Structural and Electronic Characterization of Nitrosyl(Octaethylporphinato)iron(III) Perchlorate Derivatives

Mary K. Ellison,[†] Charles E. Schulz,*[,‡] and W. Robert Scheidt*[,†]

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, and Department of Physics, Knox College, Galesburg, Illinois 61401

Received July 17, 2000

The synthesis and crystallographic characterization of the five-coordinate iron(III) porphyrinate complex [Fe(OEP)(NO)]ClO_4 are reported. This {FeNO}^{6} complex has a nearly linear Fe−N−O group (angle = 173.19(13)°) with a small off-axis tilt of the Fe−N(NO) vector from the heme normal (angle = 4.6°); the Fe−N(NO) distance is 1.6528(13) Å and the iron is displaced 0.32 Å out-of-plane. The complex forms a tight cofacial $\pi-\pi$ dimer in the solid state. Mössbauer spectra for this derivative as well as for a related crystalline form are measured both in zero applied magnetic field and in a 7 T applied field. Fits to the measurements made in applied magnetic field demonstrate that both crystalline forms of [Fe(OEP)(NO)]ClO_4 have a diamagnetic ground state at 4.2 K. The observed isomer shifts (δ = 0.22−0.24 mm/s) are smaller than those typically observed for low-spin iron(III) porphyrinates. Analogous Mössbauer measurements are also obtained for a six-coordinate derivative, [Fe(OEP)(Iz)(NO)]ClO_4 (Iz = indazole). The observed isomer shift for this species is smaller still (δ = 0.02 mm/s). All derivatives show a strong temperature dependence of the isomer shift. The data emphasize the strongly covalent nature of the FeNO group. The Mössbauer isomer shifts suggest formal oxidation states greater than +3 for iron, but the NO stretching frequencies are not consistent with such a large charge transfer to NO. Differences in the observed nitrosyl stretching frequencies of the two crystalline forms of [Fe(OEP)(NO)]ClO_4 are discussed.

Introduction

Since the discovery that mammalian cells produce nitric oxide (NO) there has been a resurgence of interest in NO in many areas of chemistry and biology. NO has been found to play an important role in mammalian regulatory functions such as neurotransmission, blood pressure regulation, inhibition of platelet aggregation, and cytotoxic action of macrophages.[1] Many of these mammalian responses result from the interaction of NO with formally iron(II) heme proteins best described as {FeNO}^{7} species using the notation of Enemark and Feltham.[2] More recently, moreover, formally iron(III) nitrosyl {FeNO}^{6} heme proteins (nitrophorins) were discovered in the salivary glands of bloodsucking insects.[3] These nitrophorins can reversibly bind NO to allow both the storage of NO in the bug's salivary glands and the release of NO in host tissues. Surprisingly, unlike {FeNO}^{6} porphyrin model complexes, these nitrophorins resist chemical reduction to the iron(II) form of the heme. However, the structure of the {FeNO}^{6} nitrophorin complex remains elusive owing to reduction of the iron to give an {FeNO}^{7} species upon exposure to radiation during X-ray experiments.[4−6] {FeNO}^{6} hemes are also proposed intermediates in fungal and bacterial denitrification processes. One of the proposed intermediates that catalyzes the reduction of NO to N_2O by cytochrome P450 nitric oxide reductase in the fungus *Fusarium oxysporum* is an {FeNO}^{6} heme.[7] An {FeNO}^{6} heme is also likely involved in the reduction of nitrite to NO by heme cd_1 nitrite reductase in denitrifying bacteria.[8,9]

Until just recently there were only a few structurally characterized {FeNO}^{6} porphyrin complexes. Early examples include the five-coordinate species [Fe(OEP)(NO)]$^+$ and the six-coordinate species [Fe(TPP)(H_2O)(NO)]$^+$.[10,11] Other {FeNO}^{6}

† University of Notre Dame.
‡ Knox College.
* To whom correspondence should be addressed. E-mail Scheidt.1@nd.edu. Fax: (219) 631-4044.

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10.1021/ic000789e CCC: $19.00 © 2000 American Chemical Society
Published on Web 10/10/2000

species that have been structurally characterized are the nitro−nitrosyl derivatives [Fe(Porph)(NO_2)(NO)],[12] the six-coordinate neutral nitrogen-donor species [Fe(OEP)(L)(NO)]$^+$,[13] and [Fe(TPP)(HO-*i*-C_5H_{11})(NO)]$^+$.[14] Even less information is available concerning the electronic structure of {FeNO}^{6} species, and there is some controversy about the best description of the electronic ground states for iron nitrosyl species. An early measurement[10] of the magnetic moment of [Fe(OEP)(NO)]$^+$ yielded a nonzero value for the susceptibility and suggested the need for additional study. Westcott and Enemark[15] have tabulated some of the possible coupling interactions between the two centers; the possibility of coupling d^4 iron centers and NO^- should also be included. Mössbauer data have now been obtained for several nonporphyrinic {FeNO}^{6} species: [Fe(HL)NO]NO_3 and [Fe(R_2Q)NO].[16] The conclusion drawn from the data is that it is difficult to assign a precise description of the ground state because of the highly covalent nature of the FeNO unit. Quite recently, Mössbauer data have been reported for *trans*-[(cyclam)Fe(NO)Cl]$^+$ and its oxidized and reduced products.[17] These authors proposed that, for the {FeNO}^{6} species, the diamagnetic ground state results from the coupling a d^4 iron center and NO^-. As described below, we interpret our newly obtained Mössbauer spectral data for five- and six-coordinate porphyrinic {FeNO}^{6} systems as showing that the FeNO unit is strongly covalent in nature. However, attempts to pinpoint the location of the electrons (i.e., assign formal oxidation states) are complicated by inconsistencies between Mössbauer results and the changes in ν(NO).

The work in this study began with the preparation of five- and six-coordinate {FeNO}^{6} porphyrinates for characterization by Mössbauer spectroscopy in applied magnetic fields. Unexpectedly, our preparation of the five-coordinate derivative [Fe(OEP)(NO)]ClO_4 led to a new crystalline phase which differed from the original known phase in solvent content. The solid-state nitrosyl infrared stretching frequencies of the two crystalline forms differ by 30 cm^{-1}. Electrochemical and chemical oxidation of [Fe(Porph)(NO)] to five-coordinate [Fe(Porph)(NO)]$^+$ has been followed by IR and UV−vis spectroelectrochemical studies.[18−20] A range of nitrosyl stretching frequencies for the OEP derivatives (1830−1868 cm^{-1}) was observed, depending on the solvent used to prepare the samples and the media in which the frequencies are measured. Nitrosyl infrared stretching frequencies are expected to be quite sensitive to the nitrosyl environment and electronic structure at iron. We thought that an understanding of the origin of the differing IR stretches for the two forms could prove insightful in understanding the trends in stretching frequencies for the naturally occurring heme proteins.

This work compares the structures and electronic properties of the two crystalline forms of the five-coordinate {FeNO}^{6} complex. The structure of the new crystalline form, [Fe(OEP)(NO)]ClO_4, differs from that of the previously reported form, [Fe(OEP)(NO)]ClO_4·$CHCl_3$,[10] primarily in the solvent content and the arrangement of the molecules in the cell. Both forms have similar structural features, which is expected for {FeNO}^{6} species. The unit cells of both crystalline forms contain tightly interacting molecules that form $\pi-\pi$ dimers. Although the overlap patterns of the dimers are distinctly different in the crystalline forms, the separation parameters between molecules are essentially the same. The solid-state Mössbauer parameters of the two crystalline forms of [Fe(OEP)(NO)]$^+$ are also presented and compared with those of the six-coordinate species [Fe(OEP)(Iz)(NO)]ClO_4 (Iz = indazole (benzopyrazole)).

Experimental Section

General Information. All manipulations involving the addition of NO were carried out in an oxygen- and water-free environment using a double-manifold vacuum line, Schlenkware, and cannula techniques. Methylene chloride was distilled over CaH_2, hexanes were distilled over sodium benzophenone, and NO gas was purified by passing it through 4 Å molecular sieves immersed in a dry ice/ethanol slush bath to remove higher oxides of nitrogen.[21] All other chemicals were used as received from Aldrich or Fisher. IR spectra were recorded on a Perkin-Elmer 883 IR spectrophotometer for samples in Nujol mulls or KBr pellets; electronic spectra were recorded on a Perkin-Elmer Lambda 19 UV−vis/near-IR spectrometer. The solid-state Mössbauer samples were immobilized in Apiezon grease. Mössbauer measurements were performed on a constant-acceleration spectrometer from 4.2 to 293 K with optional zero field and in a 7 T superconducting magnet system (Knox College). The free base H_2OEP was purchased from Midcentury Chemicals. The chloro- and perchloratoiron(III) derivatives were synthesized by modified literature methods.[22,23] *Caution*! Although we have experienced no problems with the procedures described in dealing with systems containing perchlorate ion, these materials can detonate spontaneously and should be handled only in small quantities; in no case, should such a system be heated above 30 °C, and other safety precautions are also warranted.[24]

Preparation of [Fe(OEP)(NO)]ClO_4. The complex was prepared by a method similar to that of Scheidt et al.[10] To 20 mg (0.028 mmol) of [Fe(OEP)$OClO_3$] was added ∼3 mL CH_2Cl_2. NO gas was bubbled into the solution for several minutes. A dramatic color change from brownish-red to purple/pink occurred. A 1:1 mixture of hexanes and CH_2Cl_2 was used as the nonsolvent in the vapor diffusion experiment under an NO atmosphere to obtain X-ray-quality crystals. Bulk powder samples for Mössbauer measurements were obtained by adding hexanes under an NO atmosphere to a CH_2Cl_2 solution of the compound. The compound slowly effloresces NO in the solid state to give the starting perchlorate compound, and it immediately loses NO in solution if an NO atmosphere is not present. The iron(III) complex, in the presence of excess NO, is easily reduced (by reductive nitrosylation) if a trace amount of ethanol is present. IR (Nujol, KBr): ν(NO) = 1838 cm^{-1}. UV−vis/near-IR (CH_2Cl_2): 359, 410 (sh), 557 nm. X-ray-quality crystals of [Fe(OEP)(NO)]ClO_4·$CHCl_3$, the crystalline form previously isolated by Scheidt et al.,[10] can also be obtained by using ethanol-free $CHCl_3$ instead of CH_2Cl_2. Bulk powder samples were prepared by adding hexanes under an NO atmosphere to an ethanol-free $CHCl_3$ solution of the compound. Similarly, bulk powder samples of [Fe(OEP)(Iz)(NO)]ClO_4 for Mössbauer spectroscopy were prepared by adding NO-saturated hexanes to a solution of [Fe(OEP)$OClO_3$] (120 mg, 0.17 mmol) and indazole (benzopyrazole) (160 mg, 1.35 mmol) in 15 mL

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Table 1. Crystallographic Details for $[Fe(OEP)(NO)]ClO_4$

empirical formula	$C_{36}H_{44}ClFeN_5O_5$
fw	718.06
a, Å	13.7877(16)
b, Å	15.3611(11)
c, Å	16.8511(7)
β, deg	106.241(6)
V, Å^3	3426.5(5)
Z	4
space group	$P2_1/n$
D_c, g/cm^3	1.392
F(000)	1512
μ, mm^{-1}	0.568
crystal dimens, mm	0.53 × 0.53 × 0.25
abs corr	DIFABS
λ, Å	0.71073
T, K	130(2)
no. of total data collcd	73 545
no. of unique data	24 570 (R_{int} = 0.086)
no. of unique obsd data [$I > 2\sigma(I)$]	14 979
refinement method	on F^2 (SHELXL)
final *R* indices for $I > 2\ \sigma(I)$	$R1 = 0.0651$, $wR2 = 0.1669$
final *R* indices for all data	$R1 = 0.1111$, $wR2 = 0.2032$

of CH_2Cl_2. IR (Nujol): ν(NO) = 1914 cm^{-1}. UV−vis (CH_2Cl_2): 408, 524, 556 nm. Structural data for $[Fe(OEP)(Iz)(NO)]ClO_4$ have been reported previously.[13]

X-ray Structure Determination. The structure determination was carried out on a Nonius FAST area-detector diffractometer with a Mo rotating-anode source ($\bar{\lambda}$ = 0.710 73 Å). Our detailed methods and procedures for small-molecule X-ray data collection with the FAST system have been described previously.[25] Data collection was performed at 130(2) K. The crystal diffracted to a very high scattering angle (2θ = 90° with Mo radiation). Data collections were performed at two detector θ angles with requisite adjustments in X-ray power. A scale factor was applied to the low-angle data to account for the difference in the applied power.

A dark purple crystal of $[Fe(OEP)(NO)]ClO_4$ (0.53 × 0.53 × 0.25 mm^3) was used for the structure determination. The structure was solved using the direct methods program SHELXS-86;[26] subsequent difference Fourier syntheses led to the location of the remaining atoms. The structure was refined against F^2 with the program SHELXL,[27,28] in which all data collected were used, including negative intensities. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were idealized with the standard SHELXL idealization methods. A modified[29,30] version of the absorption correction program DIFABS was applied. Brief crystal data for $[Fe(OEP)(NO)]ClO_4$ are listed in Table 1. Complete crystallographic details, atomic coordinates, thermal parameters, and fixed hydrogen atom coordinates are included in the Supporting Information.

Results

Figure 1 is an ORTEP diagram of $[Fe(OEP)(NO)]ClO_4$ illustrating the Fe−N−O group and the relationship between the cation and anion in the cell. The labeling scheme depicted is that used in all of the diagrams and tables. Values of selected bond distances and angles for $[Fe(OEP)(NO)]ClO_4$ are listed in Table 2. Complete listings of bond lengths and angles are given in the Supporting Information. Averaged values for the different types of bonds in the porphyrin core are given in Figure 2. Also displayed in this diagram are the perpendicular displacements of the atoms from the mean plane of the 24-atom porphyrin core in units of 0.01 Å. There is a very small ruffling of the porphyrin core as well as a very slight reverse doming. The deviations from planarity, however, are not large.

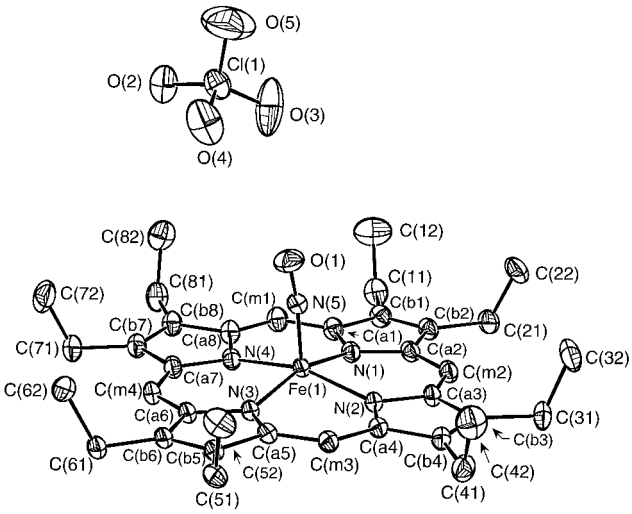

Figure 1. ORTEP diagram of $[Fe(OEP)(NO)]ClO_4$. The closest perchlorate anion is shown. Thermal ellipsoids are contoured at the 50% probability level. The labeling scheme is also shown.

Table 2. Selected Comparisons for $[Fe(OEP)(NO)]^+$ Derivatives

	$[Fe(OEP)(NO)]ClO_4{\cdot}CHCl_3$ [10]	$[Fe(OEP)(NO)]ClO_4$
	IR Data	
ν (NO)[a]	1868	1838
	Coordination Group Distances and Angles	
Fe−N_{NO} [b]	1.644(3)	1.6528(13)
N−O[b]	1.112(4)	1.140(2)
Fe−N_P [b]	1.994(1)	1.994(5)
Fe−N−O[c]	176.9(3)	173.19(13)
ΔFe[b,d]	0.29	0.32
tilt[c]	0.6	4.6
	Intermolecular Distances	
Fe···Fe[b]	4.24	4.26
MPS[b,e]	3.36	3.41
Ct···Ct[b,f]	3.65	3.65
LS[b,g]	1.43	1.32

[a] Nujol or KBr (cm^{-1}). [b] Values in angstroms. [c] Values in degrees. [d] Displacement from the 24-atom mean porphyrin plane. [e] Mean separation between the two planes. [f] Distance between two porphyrin centers. [g] Lateral shift.

The average Fe−N_P bond length for $[Fe(OEP)(NO)]ClO_4$ is 1.994(5) Å. The Fe−N_{NO} bond length is quite short at 1.6528(13) Å. The Fe−N−O angle is 173.19(13)°. The average N_{NO}···N_P nonbonded distance is 2.79(8) Å; the range is 2.71−2.88 Å. The iron is displaced out of the plane toward NO by 0.32 Å. The Fe−N−O group is tilted off the normal to the mean porphyrin plane by 4.6°.

Parts A and B of Figure 3 show how two $[Fe(OEP)(NO)]^+$ cations interact in pairs to form cofacial $\pi-\pi$ dimers in the solid state. On the top left is a view of the $[Fe(OEP)(NO)]^+$ cations perpendicular to the porphyrin mean planes. The top right shows the pair of $[Fe(OEP)(NO)]^+$ cations rotated 90° from the view on the left. The two molecules are related by an inversion center, and so the two porphyrinato planes are precisely parallel. The separation between the porphyrin planes is 3.41 Å. Other separation parameters are given in Table 2.

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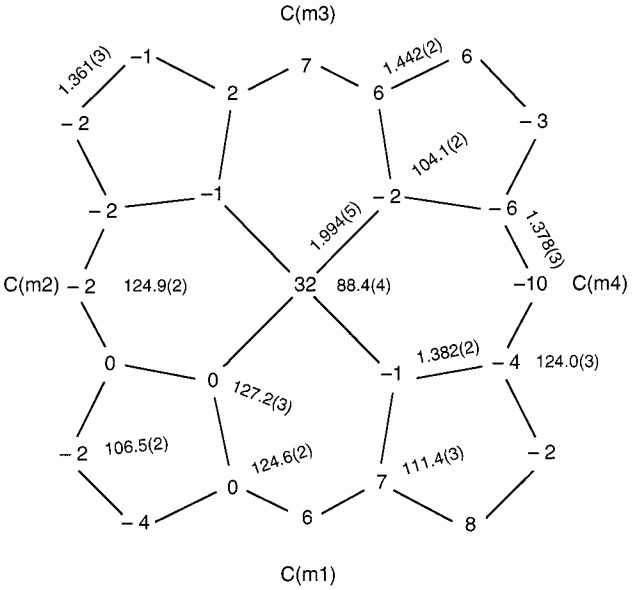

Figure 2. Formal diagram of the porphinato core of [Fe(OEP)(NO)]ClO_4 illustrating the labeling scheme and the displacement of each unique atom from the mean plane of the 24-atom porphinato core (in units of 0.01 Å). Also displayed are the averaged values of each type of bond distance and angle in the porphinato core.

This $\{FeNO\}^6$ species was also characterized by IR and Mössbauer spectroscopies. The nitrosyl stretching frequency appears at 1838 cm^{-1} in the solid state (Table 3). Mössbauer data confirm the low-spin-state assignment for this species, and on the basis of the agreement of the fit to data collected in an applied field, a diamagnetic ground state is assigned. Mössbauer spectra were also obtained in zero field and in an applied field for [Fe(OEP)(NO)]ClO_4·$CHCl_3$ and [Fe(OEP)(Iz)(NO)]ClO_4. The Mössbauer parameters are given in Table 4 and Figures 4 and 5.

Discussion

The molecular structure of the $\{FeNO\}^6$ complex [Fe(OEP)(NO)]ClO_4 has been determined. This new five-coordinate crystalline complex was initially isolated in attempts to crystallize six-coordinate $\{FeNO\}^6$ species $[Fe(Porph)(L)(NO)]^+$. Subsequently, this new unsolvated crystalline species, [Fe(OEP)(NO)]ClO_4, was obtained by the straightforward synthesis described in the Experimental Section. Although the molecular structure of a solvated form of [Fe(OEP)(NO)]ClO_4 had been previously determined, an initial IR spectrum showed that our new crystalline form had a nitrosyl stretching frequency significantly different from that reported earlier for the solvated form [Fe(OEP)(NO)]ClO_4·$CHCl_3$[10] even though both have the same molecular formula; therefore, we wished to characterize the new form in detail. Since nitrosyl stretching frequencies are an important spectroscopic probe of nitric oxide complexes and heme proteins containing NO, we thought that further investigation of the origin of the NO stretching frequency shift was merited. An investigation of this question clearly requires a detailed knowledge of the molecular structure and a knowledge of the intermolecular interactions. Since the details of the electronic structure of $\{FeNO\}^6$ species have not been thoroughly investigated and are not well understood, we also carried out Mössbauer spectroscopic measurements to define the ground state of [Fe(OEP)(NO)]ClO_4; the measurements were performed in the presence and absence of an applied magnetic field. All measurements are consistent with the assignment of a diamagnetic ground state to [Fe(OEP)(NO)]ClO_4 and will be discussed subsequently.

[Fe(OEP)(NO)]ClO_4 is a low-spin $\{FeNO\}^6$ species, as denoted by Enemark and Feltham.[2] In this $\{FeNO\}^6$ model, the iron is considered to be most similar to a d^5 ion, and thus the geometric parameters at iron should be similar to those of other low-spin iron(III) porphyrinates. The average $Fe-N_P$ bond length for [Fe(OEP)(NO)]ClO_4 is 1.994(5) Å, which is consistent with the low-spin-state assignment for this species.[31] The iron is displaced out of the 24-atom mean porphyrin plane toward NO by 0.32 Å. This displacement is slightly larger than one might predict for a low-spin, five-coordinate iron(III) complex. However, the iron may be displaced farther from the porphyrin plane to alleviate nonbonded repulsions between the nitrogen atom of the nitrosyl ligand and atoms of the core that result from the very short $Fe-N_{NO}$ bond length of 1.6528(13) Å. The average $N_{NO}\cdots N_P$ nonbonded distance is 2.79(8) Å; the range is 2.71−2.88 Å. This nonbonded interaction is nearly the same as that seen in five-coordinate $\{FeNO\}^7$ species that have an average $N_{NO}\cdots N_P$ distance of 2.82 Å.[32] Six-coordinate $\{FeNO\}^6$ species have an even closer average $N_{NO}\cdots N_P$ nonbonded distance of 2.63 Å, which results from similar $Fe-N_{NO}$ bond lengths with an in-plane iron atom.[13] Another consequence of the short $Fe-N_{NO}$ bond length is small porphyrin nitrogen atom displacements from the nitrosyl ligand, as seen in Figure 2. These nitrogen atom displacements lead to a small reverse doming; a modest core ruffling is also superimposed.

There are only a few previously structurally characterized five-coordinate, low-spin iron(III) complexes. These derivatives all share common characteristics, which include small iron atom displacements from the mean porphyrin plane and short $Fe-N_P$ bond lengths. The previously structurally characterized examples include σ-bonded phenyl,[33] alkyl,[34] and acyl[34] derivatives. The range of $Fe-N_P$ distances in these complexes is 1.961(7)−1.974(13) Å, and the iron atom out-of-plane displacements range from 0.15 to 0.22 Å. The $Fe-N_P$ bond length of 1.994(5) Å in [Fe(OEP)(NO)]ClO_4 is longer than the $Fe-N_P$ bond length of the σ-bonded carbon derivatives owing to a combination of the larger displacement of the iron atom and essentially planar porphyrin cores. The cores of the σ-bonded carbon derivatives are quite ruffled, leading to shorter $Fe-N_P$ bond lengths.

The $Fe-N_P$ bond length of 1.994(5) Å in [Fe(OEP)(NO)]ClO_4 is identical to those found in six-coordinate $\{FeNO\}^6$ porphyrin complexes with a neutral sixth ligand trans to the nitrosyl, where the range is 1.995(8)−2.004(4) Å,[10,13] and with nitrite trans to the nitrosyl, as in [Fe(TpivPP)(NO_2)(NO)], where $Fe-N_P$ is 1.996(4) Å.[12]

The axial $Fe-N_{NO}$ bond length of 1.6528(13) Å in [Fe(OEP)(NO)]ClO_4 is substantially shorter than the Fe−C axial bond lengths in the σ-bonded carbon derivatives mentioned above, which range from 1.955(3) to 1.979(9) Å. These very short distances in the nitrosyl complex again lead to a larger out-of-plane displacement of the iron atom, which helps to alleviate the close contact between the nitrogen atom of the nitrosyl ligand and the nitrogen atoms of the porphyrin core. Surprisingly, the $Fe-N_{NO}$ bond length in [Fe(OEP)(NO)]ClO_4 is at the high end of the range of those found in the six-coordinate $\{FeNO\}^6$

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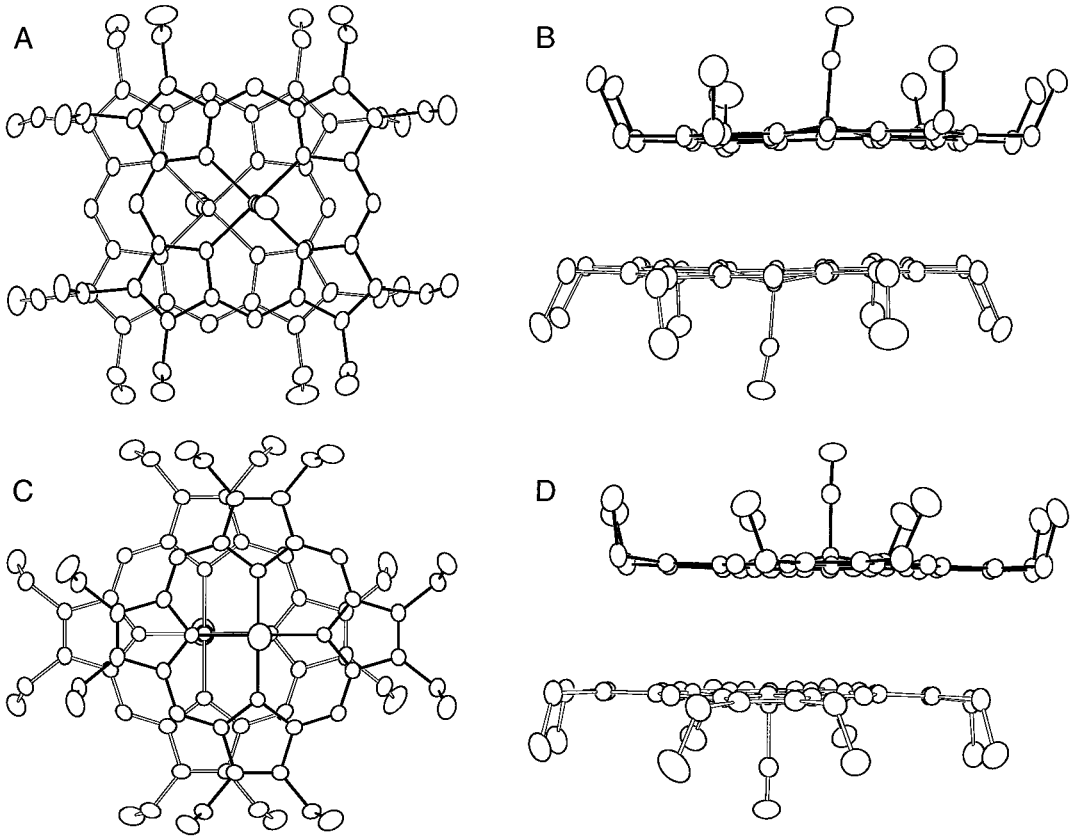

Figure 3. ORTEP diagrams of the two closely interacting cations in [Fe(OEP)(NO)]ClO_4: (A) view perpendicular to the mean porphyrin plane and (B) view parallel to the mean porphyrin plane. ORTEP diagrams of the two closely interacting cations of the solvated form [Fe(OEP)(NO)]-ClO_4·$CHCl_3$: (C) view perpendicular to the mean porphyrin plane and (D) view parallel to the mean porphyrin plane. The differences in the bendings and tiltings of the nitrosyl groups are readily seen in views B and D.

Table 3. Nitrosyl Stretching Frequencies for Five-Coordinate $\{FeNO\}^6$ Complexes

complex	state	ν(NO), cm^{-1}	medium	ref
$[Fe(OEP)(NO)]^+$ [a]	soln	1853	CH_2Cl_2	18
$[Fe(OEP)(NO)]^+$ [b]	soln	1854	CH_2Cl_2	19
$[Fe(OEP)(NO)]^+$ [c]	powder	1830	Nujol	20
[Fe(OEP)(NO)]ClO_4·$CHCl_3$ [d]	crystal	1862	KBr	10
[Fe(OEP)(NO)]ClO_4·$CHCl_3$ [d]	crystal	1868	Nujol, KBr	this work
[Fe(OEP)(NO)]ClO_4 [e]	crystal	1838	Nujol, KBr	this work
[Fe(OEP)(NO)]ClO_4 [f]	crystal	1852	Nujol	this work

[a] Prepared by chemical oxidation in CH_2Cl_2. [b] Prepared by electrooxidation in situ. [c] Prepared by electrooxidation in CH_2Cl_2 followed by solvent removal. [d] Prepared in $CHCl_3$ solution. [e] Prepared in CH_2Cl_2 solution; unsolvated. [f] Prepared in C_6H_5Cl solution.

species $[Fe(Porph)(L)(NO)]^+$ (1.627(2)−1.652(5) Å). However, the Fe−N_{NO} bond length in [Fe(TpivPP)(NO_2)(NO)] is longer at 1.671(2) Å. This small increase is likely due to the presence of the trans π-accepting ligand NO_2^-.

As expected for an $\{FeNO\}^6$ species, the Fe−N−O group in [Fe(OEP)(NO)]ClO_4 is nearly linear, with an angle of 173.19-(13)°. The Fe−N−O angle in [Fe(OEP)(NO)]ClO_4 is at the more bent end of the range of angles for other $\{FeNO\}^6$ porphyrin complexes (169.3(2)−177.6(3)°). The most bent is that of [Fe-(TpivPP)(NO_2)(NO)]. A near-linear nitrosyl group (176.9(3)°) is also seen in the previously characterized solvated form, [Fe-(OEP)(NO)]ClO_4·$CHCl_3$.[10] In fact, most of the coordination group parameters of the two five-coordinate nitrosyl complexes are, not surprisingly, quite similar; these are summarized in Table 2. Also given in Table 2 is the degree to which the Fe−N−O group is tilted from the heme normal in both species. The nitrosyl group in [Fe(OEP)(NO)]ClO_4 is tilted from the heme normal in the direction of the slight Fe−N−O bend by 4.6°. There is virtually no tilt (0.6°) observed in the previously characterized species, [Fe(OEP)(NO)]ClO_4·$CHCl_3$. This can be seen most clearly in the two diagrams on the right-hand side of Figure 3.

Also tabulated in Table 2 are selected distances describing the cofacial $\pi-\pi$ dimers formed by both derivatives in the crystalline state. In both species, the two cations are related by an inversion center and thus the porphyrin planes are precisely parallel. Figure 3 shows the relationship between the two interacting molecules in [Fe(OEP)(NO)]ClO_4 (top) and [Fe-(OEP)(NO)]ClO_4·$CHCl_3$ (bottom). In both species, the molecules form quite close cofacial dimers (Table 2). The mean-plane separations are 3.41 Å for [Fe(OEP)(NO)]ClO_4 and 3.36 Å for [Fe(OEP)(NO)]ClO_4·$CHCl_3$. The distances between the two metal centers and the Ct···Ct distances are also equivalent. Thus, all parameters that describe distances between the two molecules are nearly the same. However, the manners in which the two molecules overlap are quite different, as can be seen from the top view of the molecules on the left-hand side of Figure 3. In [Fe(OEP)(NO)]ClO_4, a pair of α carbons overlay a pair of nitrogen atoms. The two molecules are slipped by 1.32 Å at 45° from an Fe−N_P bond. In [Fe(OEP)(NO)]ClO_4·$CHCl_3$, the molecules are slipped by 1.43 Å *along* a pair of Fe−N_P bonds to put the iron atom nearly over a nitrogen atom of the other porphyrin ring.

The immediate nitrosyl environments are also different in the two five-coordinate complexes. In [Fe(OEP)(NO)]ClO_4, there is no solvent molecule present in the cell whereas, in [Fe(OEP)-(NO)]ClO_4·$CHCl_3$, there is a molecule of chloroform. As can

Table 4. Solid-State Mössbauer Parameters for Nitrosyl and Related Derivatives in Zero Applied Field

complex	ΔE_q, mm/s	δ_{Fe}, mm/s	T, K	ref
	{FeNO}^{6} Complexes			
[Fe(OEP)(NO)]ClO_4·$CHCl_3$	1.63	0.12	293	this work
	1.65	0.20	4.2	this work
[Fe(OEP)(NO)]ClO_4	1.55	0.13	293	this work
	1.64	0.20	4.2	this work
[Fe(OEP)(Iz)(NO)]ClO_4	1.99	−0.07	293	this work
	1.92	0.02	4.2	this work
[Fe(TPP)(NO_2)(NO)]	1.37	0.02	293	12
	1.36	0.13	4.2	12
	1.36	0.13	77	41
[Fe(T-*p*-OCH_3PP)(NO_2)(NO)]	1.43	0.04	293	12
[Fe(TpivPP)(NO_2)(NO)]	1.48	0.01	293	12
	1.43	0.09	4.2	12
[Fe(OE-corrole)(NO)]	1.81	0.01	*a*	42
[Fe(OE-corrole)(NO)]$FeCl_4$	1.98	0.00	*a*	42
[Fe(HL)NO]NO_3	1.18	0.24	300	16
	1.18	0.30	80	16
[Fe(CH_3)$_2$Q)NO]	1.64	0.16	300	16
	1.67	0.23	80	16
trans-[(cyclam)Fe(NO)Cl]$^{2+}$	2.04	0.04	4.2	17
[L′Fe(NO)(ONO)(NO_2)]$^+$	1.37	0.03	4.2	17
	Iron(IV) Complexes			
[Fe(TPP)(O)(1-MeIm)]^b	1.26	0.11	4.2	43
[Fe(TPP)(O)(Py)]^b	1.56	0.10	4.2	43
{[Fe(TPP)]$_2$N}$^+$	2.04	−0.13	293	44
	Iron(II) CO Complexes			
[Fe(TPP)(1-MeIm)(CO)]	0.35	0.20	293	45
[Fe(TPP)(Py)(CO)]	0.57	0.28	293	45
	Iron(III) Cyanide Complexes			
[Fe(OEP)(*t*-BuNC)$_2$]$^+$	1.67	0.08	300	46
	1.98	0.16	120	46
	2.06	0.18	4.2	46
[Fe(TPP)(*t*-BuNC)$_2$]$^+$	2.12	0.13	120	46
MbCN	1.46	0.16	4.2	47
CCPCN	1.60	0.21	4.2	47
	Iron(III) Complexes (⊥ Ligand Orientation)			
[Fe(TMP)(2-MeHIm)$_2$]$^+$	1.48	0.20	77	48
[Fe(TMP)(3-EtPy)$_2$]$^+$	1.25	0.18	77	48
[Fe(TMP)(3-ClPy)$_2$]$^+$	1.36	0.20	77	48
[Fe(TMP)(4-NMe_2Py)$_2$]$^+$	1.75	0.18	4.2	49
[Fe(TMP)(1,2-Me_2Im)$_2$]$^+$	1.25	0.14	250	50
	1.26	0.17	120	50
[Fe(TPP)(4-CNPy)$_2$]$^+$	0.65	0.19	120	51
[Fe(TPP)(Py)$_2$]$^+$	1.25	0.16	77	52
[Fe(TPP)(2-MeHIm)$_2$]$^+$	1.77	0.22	150	53
	Iron(III) Complexes (∥ Ligand Orientation)			
[Fe(TMP)(1-MeIm)$_2$]$^+$	2.31	0.28	4.2	49
[Fe(OEP)(4-NMe_2Py)$_2$]$^+$	2.15	0.26	4.2	49
[Fe(T-*p*-OCH_3PP)(HIm)$_2$]$^+$	2.06	0.17	298	54
[Fe(T-*p*-ClPP)(HIm)$_2$]$^+$	2.01	0.15	298	54
	{FeNO}^{7} Complexes			
[Fe(TpivPP)(NO_2)(NO)]$^-$ (form 1)	1.78	0.22	200	39
[Fe(TpivPP)(NO_2)(NO)]$^-$ (form 2)	1.20	0.35	4.2	39
[Fe(TPP)(NO)]	1.24	0.35	4.2	39
[Fe(OEP)(NO)]	1.26	0.35	100	40

[a] Temperature not reported; expected temperature 4.2 K. [b] Frozen toluene solutions.

be seen from Figure 1, in [Fe(OEP)(NO)]ClO_4, the nearest perchlorate anion is located almost directly above the nitrosyl ligand. The closest oxygen−oxygen distance in this structure is 3.59 Å (O(1)···O(3)). In [Fe(OEP)(NO)]ClO_4·$CHCl_3$, the closest O···O distance between the perchlorate anion and the nitrosyl oxygen atom is 0.5 Å shorter at 3.09 Å (O(1)···O(3)) and the anion is located farther off to the side, as can be seen in Figure 2 of ref 10.

The closest contacts between the nitrosyl ligand and atoms of nearby molecules were also examined; there are no striking differences. In [Fe(OEP)(NO)]ClO_4, the closest nitrosyl interaction is between the oxygen atom and a hydrogen atom (H(61a)) of an ethyl carbon (C(61)) on an adjacent molecule. The O···H distance is 2.78 Å. In [Fe(OEP)(NO)]ClO_4·$CHCl_3$, the closest contact is between the oxygen atom and a methyl group hydrogen atom (H(72c)) at 2.71 Å. ORTEP diagrams illustrating the closest contacts are given in the Supporting Information (Figures S1 and S2).

A detailed structural study of [Fe(OEP)(NO)]ClO_4 was undertaken to help elucidate the environmental factors that led to the 30 cm^{-1} difference in the nitrosyl stretching frequencies seen in the two five-coordinate nitrosyl species. In fact, there

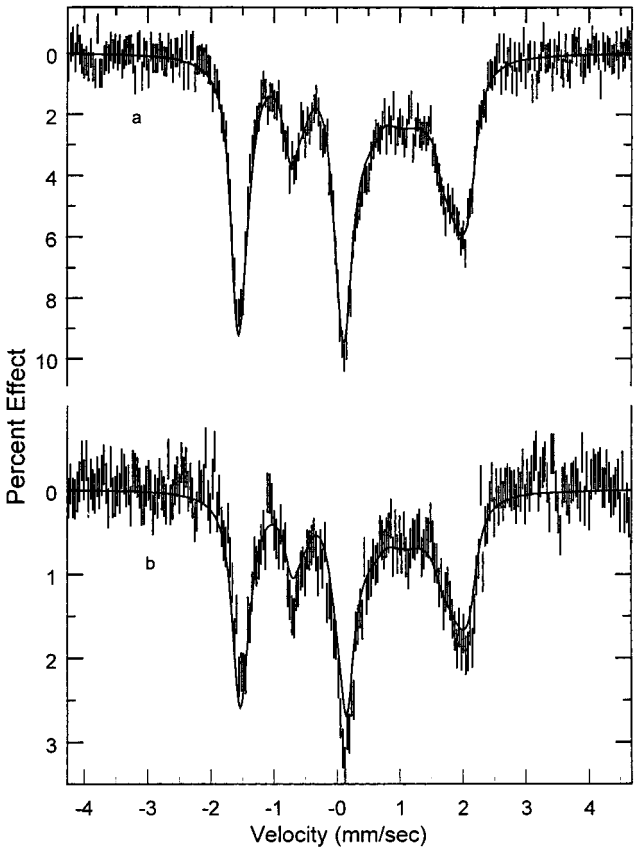

Figure 4. Mössbauer spectra of [Fe(OEP)(NO)]ClO_4 (top) and [Fe(OEP)(NO)]ClO_4·$CHCl_3$ (bottom) recorded at 4.2 K with an applied magnetic field of 7 T parallel to the γ-ray beam. The solid lines are diamagnetic fits to the data, yielding the following parameters. [Fe(OEP)(NO)]ClO_4: quadrupole splitting, $\Delta E_q = 1.64$ mm/s; asymmetry parameter, $\eta = 0.2(4)$; isomer shift, $\delta_{Fe} = 0.22$ mm/s; Lorentzian width, Γ (fwhm) = 0.26 mm/s. [Fe(OEP)(NO)]ClO_4·$CHCl_3$: quadrupole splitting, $\Delta E_q = 1.64$ mm/s; asymmetry parameter, $\eta = 0.0(4)$; isomer shift, $\delta_{Fe} = 0.24$ mm/s; Lorentzian width, Γ (fwhm) = 0.27 mm/s.

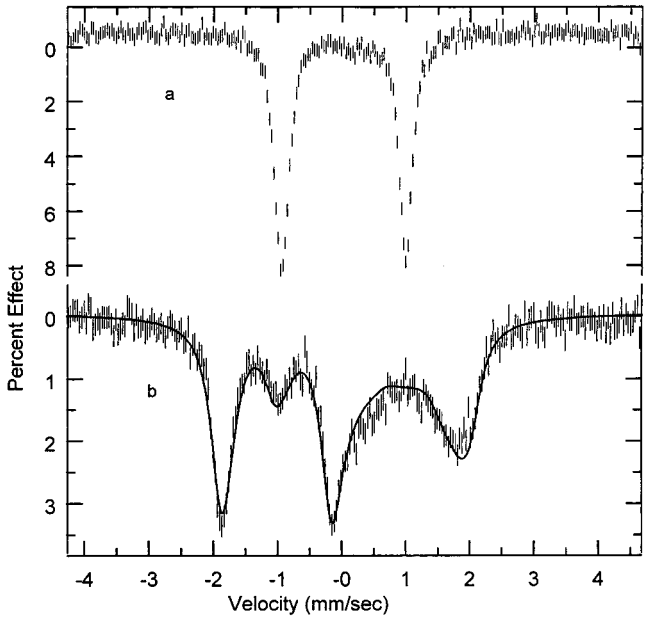

Figure 5. Mössbauer spectra of [Fe(OEP)(Iz)(NO)]ClO_4 recorded at 4.2 K in zero applied field (top) and in an applied magnetic field of 7 T parallel to the γ-ray beam (bottom). The solid line in the bottom figure is a diamagnetic fit to the data, yielding the following parameters: quadrupole splitting, $\Delta E_q = 1.88$ mm/s; asymmetry parameter, $\eta = 0.0$; isomer shift, $\delta_{Fe} = 0.02$ mm/s; Lorentzian width, Γ (fwhm) = 0.38 mm/s.

is a wide range of reported nitrosyl stretching frequencies for [Fe(OEP)(NO)]$^+$ species which depend, inter alia, on the solvent used to prepare the compounds and the medium in which the spectra are recorded. As can be seen from Table 3, when [Fe(OEP)(NO)]$^+$ is prepared by oxidation of [Fe(OEP)(NO)] in CH_2Cl_2 by adding a chemical oxidant[18] and by electrochemical means[19] and the spectra are recorded in CH_2Cl_2, both species exhibit the same ν(NO) values (1853 and 1854 cm^{-1}). When [Fe(OEP)(NO)]$^+$ is electrochemically generated in CH_2Cl_2 but a *solid-state* spectrum is recorded (Nujol mull), ν(NO) shifts to 1830 cm^{-1}.[20] A similar stretching frequency (1838 cm^{-1}) is observed when [Fe(OEP)(NO)]$^+$ is prepared by ligand substitution ([Fe(OEP)$OClO_3$] + NO) *in* CH_2Cl_2 and a solid-state spectrum is recorded for a sample either in Nujol mull or in KBr pellet (this work). When [Fe(OEP)(NO)]$^+$ is prepared by ligand substitution *in* $CHCl_3$, the isolated crystalline form contains a molecule of chloroform in the asymmetric unit and the solid-state NO stretching frequency shifts to 1868 cm^{-1}, recorded for a sample either in a Nujol mull or in a KBr pellet (this work), or to 1862 cm^{-1}, previously recorded for a sample in a KBr pellet.[10] Presumably, a third crystalline form (X-ray-quality crystals not obtained) exists, which is obtained by ligand substitution ([Fe(OEP)$OClO_3$] + NO) in chlorobenzene and exhibits ν(NO) at 1852 cm^{-1} in the solid state. These shifts in ν(NO) must originate in the solid-state structure differences.

We are able to identify a number of features in the two structurally characterized forms of [Fe(OEP)(NO)]$^+$ that are consistent with the observed NO stretching frequency differences. However, we cannot identify a single dominant feature and indeed the identified features may be interrelated. The most obvious difference in the two five-coordinate nitrosyl species that may explain the 30 cm^{-1} difference in ν(NO) is the bending of the nitrosyl group. The Fe−N−O group is more bent in [Fe(OEP)(NO)]ClO_4, at 173.19(13)°, than in [Fe(OEP)(NO)]ClO_4·$CHCl_3$, where the angle is 176.9(3)°. The species with the more bent angle and thus decreased NO bond order, albeit slight, has the lower NO stretching frequency. Another difference seen in the two examples is the degree to which the Fe−N−O group is tilted off the heme normal. In [Fe(OEP)(NO)]ClO_4, the Fe−N−O group is tilted off-axis by 4.6° in the direction of the bend. In [Fe(OEP)(NO)]ClO_4·$CHCl_3$, there is virtually no tilting of the more nearly linear Fe−N−O group. This observation agrees with the findings of Ghosh and Bocian, who have shown that tilting and bending of CO in carbon monoxyheme is strongly coupled.[35] Such tilting/bending has also been observed in all sufficiently characterized five-coordinate {FeNO}^{7} porphyrin species,[32] where it was suggested that the tilting is a consequence of better overlap of the π^* orbital of NO with the metal d_{z^2} orbital. In these {FeNO}^{7} species, tilting is clearly favorable whereas in the {FeNO}^{6} species, where we see groups that are both tilted and not tilted, the energy difference between the two must be quite small.

The energy difference may arise from the different manner in which the two [Fe(OEP)(NO)]$^+$ cations interact in pairs in the two crystalline forms to form $\pi-\pi$ dimers. From Figure 3C, it is seen that, in [Fe(OEP)(NO)]ClO_4·$CHCl_3$, a porphyrinato nitrogen atom is located almost directly above the iron atom of the closest molecule. This interaction could be interpreted as a pseudo-sixth-ligand interaction which may reduce the bending and tilting of the nitrosyl group. In addition, we have seen that

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adding a sixth ligand to an $\{FeNO\}^6$ species increases the nitrosyl stretching frequency (vide infra). It is therefore consistent that ν(NO) for $[Fe(OEP)(NO)]ClO_4 \cdot CHCl_3$ increases to 1868 cm^{-1} from the 1838 cm^{-1} value seen for $[Fe(OEP)(NO)]ClO_4$, where the interaction between the two closest molecules is clearly different. It is also possible that the differences in Fe−N−O geometry in the two crystalline forms may simply be an effect of crystal packing. Finally, electrostatic effects may have an influence on the observed NO frequency. There is a difference in the immediate nitrosyl environments in the two structures. Although the counterion is the same in both complexes, in $[Fe(OEP)(NO)]ClO_4 \cdot CHCl_3$ an oxygen atom of the perchlorate anion is 0.5 Å closer to the nitrosyl oxygen atom. We would thus expect a frequency shift to a higher value, consistent with the effects of more polar solvents that we have observed for other nitrosyl derivatives.[12]

The NO stretching frequencies of both five-coordinate $[Fe(OEP)(NO)]^+$ species are surprisingly lower than those of the six-coordinate $\{FeNO\}^6$ species where the trans ligand is water (1937 cm^{-1}),[10] alcohol (1935 cm^{-1}),[14] or a neutral nitrogen-donor ligand (1890−1921 cm^{-1}).[13] However the nitrosyl stretching frequencies for the five-coordinate species are higher than those reported for the six-coordinate $\{FeNO\}^6$ octaethylporphyrin species where the trans ligand is a σ-bonded alkyl or aryl group (1766−1839 cm^{-1}).[36] The observation of nitrosyl stretches that either increase or decrease upon addition of a sixth ligand is in distinct contrast to what is seen in the $\{FeNO\}^7$ cases. In these systems, ν(NO) uniformly decreases upon addition of any sixth ligand. The common explanation for this effect is that the sixth ligand leads to increased π donation by iron into the π^* orbital of NO. That the $\{FeNO\}^6$ species do not show a uniform direction of shift upon addition of the sixth ligand suggests that the orbital energy matchings of Fe and NO are very different in the $\{FeNO\}^6$ and $\{FeNO\}^7$ systems.

An important question concerning these nitrosyl complexes regards their electronic structures. One significant issue is the ultimate nature of the interaction between the initial d^5 iron(III) center and the $S = 1/2$ nitric oxide ligand upon formation of the nitrosyl complex. We have used Mössbauer spectroscopy to examine this issue, obtaining spectra for both $[Fe(OEP)(NO)]ClO_4$ and $[Fe(OEP)(NO)]ClO_4 \cdot CHCl_3$ in zero applied field at 4.2 K and room temperature and in a 7 T applied magnetic field at 4.2 K (Table 4). The Mössbauer measurements in an applied magnetic field for both species are essentially identical. Both can be well-fitted to a diamagnetic model. The fits to the experimental data (Figure 4) make it evident that both five-coordinate species have diamagnetic ground states. The best fit parameters are $\Delta E_q = 1.64$ mm/s, $\delta = 0.22$ mm/s, $\Gamma = 0.26$ mm/s, and $\eta = 0.2(4)$ for $[Fe(OEP)(NO)]ClO_4$ and $\Delta E_q = 1.64$ mm/s, $\delta = 0.24$ mm/s, $\Gamma = 0.27$ mm/s, and $\eta = 0.0(4)$ for $[Fe(OEP)(NO)]ClO_4 \cdot CHCl_3$.

The isomer shifts for the two complexes display a rather large temperature dependence with $\delta = 0.13$ mm/s at 293 K and 0.20 mm/s at 4.2 K for $[Fe(OEP)(NO)]ClO_4$ and $\delta = 0.12$ mm/s at 293 K and 0.20 mm/s at 4.2 K for $[Fe(OEP)(NO)]ClO_4 \cdot CHCl_3$. Isomer shifts usually provide an indication of the formal oxidation state of the central iron atom when closely related structures are compared.[37,38] The isomer shifts for these two five-coordinate nitrosyls are most similar to those observed for low-spin iron(III) porphyrinate systems of the type $[Fe(Porph)L_2]^+$. The values appear to be slightly smaller than those for most low-spin iron(III) porphyrinates, consistent with strong π donation from iron to NO. This pattern is similar to that observed for the five-coordinate $\{FeNO\}^7$ species that also have isomer shifts[39,40] somewhat smaller than those observed for the analogous low-spin iron(II) derivatives.[37] A similar effect is also seen for CO complexes that have reduced isomer shifts (0.20, 0.28 mm/s)[45] compared to more typical low-spin iron(II) porphyrinates (0.41−0.51 mm/s).[37] Despite the observed diamagnetism at 4.2 K, there are several possible descriptions for the ground state. The first of these formal descriptions is that of a low-spin iron(II) coordinated to neutral NO. A second is that of a low-spin iron(III) center antiferromagnetically coupled to the $S = 1/2$ nitric oxide ligand. Another is an iron(IV) ion ($S = 1$) coupled to an NO^- ligand ($S = 1$). A final, yet less likely, possibility,[55] is an iron(IV) ion ($S = 0$) interacting with NO^- ($S = 0$). As discussed subsequently, each of these descriptions has some deficiencies when all of the physical data are considered. We note that nitric oxide is a noninnocent ligand and that the {FeNO} unit is a highly covalent entity.

The quadrupole splitting constants of 1.64 mm/s for the two forms of $[Fe(OEP)(NO)]ClO_4$ are closer to the splitting values found for bis(planar axial ligand)iron(III) porphyrinates in which the two planar ligands have relative perpendicular orientations than to the splitting constants for similar complexes in which the two planar ligands have relative parallel orientations. For the species with perpendicular ligand orientations, there is a near degeneracy of the d_{xz} and d_{yz} orbitals,[56,57] resulting from the symmetrical interaction of the two ligands with the two d_π

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orbitals. The electronic states are correlated with Mössbauer quadrupole splittings of less than 1.75 mm/s for species with perpendicular orientations and greater than 2.00 mm/s for species with parallel orientations.[49,58] A near degeneracy of the d_{xz} and d_{yz} orbitals would be expected when the iron−NO π interaction is large.

Mössbauer measurements have also been made for a six-coordinate $\{FeNO\}^6$ species, $[Fe(OEP)(L)(NO)]^+$. In our experience, very pure bulk samples of six-coordinate species are difficult to prepare owing to either NO loss/replacement or problems of reductive nitrosylation. We chose to use the indazole derivative $[Fe(OEP)(Iz)(NO)]ClO_4$, as its preparation is least hindered by these difficulties.[59] The Mössbauer spectrum verified the purity of the bulk sample. Fits to the spectrum obtained in an applied magnetic field confirmed that the ground state is diamagnetic (Figure 5 (bottom)). The best fit parameters from the magnetic spectrum are $\Delta E_q = 1.88$ mm/s, $\delta = 0.02$ mm/s, $\Gamma = 0.38$ mm/s, and $\eta = 0.0$ at 4.2 K. Measurements in zero applied field show that the isomer shift has a temperature dependence and decreases to −0.07 mm/s at 293 K.

There is a significant effect on the Mössbauer parameters as a result of coordinating a sixth ligand. Compared to that of the five-coordinate nitrosyl species, the quadrupole splitting of $[Fe(OEP)(Iz)(NO)]ClO_4$ has a larger value of 1.92 mm/s, consistent with an increased energy separation between the d_{xz} and d_{yz} orbitals and a π interaction between the indazole ligand and iron. The already low isomer shift values for the five-coordinate $\{FeNO\}^6$ species are seen to be lower still for the six-coordinate species. Indeed, the isomer shift values of 0.02 mm/s at 4.2 K and −0.07 mm/s at 293 K are those typically expected for iron(IV) porphyrin derivatives.[37] From the Mössbauer data alone, the ground-state diamagnetism in this case may be best described as coupling between an iron(IV) ion ($S = 1$) and an NO^- ligand ($S = 1$). However, this description is less satisfactory when all of the experimental data are considered (vide infra).

The quadrupole splitting and isomer shift values for these $\{FeNO\}^6$ species and the previously reported nitro−nitrosyl complexes $[Fe(Porph)(NO_2)(NO)]$ are listed in Table 4, along with values for a number of additional iron porphyrinates. The nitro−nitrosyl complexes are also seen to have unusually small isomer shift values for iron that also display a strong temperature dependence. A straightforward analysis of the isomer shifts is that the addition of NO to a formally iron(III) porphyrinate increases the apparent formal charge on iron and NO, being an extremely good π-accepting ligand, accepts electron density. The high formal charge emphasizes the strongly covalent nature of the $\{FeNO\}^6$ entity. The addition of the sixth ligand to five-coordinate $\{FeNO\}^6$ complexes tends to increase the formal charge on iron even further, whether the sixth ligand is a neutral nitrogen donor or a nitrite anion. With this "transfer" of electron density, one would expect a decrease in the nitrosyl stretching frequency as the π^* orbitals of NO become more populated. However, this is not what is observed. The nitrosyl stretching frequencies in fact *increase* by more than 60 cm^{-1} [13] and indeed are higher than that seen for neutral NO. An apparent increase in the formal charge of $[Fe(Porph)(NO_2)(NO)]$ species compared to the five-coordinate parent species $[Fe(OEP)(NO)]^+$ is consistent with modest π-accepting character for the nitrite ligand. The effects of the neutral sixth ligand on the isomer shift of $[Fe(OEP)(Iz)(NO)]ClO_4$ are somewhat more unexpected. The π interaction between indazole and iron must be less important than that between iron and nitrite. Hence, we could expect that the formal charge on iron would be lower than that in the nitro−nitrosyl species, leading to a somewhat larger isomer shift. Yet the isomer shift trend is opposite to this expectation, with the indazole derivative having the smallest isomer shift of any of the $\{FeNO\}^6$ species *and* the highest nitrosyl stretching frequency. Clearly, these two indicators of charge distribution are inconsistent and a definitive assignment of electronic ground states for these species cannot be made without further study. Investigations of other $\{FeNO\}^6$ species to understand the interaction of NO with iron and the effects of Mössbauer isomer shifts are in progress. We can only reiterate that nitric oxide is a noninnocent ligand and that the {FeNO} unit is a highly covalent entity. The assignment of a formal oxidation state to iron is accordingly unlikely to be completely satisfactory.

Summary. The five-coordinate species $[Fe(OEP)(NO)]ClO_4$ has been characterized by X-ray crystallography and IR and Mössbauer spectroscopies. The structural study reveals subtle differences between this new form and the previously reported species with the same molecular formula[10] that may be responsible for the surprising 30 cm^{-1} difference in the nitrosyl stretching frequencies. Mössbauer studies confirm a diamagnetic ground state for both crystalline forms of $[Fe(OEP)(NO)]ClO_4$ and the related six-coordinate complex $[Fe(OEP)(Iz)(NO)]ClO_4$. The three $\{FeNO\}^6$ species studied reveal unusual quadrupole splitting and isomer shift parameters compared to the typical iron(III) porphyrinates.

Note Added in Proof. A recent contribution reports Mössbauer spectra for a mixture of $[Fe(OEP)(1\text{-MeIm})(NO)]^+$ and $[Fe(OEP)(1\text{-MeIm})_2]^+$ in dimethylacetamide solution at 4.2 K.[60] The best fit parameters for the nitrosyl complex are $\Delta E_q = 1.64$ mm/s and $\delta_{Fe} = 0.02$ mm/s. Our data support the assignment of these Mössbauer parameters to a six-coordinate $\{FeNO\}^6$ species.

Acknowledgment. We thank the National Institutes of Health for support of this research under Grant GM-38401 to W.R.S. Funds for the purchase of the FAST area detector diffractometer were provided through NIH Grant RR-06709 to the University of Notre Dame. We thank Prof. W. R. Monfort for a preprint of reference 6.

Supporting Information Available: Tables S1−S6, giving complete crystallographic details, atomic coordinates with U(eq) values, bond distances and angles, anisotropic temperature factors, and fixed hydrogen atom positions with U(eq) values for $[Fe(OEP)(NO)]ClO_4$, Figures S1 and S2, showing the closest intermolecular interactions involving the nitrosyl ligands $[Fe(OEP)(NO)]ClO_4$ and $[Fe(OEP)(NO)]ClO_4 \cdot CHCl_3$, respectively, Figure S3, showing the Mössbauer spectra of $[Fe(OEP)(NO)]ClO_4$ and $[Fe(OEP)(NO)]ClO_4 \cdot CHCl_3$ at 4.2 K in zero applied field, and an X-ray crystallographic file, in CIF format, for $[Fe(OEP)(NO)]ClO_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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