strained η^4-naphthalene, but this is not unreasonable since the η^4-naphthalene should be a significantly better π-acceptor. The displacement of methylcyclopentadiene from the protonation product has been confirmed by HPLC of a 100-μL aliquot of a reaction mixture protonated at 0 °C, maintained at this temperature for 2 h, and then cooled to −78 °C. This unambiguously established the formation of a 90 ± 3% yield of monomeric methylcyclopentadiene.

The suggestion that the methylcyclopentadienyl ligand in $\mathbf{4}^{2-}$ adopts an η^3 conformation is partially based on 18-electron considerations: as noted in an authoritative recent review,[9] the η^3-cyclopentadienyl ligand was a controversial species for a number of years, but there is now a structurally characterized example of this bonding mode,[10] and Casey's work on PMe_3 addition to $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$ provides an example in which kinetic data implicate an η^3-cyclopentadienyl complex as a labile intermediate following coordination of a two-electron donor.[11] The importance of ring slippage to the η^3-coordination mode in reactions of cyclopentadienyl complexes also receives circumstantial support from the recent body of work establishing that indenyl ligands can readily adopt η^3-coordination modes.[12]

The reduction of **3** to $\mathbf{4}^{2-}$ would suggest that reductively induced hapticity changes of the type established for arene ligands[1-3,13] can also be induced with other aromatic ligands such as the cyclopentadienyl ligand and that, as in the arene case, such hapticity shifts result in ligand activation toward electrophiles.[14] The only prior evidence for reductive activation of a cyclopentadienyl ligand comes from the electrochemical studies of cobaltocene reduction by El Murr, in which he establishes that $[Co(C_5H_5)_2]^-$ can be trapped by exo CO_2 addition and esterification to give $[Co(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_5CO_2CH_3)]$.[15] Reductively induced hapticity shifts of cyclopentadienyl ligands have important implications for synthetically interesting sequences like those employed by Jonas, in which complexes of highly reduced transition-metal centers are formed by reduction of η^5-cyclopentadienyl precursors like ferrocene[16] (and more specifically for the observation by Ellis that Na/HMPA reduction of $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ gives $[Mn(CO)_4]^{3-}$ [17]), and suggest that such reductions probably involve a series of discrete intermediates differing by two-electron hapticity shifts.

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Nitrite-Bound Five-Coordinate Low-Spin Iron(II) Model Complex for the Prosthetic Group of Nitrite Reductase with an Unusually Large Quadrupole Splitting. Synthesis, Mössbauer Properties, and Molecular Structure of the Complex (Nitro)(α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphinato)iron(II)

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We report the synthesis, molecular structure, and Mössbauer properties of a new N-bound five-coordinate (nitro)(porphinato)iron(II) complex which is relevant as a model for enzymatic nitrite reduction. Most interestingly, the ferrous iron is low spin ($S = 0$) and its Mössbauer spectrum shows an unusually large quadrupole splitting for low-spin (porphinato)iron(II). Such large splittings have been previously observed only for oxygenated hemes such as oxyhemoglobin.

Crystalline $[K(222)][Fe(NO_2)(TpivPP)]\cdot H_2O\cdot C_6H_5Cl$[2] was prepared by reaction, under argon, of $[Fe(SO_3CF_3)(H_2O)(TpivPP)]$[3] (0.08 mmol) and 1 mL of zinc amalgam in 10 mL of C_6H_5Cl and filtered into a solution of Kryptofix-222 (0.8 mmol) and KNO_2 (2.4 mmol) in C_6H_5Cl (10 mL).[4] The red-yellow solution was filtered, and crystals were prepared by diffusion of pentane into the C_6H_5Cl. The crystalline material was washed with several portions of degassed water and then with pentane. UV-vis (C_6H_5Cl): λ_{max} (log ϵ) 428 (5.01) (sh), 441 (5.11), 543 (4.01) (sh), 569 (4.17), 608 (3.83).

An X-ray crystal structure determination[6] shows that the complex is five-coordinate with an N-coordinated nitrite ion in the ligand binding pocket of the picket fence porphyrin (Figure 1). An adventitious water molecule is found at the mouth of the ligand-binding pocket; the $O(w)\cdots O(NO_2)$ distances of 3.17 and 3.36 Å suggest a weak hydrogen bond. Figure S1 (supplementary material) shows average bond distances in the porphinato core and atom displacements from the 24-atom mean plane.[9] Both the short average $Fe-N_p$ bond distance of 1.970 (4) Å and the small (0.18 Å) displacement of iron out-of-plane are consistent with those expected[10,11] for a low-spin five-coordinate iron(II)

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(1) (a) University of Notre Dame. (b) Emory University.

(2) Abbreviations used: H_2TPP, *meso*-tetraphenylporphyrin; $H_2TpivPP$, picket fence porphyrin; Kryptofix-222 or 222, 4,7,13,16,21,24-hexaoxo-1,10-diazabicyclo[8.8.8]hexacosane.

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(4) Kryptofix-222 was recrystallized from benzene, and KNO_2 was recrystallized from distilled water, dried under vacuum, and stored under argon. These compounds must be carefully recrystallized to remove the halide impurities known to coordinate[5] to Fe(II) porphyrin species.

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(6) The complex crystallizes in the monoclinic space group $P2_1/n$, $a = 17.715$ (7) Å, $b = 21.341$ (5) Å, $c = 22.838$ (11) Å, $\beta = 101.86$ (3)°, $V = 8450$ Å^3, $Z = 4$. A total of 15 263 $h,k,\pm l$ reflections were measured at 123 K, and 7722 reflections having $\sin\theta/\lambda < 0.602$ and $F_o \geq 3.0\sigma(F_o)$ were taken as observed. The structure was solved by using the coordinates for the iron porphyrin and [K(222)] cation of the isomorphous nitrato[7] and acetato[8] structures. The remaining atoms were found from difference Fouriers. Least-squares refinement of the model based on 917 variables with anisotropic thermal parameters for all non-hydrogen atoms and fixed, idealized hydrogen atoms leads to $R_1 = 0.079$, $R_2 = 0.087$. Confer Table SI (supplementary material).

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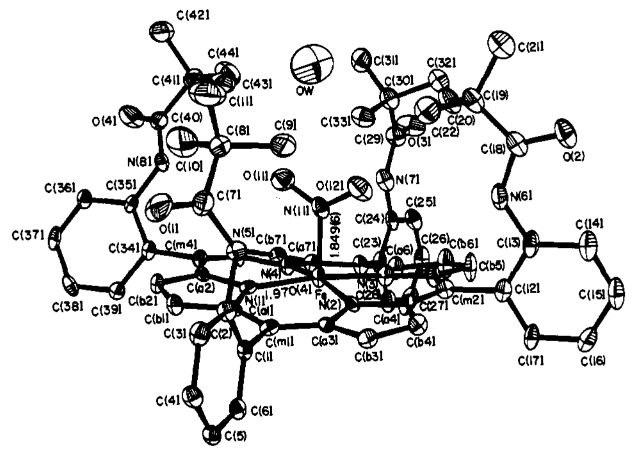

Figure 1. ORTEP diagram showing the molecular structure of the [Fe(NO_2)(TpivPP)]$^-$ ion and the atom-labeling scheme; 30% probability surfaces are shown.

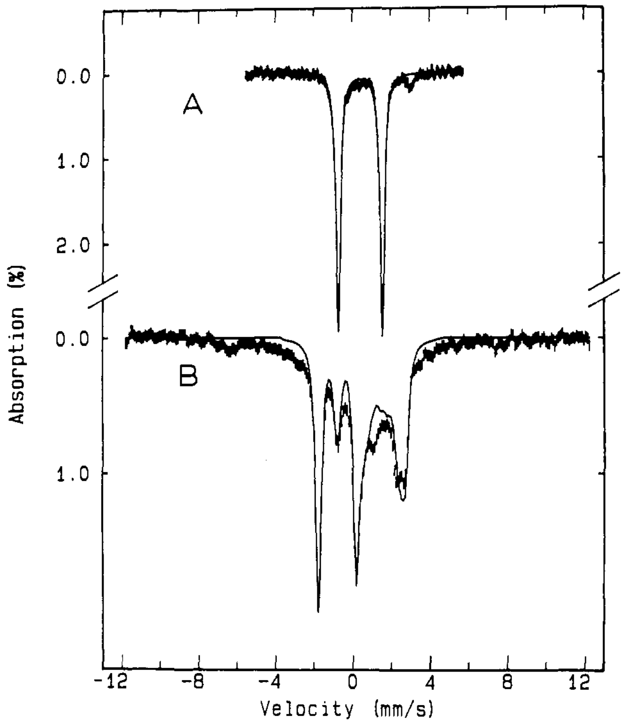

Figure 2. Mössbauer spectrum of [Fe(NO_2)(TpivPP)]$^-$ at 4.2 K in (A) zero applied field and (B) an 8-T field.

complex. The axial Fe–N(NO_2) distance of 1.849 (6) Å is also extremely short. For comparison, the Fe–N(NO_2) distances in several six-coordinate (nitro)iron(III) porphyrinates[12-14] range from 1.949 to 2.001 Å; the Co–N(NO_2) distances in two (isoelectronic) six-coordinate Co(III) porphyrinates are 1.90 (1)[15] and 1.948 (4) Å.[16] The nitrite ligand plane makes a dihedral angle of 40.4° with the closest Fe–N_p vector; the same value (to within ~3°) is seen in all of the related iron(III) complexes. The nitrite is ordered even though it is entirely within the ligand-binding pocket; a view of the orientations of nitrite, iron porphyrin, and the pickets is given in Figure S3 (supplementary material).

A 4.2 K, zero-field Mössbauer spectrum of [Fe(NO_2)(TpivPP)]$^-$ [17] (Figure 2A) shows an intense quadrupole doublet with an isomer shift (δ) of 0.41 mm/s and a quadrupole splitting (ΔE_q) of 2.28 mm/s.[18] The observed δ is characteristic for low-spin (porphinato)iron(II) complexes, while the ΔE_q value is unusually large and has only been reported previously for oxygenated heme compounds.[19] In distinct contrast to the oxyhemes,[20] we do not observe a significant temperature dependence for ΔE_q (=2.23 mm/s at 190 K). The spectrum also shows the presence of a small high-spin iron(II) ($S = 2$) impurity as indicated by a small absorption peak and shoulder, respectively at ~+2.4 mm/s and ~-0.2 mm/s. A 4.2 K spectrum in an 8-T applied field (Figure 2B) unambiguously demonstrates the diamagnetism. The solid line (Figure 2B) is a theoretical simulation assuming diamagnetism and the observed zero-field values of δ and ΔE_q. The perfect agreement in the magnetic splitting between experiment and theory indicates that the effective field at the iron nucleus is equal to the applied field (i.e., $S = 0$). Clearly, the axial ligand field of a *single* axial nitrite is sufficient to lead to a low-spin iron(II) porphyrinate. Although an analogous five-coordinate iron(III) complex has not been isolated, spectroscopic titration data[12] were interpreted in terms of any mononitroiron(III) species as high spin; an isolated bis(nitro)iron(III) derivative is low spin.[12] Finally, we note that although a number of iron(II) complexes with an anionic axial ligand have been previously synthesized,[21] all derivatives have high-spin ($S = 2$) states.

The large quadrupole splitting (~2 mm/s) observed for oxyheme compounds has generated much controversy and has been considered to be unique for low-spin ferrous complexes. Early investigators proposed that the large ΔE_q was consistent with low-spin Fe(III) ($S = {}^1/_2$) coordinated to superoxide anion ($S = {}^1/_2$) with the diamagnetism the result of spin pairing between the two ions.[22] A later calculation[23] suggested that asymmetric binding of dioxygen to heme caused a large rhombic distortion in the dπ orbitals which gave the observed large ΔE_q rather than the postulated iron(III) state. More recent Mössbauer studies of oxyhemoproteins[24] also found no evidence for a thermally accessible triplet excited state. We have now found another low-spin iron(II) heme, [Fe(NO_2)(TpivPP)]$^-$, with a ΔE_q similar to that of the oxyhemes. A Fe(III)–NO_2^{2-} formulation for the nitro complex is highly improbable, and thus the large ΔE_q cannot be explained by postulation of low-spin Fe(III). Mössbauer studies, molecular structures, and single-crystal EPR studies for related (nitro)iron(III) derrivatives[13,14,25] indicate that the orientation of the two dπ orbitals is determined by the nitrite ligand(s); furthermore, strong π-bonding between iron(III) and nitrite is evident in the observed large rhombicities. A significant difference in the energies of the d_{xz} and d_{yz} orbitals from binding nitrite to iron(II) can also be expected. It is thus reasonable to conclude that the origin of the large ΔE_q for the nitro- and oxyheme derivatives is the same, namely, a large rhombicity in the heme plane.[26]

Nitrite reductases are a heterogeneous group of enzymes differing in molecular composition, prosthetic group, and physiological function. This diversity exists even among the heme-containing nitrite reductases which include a siroheme exchange-coupled to a Fe_4S_4 cluster,[27] and dissimilatory reductases

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containing both *c*- and d_1-type hemes[28,29] or six *c*-type hemes per molecule.[30] Some reductases react with nitrite in their oxidized form,[31,32] but all, in their reduced state, react with nitrite and form NO-bound heme species. The NO-bound d_1-heme is six-coordinated with histidine as the other axial ligand,[33] while the axial ligand for the siroheme remains undetermined. Most interestingly, the EPR spectrum for the NO-bound heme in the hexaheme nitrite reductase appears to be of the five-coordinate type.[34] Consistent with this observed diversity, our present results make evident that a low-spin state for the initial complex formed between substrate and reductase heme does not have significant other axial ligand requirements.

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Supplementary Material Available: Figures S1–S3 depicting a formal diagram of the core, an ORTEP plot of $[K(222)]^+$ cryptand, and a drawing showing the relative orientation of nitrite ion and Fe–N_p vectors and Tables SI–SV giving complete crystallographic details, final atomic coordinates, anisotropic thermal parameters, fixed hydrogen atom positions, and a complete listing of bond distances and angles for $[K(222)][Fe(NO_2)(TpivPP)]\cdot H_2O\cdot C_6H_5Cl$ (20 pages); listing of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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Photoinduced Electron Transfer in the Solid State: Rate vs Free Energy Dependence in Fixed-Distance Porphyrin–Acceptor Molecules

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Recent interest in the role of the solvent in electron-transfer reactions has focused on ultrafast photoinduced electron transfers,[1] highlighted by investigations into the primary events of bacterial photosynthesis.[2] In contrast to photosynthesis, which exhibits a quantum yield of primary charge separation near unity at cryogenic temperatures, most photosynthetic model systems based on chlorophyll or porphyrin electron donors exhibit significantly reduced efficiencies of light-initiated, singlet-state electron transfer whenever they are dissolved in rigid glass media.[3] This occurs because solvent dipoles reorient around an ion pair in a polar liquid, decreasing the energy of the ion pair, while solvent dipoles cannot reorient around an ion pair produced within a frozen solvent and, thus, provide little stabilization of the ion pair.[4,5] As a result, the energy level of the ion pair is much higher in the rigid glass than in the liquid. In fact, the ion pair state energy may be so high that it lies above the energy of the excited state, in which case photoinduced electron transfer cannot occur.

We recently reported that the ion-pair states in two porphyrin–triptycene–acceptor molecules are destabilized by as much as 0.9 eV in going from a polar liquid to a rigid glass.[6] To obtain a quantitative picture of the dependence of charge-separation rate on free energy of reaction in the rigid glass, we present electron transfer rate data on 14 porphyrin–triptycene–acceptor molecules, which possess sufficiently large, negative free energies for charge separation to allow electron transfer to compete with excited singlet state decay in glassy 2-methyltetrahydrofuran (MTHF) at 77 K, Figure 1. The compounds in Figure 1 were synthesized by methods described earlier,[6-9] and the details of their preparation will be presented later. Electron transfer rate constants were determined by using picosecond transient absorption and emission techniques along with fluorescence quenching measurements also described earlier.[10]

The free energy of charge separation, ΔG_{cs}, in the rigid glass is given by eq 1,

$$\Delta G_{cs} = \Delta G_{ip} - E_s \tag{1}$$

where ΔG_{ip} is the free energy of the ion pair in the rigid glass and E_s is the energy of the lowest excited singlet state of the porphyrin obtained from its fluorescence spectrum. Since ion-pair recombination in porphyrin–acceptor molecules is nonradiative, the value of ΔG_{cs} in the rigid glass is difficult to obtain. On the other hand, in polar liquids, the free energies of charge separation in these molecules, $\Delta G'_{cs}$, can be estimated by using the one-electron oxidation, E_{ox}, and reduction, E_{red}, potentials of the donor and acceptor, respectively, and the coulomb stabilization of the ion pair:

$$\Delta G'_{cs} = E_{ox} - E_{red} - e_0^2/\epsilon r_{12} - E_s \tag{2}$$

where e_0 is the charge of the electron, ϵ is the static dielectric constant of the high-polarity medium, and r_{12} is the center-to-center distance between the ions. We determined $\Delta G'_{cs}$ for the 14 compounds presented in Figure 2 in butyronitrile at 295 K containing 0.1 M tetra-*n*-butylammonium perchlorate.[11] Since $r_{12} = 11 \pm 1$ Å for these compounds,[12] the Coulombic term is only 0.065 eV and is neglected. Thus, the plot of ln k_{cs} vs $-\Delta G'_{cs}$ in Figure 2 is *based solely on experimentally determined quantities with no corrections applied.* Although the plot of ln k_{cs} vs $-\Delta G'_{cs}$ can be used as a predictive tool, $\Delta G'_{cs}$ obtained from polar solution

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