENDOR spectrum to fine structure and hyperfine parameters of the spin Hamiltonian shows ENDOR to be a valuable adjunct to CW EPR and Mössbauer spectroscopies in characterizing the properties of biologically significant high-spin Fe(III) complexes. Splitting of lines of an ENDOR pair results from interaction of hyperfine and electronic Zeeman terms in the spin Hamiltonian, the pseudo-nuclear Zeeman effect. Because of the sensitivity of this effect to zero-field splittings, fine structure as well as hyperfine parameters of the spin Hamiltonian may be estimated from the ⁵⁷Fe ENDOR spectrum.

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Electrochemical, Theoretical, and ESR Characterizations of Porphycenes. The π Anion Radical of Nickel(II) Porphycene

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Abstract: Electrochemical, optical, ESR, ENDOR, and theoretical results are presented for nickel(II) 2,7,12,17-tetrapropylporphycene and its one-electron reduction product. The nickel complex of this novel class of porphyrin isomers was chosen to probe the electronic configurations of porphycenes, to assess the role of the porphycene ligand in controlling sites of reduction (metal versus macrocycle), to determine the effects of its D_{2h} symmetry compared to the D_{4h} symmetry of porphyrins on ESR spectral resolution, and to compare with the reductive chemistry of nickel porphyrins used to model the reactions of F430, the nickel tetrapyrrole found in methanogenic bacteria. Reduction of the Ni(II) porphycene yields a π anion radical whose redox, optical, and ESR characteristics are in good agreement with extended Hückel and ZINDO molecular orbital calculations and thus begin to define the electronic configuration of this new class of porphyrin derivatives.

The seminal syntheses by Vogel and co-workers² of porphycenes, the novel porphyrin isomers, led us to investigate the reduction of nickel(II) 2,7,12,17-tetrapropylporphycene (TPrPc, see Figure 1) for several reasons. (1) Little is known about the electronic factors that determine the properties of porphycenes and the consequences of isomerization of the porphynoid structure. (2) The reduction of nickel(II) porphyrin derivatives is being extensively studied to model F430, the nickel tetrapyrrole that catalyzes CO₂ conversion to methane in methanogenesis. Ni(II) radicals and Ni(I) anions have been reported as reduction products.³⁻⁹ (3) Porphycenes are easier to reduce than porphyrins or hydro-

porphyrins and the relative reordering of the metal and π^* orbitals may therefore yield π anions unambiguously. (4) The D_{2h} symmetry of the porphycenes should remove the orbital degeneracy of the π^* orbitals found in D_{4h} porphyrins that results in a lack of ESR resolution and does not allow direct comparison with molecular orbital calculations.^{10,11}

We present here redox, ESR, ENDOR, optical, and theoretical results for the π anion of nickel(II) porphycene that help characterize this novel class of compounds.

Methods

ESR and ENDOR spectra were recorded on a Bruker-IBM ER 200D spectrometer equipped with an ER 251 double resonance system, a field frequency lock, and an Aspect 2000 data acquisition system. NMR spectra were obtained in CDCl₃ at 250 MHz on a Bruker WM-250 instrument. Mass spectra were measured on a JEOL HX 110 spectrometer. Optical spectra were recorded on a Cary 2300 spectrophotometer. Anion radicals were generated electrochemically in tetrahydrofuran (THF) at Pt electrodes in vacuo.¹² ESR samples were equipped with optical cells to allow monitoring before and after the ESR measurements.¹² Cyclic voltammograms were obtained in CH₂Cl₂ in a microcell¹³ under a N₂ atmosphere relative to a SCE electrode. THF and CH₂Cl₂ were distilled from CaH₂. The THF was degassed by freeze-

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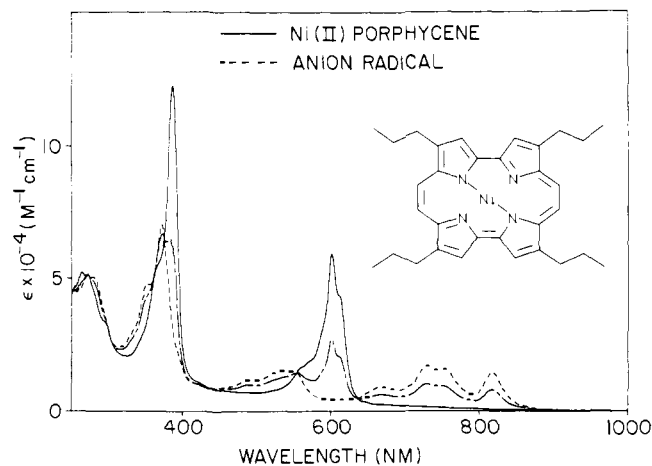


Figure 1. Optical spectra, in THF at room temperature, of Ni^{II}TPrPc (—), its anion radical (---), and an intermediate stage in the reduction (— · —). Tetrabutylammonium perchlorate (0.1 M) is the electrolyte.

thaw cycles and stored over Na–K alloy. Recrystallized tetrabutylammonium perchlorate, dried in vacuo, was used as the electrolyte. 2,7,12,17-Tetrapropylporphycene was synthesized from diethyl 3-propyl-5-methylpyrrole-2,4-dicarboxylate according to Vogel et al.²

Nickel(II) Tetrapropylporphycene. To a solution of the free base porphycene (20 mg) in acetic acid (15 mL) was added nickel(II) acetate tetrahydrate (50 mg) and sodium acetate (3 mg). The mixture was heated to reflux under nitrogen for 2 h, and the Ni(II) complex was separated as violet needles from the solution upon cooling. The crystals were collected by filtration, washed with methanol (50 mL) and dried in air. Yield 19.3 mg (86%); UV–vis, MS, and ¹H NMR spectra were identical with those reported by Vogel et al.²

Copper(II) Tetrapropylporphycene. The complex was prepared by heating a solution of tetrapropylporphycene (20 mg) in acetic acid (15 mL) with copper(II) acetate (50 mg) and sodium acetate (3 mg). After refluxing for 4 h, the solution was cooled and partitioned in CH₂Cl₂ (100 mL) and water (100 mL). The organic layer was separated, washed again with water, and evaporated. The residue was crystallized from CH₂Cl₂ and methanol. Yield 21 mg (92%); UV–vis, λ_{\max} = 366 nm (ϵ = 60800) sh, 387 (154000), 574 (15800), 613 (70500); MS, *m/z* 539/541; mp >300 °C.

2,7,12,17-Tetrapropylporphycene-9,10,19,20-d₄ was synthesized from diformyl-*d*₂-bipyrrole obtained by using deuterated DMF (*d*₇, 99.9%) in the Vilsmeier formylation reaction: mp 189–191 °C; ¹H NMR indicated that the ethylene bridge protons (9.62 s) vanished completely; MS, *m/z* 482 (M⁺). After insertion of Ni, NiTPrPc-*d*₄ contained less than 10% ¹H at those positions.

Theoretical calculations of the nickel porphycene used the published crystallographic data for Ni^{II}TPrPc.² The same structure was assumed for the anion radical.¹⁴ To shorten computation time, the propyl substituents were replaced by methyl groups. Porphine calculations used a standardized planar porphyrin skeleton based on nickel octaethylporphyrin (OEP) X-ray data.¹⁵ The iterative extended Hückel (IEH) programs were described in ref 16. Parameters were taken from Gouterman and Zerner.¹⁷ INDO/s (ZINDO) computations utilized programs developed by Zerner and co-workers for calculating the optical spectra of closed and open-shell porphyrins.¹⁸

Results and Discussion

Cyclic voltammetry of free base, Cu^{II} and Ni^{II}TPrPc in CH₂Cl₂ shows two reversible one-electron reductions and two one-electron

Table I. Half-Wave Potentials for Porphycenes, V^a

	$E_{1/2}(\text{oxidation})$		$E_{1/2}(\text{reduction})$	
H ₂	1.35	0.90	-0.97	-1.35
Cu(II)	1.07	0.77	-1.11	-1.46
Ni(II)	1.20	0.73	-1.06	-1.42

^aIn CH₂Cl₂/(C₄H₉)₄NClO₄ vs SCE.

oxidations (Table I). The porphycenes thus undergo redox changes comparable to those found in porphyrins.^{10b,19} The average difference, ΔE , between the first oxidation and reduction potentials ($E_{1/2}[\text{oxid}] - E_{1/2}[\text{red}]$) is 1.85 (± 0.04) V to be compared with $\Delta E = 2.25$ (± 0.15) V found for a series of octaethylporphyrin complexes.¹⁹ These differences in redox potentials reflect the energy levels of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the complexes.^{10b,16b} The first absorption maxima of the porphycenes should therefore appear at lower energies or to the red of those of porphyrins, as observed: $\lambda_{\max} = 536$ nm for nickel porphine and 614 (sh), 602 nm for NiTPrPc, in THF, for an energy difference of ~ 0.3 eV. The experimental trend is qualitatively predicted by IEH calculations: The energy gap between the HOMO and LUMO of Ni^{II}Pc is predicted to be 0.33 eV smaller than that of a nickel(II) porphine. (Typical gaps for porphyrins calculated by this method are ~ 2 eV.¹⁷) The major effect of the porphycene in the calculations is to drop the LUMO energy from -9.251 eV for the porphine to -9.471 eV for the porphycene, i.e., the latter should be easier to reduce, as is observed experimentally: $E_{1/2} = -1.1$ V for NiTPrPc vs -1.5 V for NiOEP.^{6,19}

Electrochemical reduction of Ni^{II}TPrPc in THF requires 1 (± 0.05) electron to yield the optical spectrum shown in Figure 1. One-electron re-oxidation regenerates better than 95% of the original spectrum. Reduction to the anion induces a diminution of the Soret band, a bleaching of the 600-nm bands, and the appearance of weak broad bands stretching into the near-infrared region. These spectral changes parallel those observed on reduction of porphyrins to π anions^{7,9,10b} and are consistent with ZINDO calculations for a Ni^{II}Pc π anion that predict new transitions at 848 nm (oscillator strength 0.0035), 814 nm (0.098), 702 nm (0.134), and 627 nm (0.033) and the loss of the original Q band which is calculated at 653 nm (0.235).

The π anion radical assignment and the lack of Ni(I) character is also supported by cyclic voltammetry of the nickel porphycene in the presence of CH₃I in THF (and in CH₂Cl₂, see Table I). Nickel(II) porphyrin derivatives and F430 exhibit irreversible catalytic voltammograms upon reduction in the presence of halogenated methanes.^{5-7,9} The porphycene does not.

Reduction of the NiTPrPc to a π anion radical is further evidenced by its ESR spectra which exhibit many resolved lines over a wide range of temperatures (200–300 K). Porphyrin π anions display no hyperfine structure¹⁰ and in the case of Ni derivatives, ESR signals are only observed at low temperatures with *g* values significantly shifted from the free-electron value.⁶⁻⁹ The ESR spectrum of the nickel(II) porphycene anion at 200 K is shown in Figure 2a with the corresponding ENDOR data (Figure 2c,d). The latter reveal three proton coupling constants of 0.89, 1.31, and 1.41 G (1 G = 2.8 MHz), which are assigned to 4, 8 and 4 equivalent protons, respectively, based on the relative intensities of the peaks and IEH calculations. The computations for the Ni^{II}TPrPc anion yield the unpaired spin densities (ρ) shown in Figure 3, i.e., spin density is distributed over the peripheral and “bridging” carbons ($\rho = 0.040$ – 0.055) with much smaller densities at the nitrogens. The ENDOR peaks are therefore assigned to two sets of four protons (9,10,19,20 and 3,6,13,16) and to eight protons due to the methylene groups at 2,7,12,17, with the latter having coupling constants comparable to one of the other sets of four protons.

One set of protons can readily be identified as arising from the protons on the bridging positions 9,10,19,20 by examining the

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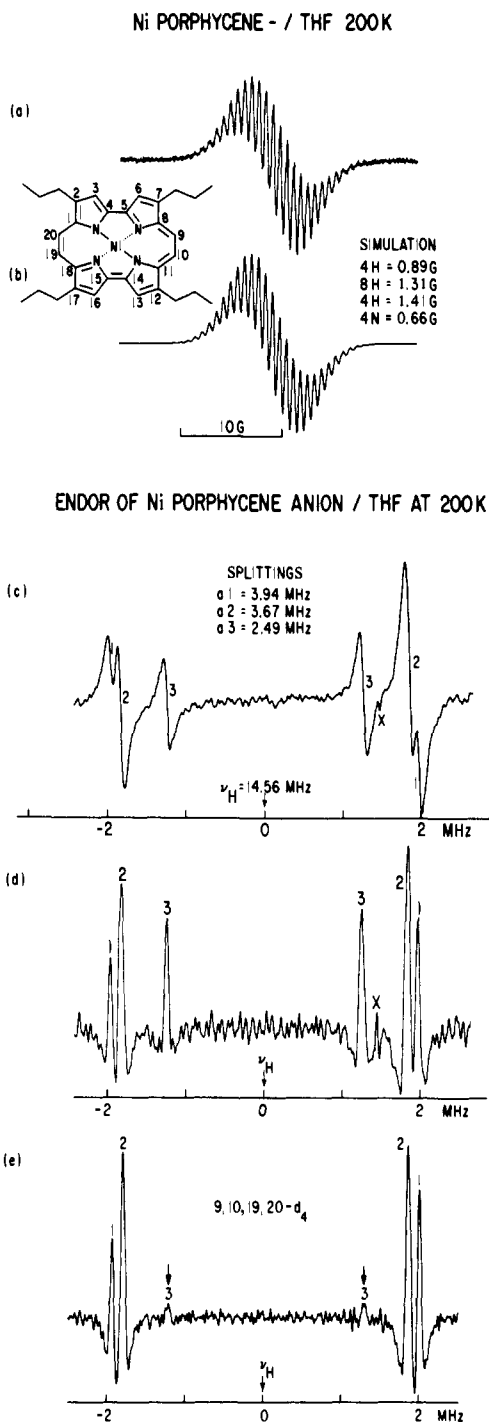


Figure 2. (a) First derivative ESR spectrum of the Ni^{II}TPPrPc anion in THF at 200 K ($g = 2.0032$). At 120 K, the spectrum collapses to a symmetrical singlet with a peak-to-peak line width of 8.1 G, the same g value, and no evidence of Ni(I) character. (b) A simulation that includes 4 protons, $a_H = 0.89$ G, 8 protons, $a_H = 1.31$ G, 4 protons, $a_H = 1.41$ G, 4 nitrogens, $a_N = 0.66$ G, and Gaussian line widths of 0.45 G.²¹ (c) Proton ENDOR spectrum of the anion radical at 200 K. 1 G = 2.8 MHz, X represents an instrumental marker. (d) Derivative of spectrum c that illustrates the clear separation of the resonances due to the methylene and skeletal protons of 1.31 and 1.41 G. (e) Derivative proton ENDOR spectrum of the 9,10,19,20-*d*₄ Ni^{II}TPPrPc anion radical. Note that peaks labeled 3 are missing.

ENDOR spectrum of the porphycene selectively deuterated (>90%) at these positions. As shown in Figure 2e, peak 3 vanishes upon deuteration. In addition, a new set of resonances centered on ν_D appears at low frequencies (Figure 4) equivalent to a deuteron splitting of 0.137 G, in excellent agreement with the deuteron splitting calculated from the gyromagnetic ratio of ¹H

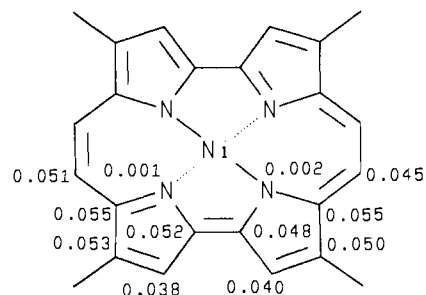


Figure 3. Unpaired spin densities for the anion radical obtained by IEH calculations. The slightly different spin densities at equivalent positions reflect the asymmetry in the X-ray data² used for the calculations and probably average out in solution.

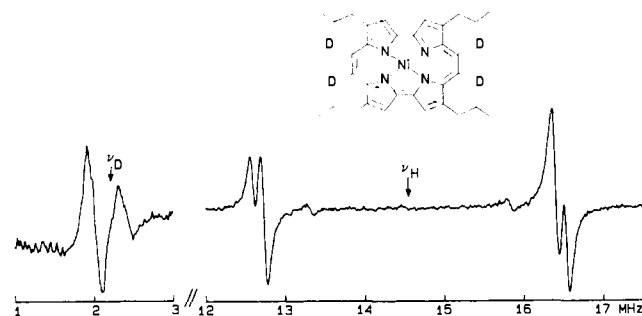


Figure 4. Proton (high frequencies) and deuteron (low frequencies) ENDOR spectra of the 9,10,19,20-*d*₄ nickel(II) porphycene anion at 200 K. $a_H = 1.31$ and 1.41 G and $a_D = 0.14$ G.

and ²H: $a_D = 0.1535 a_H$, i.e., the proton splitting of 0.89 G should yield a deuteron splitting of 0.137 G.^{10a}

The ESR spectrum at 200 K can be attributed to 4 equivalent protons (9,10,19,20) with $a_H = 0.89$ G, 8 protons (methylene groups at 2,7,12,17) with $a_H = 1.31$ G, 4 protons (3,6,13,16) with $a_H = 1.41$ G, and 4 nitrogens with $a_N = 0.66$ G, on the basis of the ENDOR results, a correlation analysis,²⁰ and trial simulations. As shown in Figure 2b, a simulation that incorporates these coupling constants agrees well with the experimental spectrum.

The multi-line spectrum of the NiTPPrPc anion is observed over a wide temperature range. The ESR and ENDOR spectra obtained at 260 K are shown in Figure 5. Small variations in the coupling constants are observed that may arise from small conformational variations as the solvent viscosity changes and/or tighter ion pairs between the radical and its Bu₄N⁺ counterion.^{10,22}

The high degree of ESR resolution that can be obtained for porphycenes¹¹ is illustrated by the spectrum of the deuterated anion in which over 100 lines are resolved at room temperature (Figure 6). A detailed analysis of the spectrum yields 4 deuterons (9,10,19,20), $a_D = 0.14$ G; 4 protons (3,6,13,16), $a_H = 1.41$ G; 8 protons (α methylenes at 2,7,12,17), $a_H = 1.28$ G; 8 protons (β methylenes), $a_H = 0.13$ G; and 4 nitrogens, $a_N = 0.68$ G. (Simulations that do not include the β methylenes do not reproduce the experimental spectrum as faithfully.) A similar spin density profile was deduced from a recent independent investigation¹¹ of the anion radical of free base porphycene (without propyl groups) at 240 K: 4 nitrogens, $a_N = 0.73$ G, 4 protons (9,10,19,20), $a_H = 0.94$ G, and two sets of 4 protons on the pyrrole β carbons (unassigned) with $a_H = 1.44$ and 1.81 G.²³

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(21) The line width used in the simulation subsumes small coupling constants expected from the other methylene and methyl proton substituents of the propyl groups. These decrease by an order of magnitude for every atom in the aliphatic chains away from the π system:^{10a} i.e. the second methylenes of the propyl groups are expected to have proton coupling constants of ~ 0.1 g and the methyl groups ~ 0.01 G (see Figure 6 in which only the latter are unresolved).

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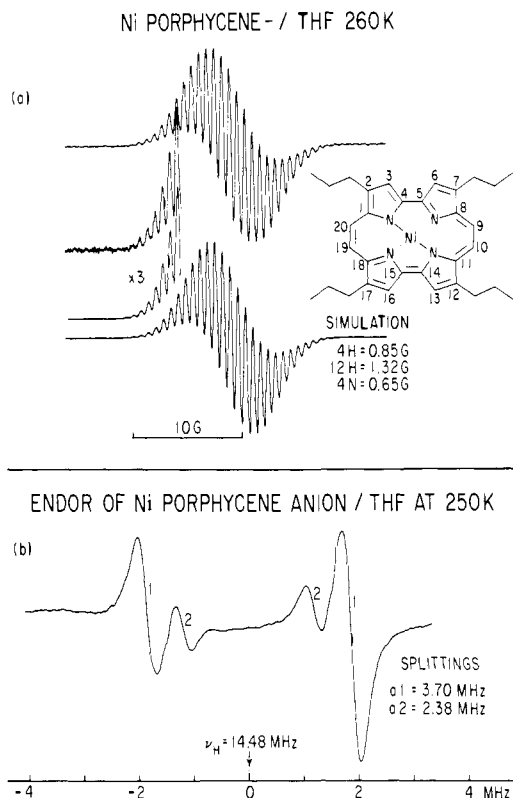


Figure 5. (a) First derivative ESR spectrum of the Ni^{II}TPPrPc anion in THF at 260 K ($g = 2.0032$), and a simulation that assumes 4 protons, $a_H = 0.85$ G; 12 protons, $a_H = 1.32$ G; 4 nitrogens, $a_N = 0.65$ G; and gaussian line widths of 0.48 G.²¹ Wings are expanded by 3 \times to show the agreement between experimental and simulated spectra. (b) Proton ENDOR spectrum of the anion at 260 K, the highest temperature at which ENDOR is obtained.

Conclusions

The ESR results for the anions of the Ni and free base¹¹ porphycenes establish that the change in symmetry from porphyrin to porphycene plays a role in the spectral resolution obtained, as was previously observed for anions of chlorins and bacteriochlorins which also possess symmetries lower than porphyrins.^{10a}

The wide range of temperatures over which the ESR spectra of the nickel(II) porphycene radical are observed excludes any Ni(I) character and the possibility that the compound can be used as a working model for F430. However, examination of porphyrin derivatives that yield Ni(I) upon reduction, i.e. F430, iso-

(23) In the case of the NiTPPrPc anion, the methylene coupling constants depend on the average dihedral angle, θ , the protons make with the p_z orbital of the carbon atom to which the methylenes are attached: $a_H = (\text{constant}) \cdot \rho(\cos^2 \theta)$. For the same ρ value, this will result in a smaller coupling constant for a methylene group than for a proton.^{10a}

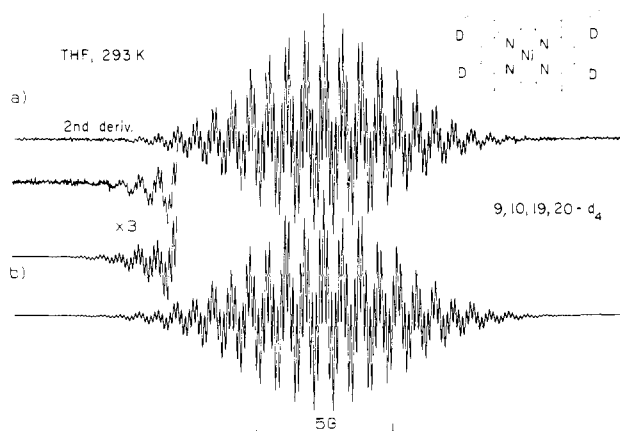


Figure 6. (a) Second derivative ESR spectrum of the 9,10,19,20- d_4 Ni^{II}TPPrPc anion at 293 K. (b) A simulation that assumes 4 nitrogens, $a_N = 0.68$ G; 4 deuterons, $a_D = 0.14$ G; 4 protons, $a_H = 1.41$ G; 8 protons, $a_H = 1.28$ G; 8 protons, $a_H = 0.13$ G; and gaussian line widths of 0.15 G that accommodate the 12 unresolved terminal methyl protons estimated at ~ 0.01 G.

bacteriochlorins, and possibly some porphyrins,⁵⁻⁹ suggests that formation of Ni(I) requires a combination of proper energy levels of the Ni relative to the π^* orbitals, and the capability of the macrocycle to accommodate the structural changes that accompany the change from d_8 to d_9 configurations. Although the Ni-N distances in the porphycene² are comparable to those found in porphyrins,¹⁵ the porphycene core is smaller²⁴ and therefore less likely to accommodate a larger Ni(I) ion. In addition, the facile reduction of the porphycene macrocycle compared to porphyrins is also likely to be a controlling factor in favoring a Ni(II) anion radical over a Ni(I) anion.

Porphycenes do display spectral²⁵ and redox features that make them potentially attractive as photosensitizers. The above combination of experimental and theoretical results helps to rationalize many of these properties and begins to define the electronic configurations of this novel class of porphyrin isomers.

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