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Nitrosyliron(III) Porphyrinates: Porphyrin Core Conformation and FeNO Geometry. Any Correlation?

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Abstract: The synthesis, structural, and spectroscopic characterization of (nitrosyl)iron(III) porphyrinate complexes designed to have strongly nonplanar porphyrin core conformations is reported. The species have a nitrogen-donor axial ligand trans to the nitrosyl ligand and display planar as well as highly nonplanar porphyrin core conformations. The systems were designed to test the idea, expressly discussed for the heme protein nitrophorin (Roberts, et al. *Biochemistry* **2001**, *40*, 11327), that porphyrin core distortions could lead to an unexpected, bent geometry for the FeNO group. For $[Fe(OETPP)(1\text{-}MeIm)(NO)]ClO_4{\cdot}C_6H_5Cl$ (H_2OETPP = octaethyltetraphenylporphyrin), the porphyrin core is found to be severely saddled. However, this distortion has little or no effect on the geometric parameters of the coordination group: $Fe{-}N_p$ = 1.990(9) Å, Fe−N(NO) = 1.650(2) Å, Fe−N(L) = 1.983(2) Å, and Fe−N−O = 177.0(3)°. For the complex $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4{\cdot}0.5CH_2Cl_2$ (H_2OEP = octaethylporphyrin), there are two independent molecules in the asymmetric unit. The cation denoted $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**) has a close-to-planar porphyrin core. For this cation, $Fe{-}N_p$ = 2.014(8) Å, Fe−N(NO) = 1.649(2) Å, Fe−N(L) = 2.053(2) Å, and Fe−N−O = 175.6(2)°. The second cation, $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**), has a ruffled core: $Fe{-}N_p$ = 2.003(7) Å, Fe−N(NO) = 1.648(2) Å, Fe−N(L) = 2.032(2) Å, and Fe−N−O = 177.4(2)°. Thus, there is no effect on the coordination group geometry caused by either type of nonplanar core deformation; it is unlikely that a protein engendered core deformation would cause FeNO bending either. The solid-state nitrosyl stretching frequencies of 1917 cm^{-1} for $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4$ and 1871 cm^{-1} for $[Fe(OETPP)(1\text{-}MeIm)(NO)]ClO_4$ are well within the range seen for linear Fe−N−O groups. Mössbauer data for $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4$ confirm that the ground state is diamagnetic. In addition, the quadrupole splitting value of 1.88 mm/s and isomer shift (0.05 mm/s) at 4.2 K are similar to other (nitrosyl)iron(III) porphyrin complexes with linear Fe−N−O groups. Crystal data: $[Fe(OETPP)(1\text{-}MeIm)(NO)]ClO_4{\cdot}C_6H_5Cl$, monoclinic, space group $P2_1/c$, $Z = 4$, with a = 12.9829(6) Å, b = 36.305(2) Å, c = 14.0126(6) Å, β = 108.087(1)°; $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4{\cdot}0.5CH_2Cl_2$, triclinic, space group $P\bar{1}$, $Z = 4$, with a = 14.062(2) Å, b = 16.175(3) Å, c = 19.948(3) Å, α = 69.427(3)°, β = 71.504(3)°, γ = 89.054(3)°.

Introduction

The interaction of nitric oxide (NO) with iron(II) hemes is now widely seen as extremely important to many mammalian biological functions including smooth muscle relaxation, inhibition of platelet aggregation, neurotransmission, and immune regulation.[1] Consequently, there has been renewed interest in the study of (nitrosyl)iron porphyrin model complexes. It is well-recognized that the geometry of the Fe−N−O group is an important feature of iron nitrosyl complexes and the FeNO group geometry is strongly correlated to the electronic structure at iron. Enemark and Feltham have developed a formalism for predicting the geometry of metal nitrosyl complexes on the basis of the number of electrons in the metal d orbitals plus the number of electrons in the π^* orbitals of NO. The number of electrons in the metal-nitrosyl unit is given by n in the notation $\{MNO\}^n$. Using this formalism, (nitrosyl)iron(II) porphyrin complexes are $\{FeNO\}^7$ species. Earlier structural studies[2−4] have shown that the $\{FeNO\}^7$ complexes are expected to have bent FeNO geometries with Fe−N−O angles in the range 142−150° and Fe−N(NO) bond lengths of 1.72−1.74 Å. In addition, there is a substantial structural trans effect due to the NO ligand in six-coordinate $\{FeNO\}^7$ species.[5]

On the other hand, until just recently, all structurally characterized $\{FeNO\}^6$ porphyrin complexes (formally iron(III) complexes) were found to exhibit linear or nearly linear Fe−N−O groups.[6] The Fe−N(NO) bond lengths fall into a narrow

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range from 1.63 to 1.67 Å. Also, the axial ligand bonds trans to NO are not lengthened because of the presence of the nitrosyl group. Interestingly, however, the recently characterized (nitrosyl)iron(III) ($\{FeNO\}^6$) porphyrin complex [Fe(OEP)(C_6H_4-*p*-F)(NO)] has a bent FeNO group (Fe−N−O = 157.4(2)°).[7,8] In this complex, the presence of the σ-bonded phenyl group trans to the nitrosyl causes a significant enough change in the electronic environment at iron to lead to bending of the FeNO group. This, in turn, gives credence to earlier studies of $\{FeNO\}^6$ species with an anionic ligand trans to NO (in particular, nitrite) which could be interpreted as suggesting that a trans anionic ligand might lead to an Fe−N−O angle that was slightly nonlinear.[9] Other changes in the iron coordination geometry of [Fe(OEP)(C_6H_4-*p*-F)(NO)] also accompany the bending of the FeNO group. The Fe−N(NO) bond length is elongated to 1.728(2) Å, and the axial Fe−C(aryl) bond length of 2.040(3) Å trans to the nitrosyl is 0.085 Å longer than the Fe−C(aryl) bond length in the most closely related structurally characterized species, [Fe(TPP)(C_6H_5)].[10] Thus, the structural parameters of [Fe(OEP)(C_6H_4-*p*-F)(NO)] are midway between the limiting characteristics of $\{FeNO\}^6$ and $\{FeNO\}^7$ porphyrin systems. The results immediately raise the question of how easily distortions in the FeNO coordination group could arise. Of particular interest is the ease of changing the FeNO angle from linearity in $\{FeNO\}^6$ complexes with its possible significant effects on properties and reactivity.

There has been corresponding interest in exploring and defining further biological roles for NO. One such role has been found that is critical to the life of some blood-sucking insects. *Rhodnius prolixus* and *Cimex lectularius* utilize ferric heme proteins (nitrophorins) to aid in their blood feeding. The nitrophorins store, transport, and release nitric oxide which causes local vasodilation and reduced blood coagulation in the victim.[11,12] The functions of these heme proteins could be structurally controlled, and the structures have been intensively investigated.[13−19] The proteins have an NO binding site and a coordinated histidine trans to the NO site. We have been able to synthesize and structurally characterize ferric porphyrin nitrosyl complexes as models for these rather unique proteins. The systems characterized had a number of different neutral nitrogen donors trans to NO; only linear nitrosyl groups have been observed.[20] Recently, however, an ultrahigh-resolution structure of an NO-bound nitrophorin revealed an unusual coordination geometry for the nitrosyl group. The Fe−N−O group was found to be bent, with an angle of 156°. The bending of the FeNO group was suggested to be connected to the high degree of heme ruffling.[19] The possibility that significant core ruffling could change the nature of the Fe−N−O interaction enough to lead to appreciable bending in the $\{FeNO\}^6$ porphyrins is a startling result. But, in the model complexes noted above, the core conformations were essentially planar and thus did not provide information on whether core conformation might lead to bending of the FeNO group.

Accordingly, we have synthesized and structurally characterized (nitrosyl)iron(III) porphyrin complexes designed to have highly nonplanar porphyrin cores. The structural studies revealed that the steric requirements of the 12 peripheral porphyrin substituents in [Fe(OETPP)(1-MeIm)(NO)]ClO_4 lead to a highly saddled heme but an otherwise normal FeNO coordination geometry. Using a more sterically hindered *axial* ligand to synthesize the complex [Fe(OEP)(2-MeHIm)(NO)]ClO_4 led to an interesting structural result: the porphyrin core of one cation in the asymmetric unit, $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**), is essentially planar, and the core of a second cation, $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**), is ruffled. In both of these cations, only nearly linear FeNO groups were found (Fe−N−O = 175.6(2)° and 177.4(2)°, respectively). These derivatives with highly nonplanar heme cores have FeNO geometries that are quite similar to those previously characterized with comparable trans axial ligands; all are effectively linear. Therefore, the structural data presented in this paper do not support nitrosyl group bending in (nitrosyl)iron(III) hemes due to highly nonplanar heme cores.

Moreover, we have also explored how the UV−visible and infrared spectra respond to core deformations. These spectroscopic probes have been shown, for other nitrosyl species, to be quite diagnostic of the coordination at iron and to the degree of bending of the FeNO group. Clearly, bending of the FeNO group must involve a change in the Fe−N and N−O bonding and should be observable by these methods. The spectroscopic data for the new species are found to be similar to those found for previously characterized species and consistent with the assignment of a linear FeNO group. Finally, Mössbauer data for $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ reveal an electronic environment at iron that is unaffected by the high degree of ruffling in the porphyrin core. The strong similarity between the Mössbauer parameters of $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ and other $\{FeNO\}^6$ porphyrin complexes with planar porphyrin cores and linear FeNO groups is further evidence that heme core distortions do not lead to significant changes in the electronic structure at iron or to FeNO bending.

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. Chlorobenzene was distilled over P_2O_5. Hexanes were distilled over sodium benzophenone. NO gas was purified by passing it through 4A molecular sieves immersed in a dry ice/ethanol slush bath to remove higher oxides of

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(8) Abbreviations: Porph, a generalized porphyrin dianion; OEP, dianion of octaethylporphyrin; OETPP, dianion of octaethyltetraphenylporphyrin; TMP, dianion of tetramesitylporphyrin; TPP, dianion of tetraphenylporphyrin; TpivPP, dianion of picket fence porphyrin; 4-CNPy, 4-cyanopyridine; 1,2-Me_2Im, 1,2-dimethylimidazole; 2-MeHIm, 2-methylimidazole; 1-MeIm, 1-methylimidazole; 2-MePrz, 2-methylpyrazine; Iz, indazole (benzopyrazole); PMS, pentamethylene sulfide; Prz, pyrazine; Pz, pyrazole; N_p, porphyrinato nitrogen.

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nitrogen.[21] All other chemicals were used as received from Aldrich or Fisher. IR spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer as Nujol mulls; electronic spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis/near-IR spectrometer. Representative electronic spectra cannot be obtained by simply dissolving the isolated $\{FeNO\}^6$ compound in an appropriate solvent due to facile dissociation of NO. Therefore, electronic spectra were obtained by preparing the compound in situ in CH_2Cl_2 under an atmosphere of NO in a specially designed anaerobic cell with adjoining 1 and 10 mm cuvettes. The solid-state Mössbauer sample was immobilized in Apiezon grease. Mössbauer measurements were performed on a constant acceleration spectrometer at 4.2 K with zero field and in a 6 T magnetic field parallel to the γ-ray beam (Knox College). The free base H_2OETPP was purchased from Frontier Scientific. The free base H_2OEP was purchased from Midcentury Chemicals. The chloro- and (perchlorato)iron(III) derivatives were synthesized by modified literature methods.[22,23] *Caution!* Although we have experienced no problem with the procedures described in dealing with systems containing the perchlorate ion, they 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] [Fe(OEP)(2-MeHIm)]-ClO_4 was prepared in methylene chloride as described previously.[25]

Preparation of [Fe(OETPP)(1-MeIm)(NO)]ClO_4·C_6H_5Cl. Chlorobenzene (~0.75 mL) was added to 9 mg (0.009 mmol) of [Fe-(OETPP)$OClO_3$] and 25 μL of a 5% solution of 1-MeHIm in C_6H_5Cl (0.015 mmol) in an 8 × 240 mm glass tube inside an extralong Schlenk tube under argon. NO gas was bubbled into the solution for several minutes. The dark olive-green color of the solution did not change noticeably upon addition of NO. X-ray quality crystals were obtained by layering NO-saturated hexanes over the solution in the tubes. An NO atmosphere *must* be maintained inside the Schlenk tube during crystallization to avoid the facile dissociation of NO. IR (Nujol): $\nu(NO) = 1871\ cm^{-1}$. UV−vis (CH_2Cl_2): 464, 577 nm.

Preparation of [Fe(OEP)(2-MeHIm)(NO)]ClO_4·0.5CH_2Cl_2. Carefully purified methylene chloride (~0.5 mL) was added to solid [Fe-(OEP)(2-MeHIm)]ClO_4 (12 mg) in an 8 × 150 mm glass tube inside an extralong Schlenk tube under argon. NO gas was bubbled into the solution for several minutes. The color of the solution changed from red/brown to purple/pink. X-ray quality crystals were obtained by layering NO-saturated hexanes over the solution in the tubes. An NO atmosphere *must* be maintained inside the Schlenk tube during crystallization. A bulk powder sample for Mössbauer measurements was obtained by adding hexanes under an NO atmosphere to a CH_2Cl_2 solution of the compound in a Schlenk tube. IR (Nujol): $\nu(NO) = 1917\ cm^{-1}$. UV−vis (CH_2Cl_2): 414, 529, 561 nm.

X-ray Structure Determinations. The structure determinations were carried out on a Bruker Apex CCD diffractometer with a Mo Kα radiation source ($\bar{\lambda} = 0.71073$ Å). A dark green crystal of [Fe(OETPP)-(1-MeIm)(NO)]ClO_4·C_6H_5Cl (0.50 × 0.27 × 0.07 mm^3) was used for the structure determination at 170(2) K. A dark purple crystal of [Fe-(OEP)(2-MeHIm)(NO)]ClO_4·0.5CH_2Cl_2 (0.50 × 0.50 × 0.20 mm^3) was used for the structure determination at 130(2) K. The absorption correction program SADABS[26] was used for both structures. The structures were solved using the direct methods program SHELXS;[27] subsequent difference Fourier syntheses led to the location of the remaining atoms. The structures were refined against F^2 with the program SHELXL-97,[28,29] in which all data collected were used including negative intensities. Hydrogen atoms were idealized with the standard SHELXL idealization methods. In [Fe(OETPP)(1-MeIm)(NO)]-ClO_4·C_6H_5Cl, there is disorder present in the axial imidazole ligand, the porphyrin ligand, and in the perchlorate ion. The 1-methylimidazole ligand is disordered over two positions. The major component has a refined occupancy of 83%. The minor component representing 17% occupancy was not anisotropically refined. One of the phenyl rings occupies two positions at 0.87 and 0.13 refined occupancies. There were also two positions of the perchlorate anion at 0.78 and 0.22 refined occupancies. Again, the minor components were not anisotropically refined. In the structure of [Fe(OEP)(2-MeHIm)(NO)]ClO_4·0.5CH_2Cl_2, all non-hydrogen atoms were refined anisotropically.

Table 1. Crystallographic Details for [Fe(OEP)(2-MeHIm)(NO)]ClO_4·0.5CH_2Cl_2 and [Fe(OETPP)(1-MeIm)(NO)]ClO_4·C_6H_5Cl

formula	$C_{40}H_{50}ClFeN_7O_5$·0.5CH_2Cl_2	$C_{70}H_{71}Cl_2FeN_7O_5$
fw	842.63	1217.09
a, Å	14.062(2)	12.9829(6)
b, Å	16.175(3)	36.305(2)
c, Å	19.948(3)	14.0126(6)
α, deg	69.427(3)	
β, deg	71.504(3)	108.0870(10)
γ, deg	89.054(3)	
V, Å^3	4005.3(11)	6278.4(5)
space group	$P\bar{1}$	$P2_1/c$
Z	4	4
D_c, g/cm^3	1.397	1.288
$F(000)$	1772	2560
μ, mm^{-1}	0.564	0.382
crystal dimens, mm	0.50 × 0.50 × 0.20	0.50 × 0.27 × 0.07
λ, Å	0.71073	
T, K	130(2)	170(2)
total data colld	37 717	69 284
absorption correction	SADABS	
unique data	22 586 ($R_{int} = 0.046$)	15 583 ($R_{int} = 0.045$)
unique obsd data [$I > 2\sigma(I)$]	14 253	10 323
refinement method	on F^2 (SHELXL)	
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0521$, $wR_2 = 0.1338$	$R_1 = 0.0659$, $wR_2 = 0.1728$
final R indices [for all data]	$R_1 = 0.0866$, $wR_2 = 0.1558$	$R_1 = 0.0864$, $wR_2 = 0.1891$

Brief crystal data for [Fe(OETPP)(1-MeIm)(NO)]ClO_4·C_6H_5Cl and [Fe(OEP)(2-MeHIm)(NO)]ClO_4·0.5CH_2Cl_2 are listed in Table 1. Complete crystallographic details, atomic coordinates, anisotropic thermal parameters, and fixed hydrogen atom coordinates for both structures are included in the Supporting Information.

Results

Two new $[Fe(Porph)(L)(NO)]^+$ species, designed to have nonplanar cores, have been synthesized under carefully controlled conditions. The structural and spectroscopic characterization of these species has also been determined. The first derivative was prepared with the highly substituted porphyrin octaethyltetraphenylporphyrin. An ORTEP diagram of [Fe-(OETPP)(1-MeIm)(NO)]ClO_4 is given in Figure 1. The strongly saddled core conformation of this derivative is evident. The second derivative synthesized utilized octaethylporphyrin and

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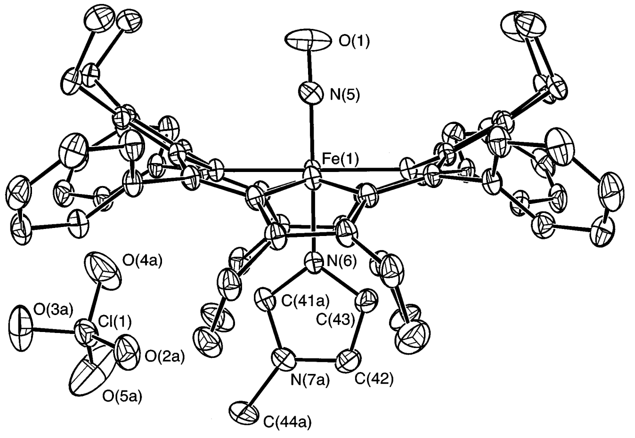

Figure 1. ORTEP diagram of [Fe(OETPP)(1-MeIm)(NO)]ClO$_4$. In this view, the N$_4$ plane is perpendicular to the plane of the drawing. Thermal ellipsoids are drawn at 30%. The labeling scheme for selected atoms is also shown. The hydrogen atoms of the porphyrin ring and imidazole ligand have been omitted for clarity.

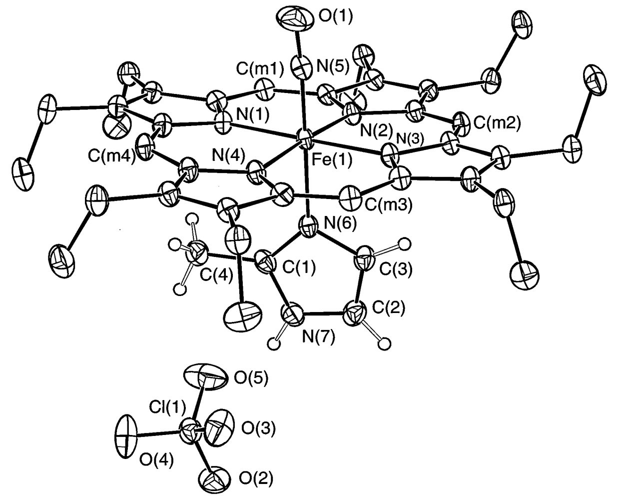

Figure 2. ORTEP diagram of [Fe(OEP)(2-MeHIm)(NO)]ClO$_4$(**pla**). Thermal ellipsoids are drawn at 50%. The labeling scheme is also shown. The hydrogen atoms of the porphyrin ring have been omitted for clarity.

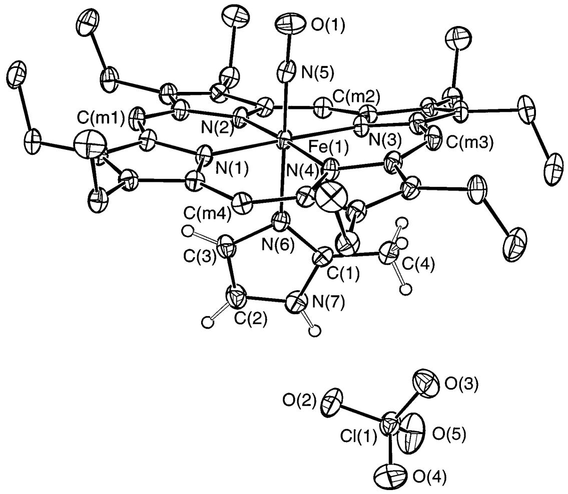

Figure 3. ORTEP diagram of [Fe(OEP)(2-MeHIm)(NO)]ClO$_4$(**ruf**). Thermal ellipsoids are drawn at 50%. The labeling scheme is also shown. The hydrogen atoms of the porphyrin ring have been omitted for clarity.

the hindered ligand 2-methylimidazole. In the structure of [Fe(OEP)(2-MeHIm)(NO)]$^+$, two independent porphyrin cations were found in the asymmetric unit. Interestingly, the two cations differ greatly in core conformation. One cation has a near-planar core conformation and is denoted [Fe(OEP)(2-MeHIm)(NO)]$^+$(**pla**); the second cation has a quite ruffled core conformation and is denoted as [Fe(OEP)(2-MeHIm)(NO)]$^+$(**ruf**). ORTEP diagrams of these molecules are given in Figures 2 and 3, where both the cation and the perchlorate counterion for each molecule are illustrated. An ORTEP diagram illustrating the arrangement of both of these molecules in the unit cell along with the counterions and solvent molecule is given in the Supporting Information. The labeling schemes depicted in these diagrams are consistent with those used in all of the diagrams and tables. Complete listings of bond lengths and angles for both structures are given in the Supporting Information. In the SI tables, the two cations in [Fe(OEP)(2-MeHIm)(NO)]$^+$ are differentiated by an underscore one (_1), which follows the label for [Fe(OEP)(2-MeHIm)(NO)]$^+$(**pla**), and an underscore two (_2), which follows that for [Fe(OEP)(2-MeHIm)(NO)]$^+$(**ruf**). Values for selected bond distances and angles for both structures are listed in Table 2. Values for related compounds are also given.[30−32]

The Fe−N(NO) bond lengths in these three [Fe(Porph)(L)(NO)]$^+$ complexes range from 1.648(2) to 1.650(2) Å. The FeNO angles are nearly linear ranging from 175.6(2)° to 177.4(2)°. The average Fe−N$_p$ bond length ranges from 1.990(9) to 2.014(8) Å. The Fe−N(2-methylimidazole) bond lengths are longer at 2.032(2) and 2.053(2) Å than for the less sterically hindering 1-methylimidazole ligand at 1.983(2) Å (Table 2).

The core conformations of the three [Fe(Porph)(L)(NO)]$^+$ cations vary greatly. The steric crowding between the four phenyl and eight ethyl substituents of the porphyrin ring in [Fe(OETPP)(1-MeIm)(NO)]$^+$ causes a severe saddling distortion. The pyrrole rings with the ethyl substituents are tilted alternately down and up with respect to the porphyrin plane. The average dihedral angle between the pyrrole ring and the porphyrin plane is quite large at 30.7°. The phenyl rings are rotated to have small dihedral angles with the porphyrin mean plane. The average of these four angles at 42.3° is smaller than the average angle for planar tetraphenyl porphyrins as expected for this saddling deformation.

The core is relatively planar in [Fe(OEP)(2-MeHIm)(NO)]$^+$(**pla**), while the core in [Fe(OEP)(2-MeHIm)(NO)]$^+$(**ruf**) is quite ruffled. One method of describing the out-of-plane distortion in the porphyrin core is to calculate the rotation angles between the five-membered pyrrole ring and the mean plane of the four pyrrole nitrogens. Ruffling is characterized by an alternating clockwise-counterclockwise pattern of rotation around the ring. Larger angles indicate more ruffling. The rotation angles for the relatively planar [Fe(OEP)(2-MeHIm)(NO)]$^+$(**pla**) are −4.5°, −0.3°, −3.4°, and +4.4°. Comparatively, for [Fe(OEP)(2-MeHIm)(NO)]$^+$(**ruf**), these angles are +8.0°, −8.4°, +12.4, and −11.2°. Positive values indicate a clockwise rotation of the pyrrole ring with respect to the four pyrrole nitrogen mean plane when looking down from the nitrosyl side of the heme plane. The perpendicular displacements of the atoms from the mean

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Table 2. Selected Comparisons for Axial Bonding Parameters in $\{MNO\}^6$ Metalloporphyrins

complex	Fe–N_p[a]	Fe–N_{NO}[a]	∠FeNO[b]	Fe–L[a]	N–O[a]	Δ[a,c]	ref
$[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$	1.990(9)	1.650(2)	177.0(3)	1.983(2)	1.130(3)	0.09	this work
$[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**)	2.014(8)	1.649(2)	175.6(2)	2.053(2)	1.132(3)	−0.02[d]	this work
$[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**)	2.003(7)	1.648(2)	177.4(2)	2.032(2)	1.139(2)	0.03	this work
$[Fe(OEP)(1\text{-}MeIm)(NO)]^+$	2.003(5)	1.6465(17)	177.28(17)	1.9889(16)	1.135(2)	0.02	20
$[Fe(OEP)(Pz)(NO)]^+$(**1**)	2.004(5)	1.627(2)	176.9(3)	1.988(2)	1.141(3)	0.01	20
$[Fe(OEP)(Iz)(NO)]^+$	1.996(4)	1.632(3)	177.6(3)	2.010(3)	1.136(4)	0.04	20
$\{[Fe(OEP)(NO)]_2Prz\}^{2+}$	1.995(8)	1.632(3)	176.5(3)	2.039(2)	1.131(4)	0.06	20
$[Fe(TPP)(H_2O)(NO)]^+$	1.999(6)	1.652(5)	174.4(10)	2.001(5)	1.150	NA[e]	30
$[Fe(TPP)(HO\text{-}i\text{-}C_5H_{11})(NO)]^+$[f]	2.013(3)	1.776(5)	177.1(7)	2.063(3)	0.925(6)	0.05[g]	31
$[Fe(TpivPP)(NO_2)(NO)]$	1.996(4)	1.671(2)	169.3(2)	1.998(2)	1.144(3)	0.09	9
$[Fe(OEP)(NO)]^+$	1.994(1)	1.644(3)	176.9(3)		1.112(4)	0.29	30
$[Fe(OEP)(NO)]^+$	1.994(5)	1.6528(13)	173.19(13)		1.140(2)	0.32	32
$[Fe(OEP)(C_6H_4\text{-}p\text{-}F)(NO)]$	2.016(11)	1.728(2)	157.4(2)	2.040(3)	1.153(3)	0.09	7
NP4(III)-NO	1.99(1)	1.66(1)	156.0(1)	2.013(9)	1.08	0.19[a]	19

[a] Value in angstroms. [b] Value in degrees. [c] Displacement of the iron from the 24-atom porphyrin plane toward the nitrosyl. [d] Displacement toward the 2-methylimidazole. [e] Metal is exactly in plane due to required symmetry. [f] This complex displayed extensive disorder. [g] Displacement of the iron atom from the 4-nitrogen mean plane.

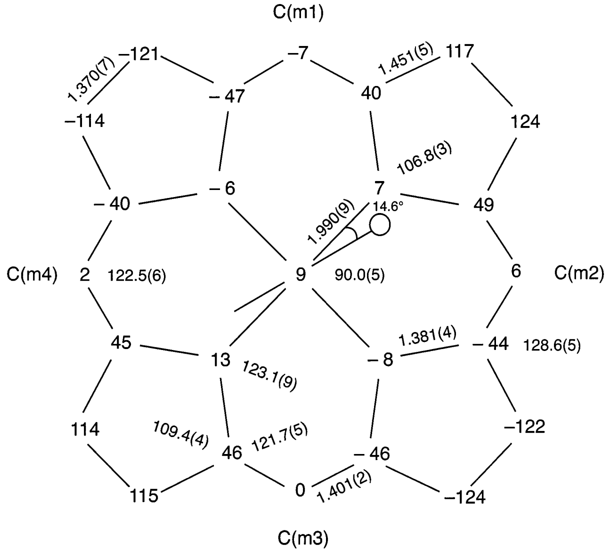

Figure 4. Formal diagram of the porphinato core of $[Fe(OETPP)(1\text{-}MeIm)(NO)]ClO_4$, illustrating the displacement of each unique atom from the mean plane of the 24-atom porphinato core in units of 0.01 Å. Positive values of displacement are toward the NO ligand. Also displayed in the diagram are the averaged values of each type of bond distance and angle in the core. The orientation of the plane of the imidazole ligand is shown with the 1-methyl group represented by the circle.

plane of the 24-atom porphyrin core in units of 0.01 Å are given in Figure 4 for $[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$. A similar mean-plane diagram for both cations in $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ is given in Figure 5. The iron atom is displaced 0.09 Å toward the NO in $[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$. The iron-atom displacement is slightly toward the 2-methylimidazole ligand in $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**) and toward the NO ligand in $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**). Averaged values for the different types of bonds in the porphyrin core are also given in these figures. The dihedral angle between the plane of the imidazole ligand and the closest Fe−N_p vector is also illustrated in Figures 4 and 5, where the circle represents the methyl group in each case. The dihedral angles are 14.6° for $[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$, 17.4° for $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**), and 30.2° for $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**).

These new $\{FeNO\}^6$ species were characterized by infrared spectroscopy. The solid-state ν(NO) frequency for $[Fe(OETPP)(1\text{-}MeIm)(NO)]ClO_4$ appears at 1871 cm^{-1}. The solid-state nitrosyl stretching frequency appears at 1917 cm^{-1} for $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4$ (a single very sharp stretch).

Mössbauer spectra have also been determined for $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4$ in the solid state at 4.2 K in zero applied field and at an applied magnetic field of 6 T (Figure 6). The quadrupole splitting value of 1.88 mm/s and isomer shift value of 0.05 mm/s, in zero applied field, are within the range of values reported for other $\{FeNO\}^6$ porphyrin complexes with linear FeNO groups.[32] Table 3 summarizes the Mössbauer parameters for the reported $\{FeNO\}^6$ and $\{FeNO\}^7$ porphyrin complexes. In an applied magnetic field, the quadrupole splitting was determined to be positive, and the experimental data are well fit assuming a diamagnetic ground state.

Discussion

As described in the Introduction, until very recently all of the structurally characterized examples of $\{FeNO\}^6$ and $\{FeNO\}^7$ porphyrin model complexes fell into two distinct geometrical categories with either linear (169−180°) or bent (142−150°) FeNO groups, respectively. The only species that does not follow this pattern is the recently characterized $[Fe(OEP)(C_6H_4\text{-}p\text{-}F)(NO)]$,[7] with an intermediate FeNO angle (157.4(2)°). The strongly σ-donating phenyl group trans to NO is thought to affect the electronic structure of iron and lead to the bending of the FeNO group. Thus, the recently published, ultrahigh-resolution structure of an $\{FeNO\}^6$ heme protein, nitrophorin NP4-NO, that also revealed a bent FeNO group (Fe−N−O = 156(1)°) was of interest.[19] It was suggested in this report that the bending of the FeNO group is possibly caused by protein-assisted ruffling of the heme plane. However, in the structure of NP4-NO, the bending of the FeNO group appears to be the only structural change in the iron coordination geometry upon distortion of the heme. The Fe−N(NO) bond length of 1.66(1) Å is within the range found for $\{FeNO\}^6$ porphyrin model complexes that have linear FeNO groups and is not lengthened as might be expected. Also, the trans Fe−N(His59) bond length of 2.01 Å in NP4-NO is within the range of Fe−N(azole) bond lengths found for porphyrin model complexes ($[Fe(Porph)(L)(NO)]^+$), all with linear FeNO groups. On the basis of the experimental data of porphyrin model complexes, the Fe−L bond length trans to the nitrosyl should be elongated with bending of the FeNO group. These apparent discrepancies between the structural results of NP4-NO and porphyrin model complexes led us to

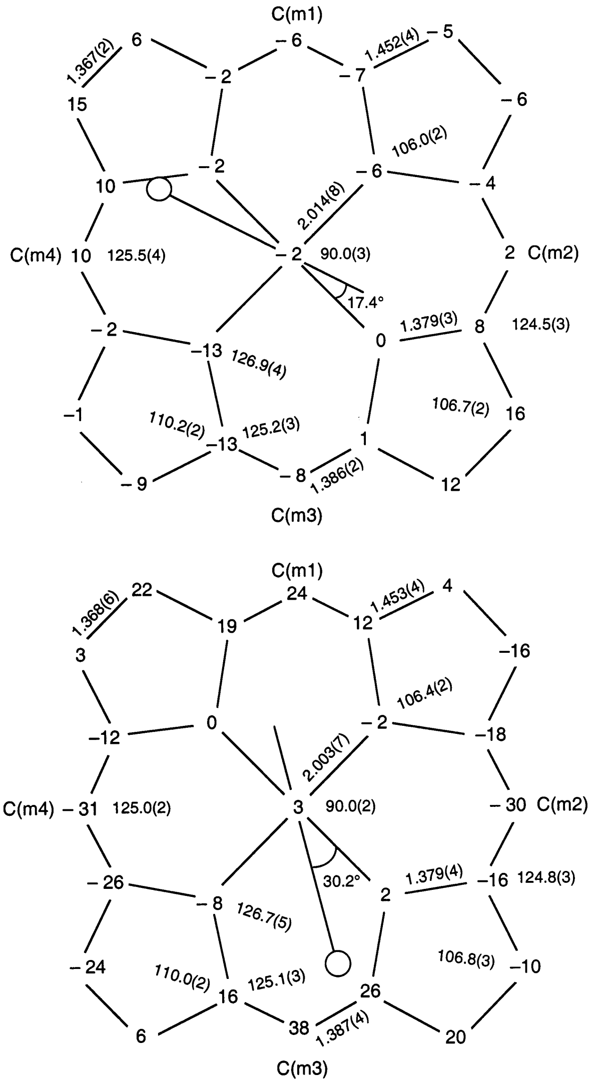

Figure 5. Formal diagrams of the porphinato core of [Fe(OEP)(2-MeHIm)(NO)]$^+$(**pla**) (top) and [Fe(OEP)(2-MeHIm)(NO)]$^+$(**ruf**) (bottom), illustrating the displacement of each unique atom from the mean plane of the 24-atom porphinato core in units of 0.01 Å. Positive values of displacement are toward the NO ligand. Also displayed in the diagrams are the averaged values of each type of bond distance and angle in the core. The orientation of the plane of the imidazole ligand is shown with the 2-methyl group represented by the circle.

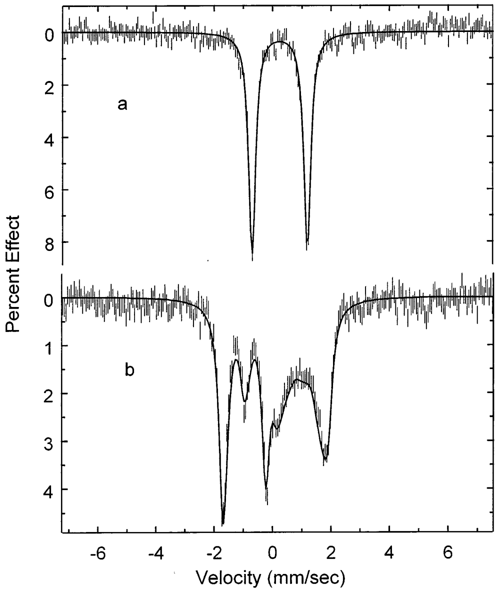

Figure 6. (a) Mössbauer spectrum of [Fe(OEP)(2-MeHIm)(NO)]$^+$ taken at 4.2 K in zero applied field. The solid line is a fit to the data which yields the following parameters: quadrupole splitting $\Delta E_Q = 1.88$ mm/s, isomer shift $\delta_{Fe} = 0.05$ mm/s, and Lorentzian width Γ(fwhm) = 0.29 mm/s. (b) Mössbauer spectrum of [Fe(OEP)(2-MeHIm)(NO)]$^+$ taken at 4.2 K in an applied magnetic field of 6 T parallel to the γ-ray beam. The solid line is a diamagnetic fit to the data which yields the following parameters: quadrupole splitting $\Delta E_Q = +1.91$ mm/s, isomer shift $\delta_{Fe} = 0.06$ mm/s, and asymmetry parameter $\eta = 0.06$.

Table 3. Solid-State Mössbauer Parameters for Nitrosyl Derivatives at Zero Applied Field

	ΔE_Q, mm/s	δ_{Fe}, mm/s	T, K	ref
	{FeNO}^{6} complexes			
[Fe(OEP)(Iz)(NO)]ClO$_4$	1.99	−0.07	293	32
	1.92	0.02	4.2	32
[Fe(OEP)(2-MeHIm)(NO)]ClO$_4$	1.88	0.05	4.2	this work
[Fe(OEP)(1-MeIm)(NO)]$^{+\,a}$	1.64	0.02	4.2	50
[Fe(OEP)(NO)]ClO$_4$	1.55	0.13	293	32
	1.64	0.20	4.2	32
[Fe(T*p*-OCH$_3$PP)(NO$_2$)(NO)]	1.43	0.04	293	9
[Fe(TpivPP)(NO$_2$)(NO)]	1.48	0.01	293	9
	1.43	0.09	4.2	9
[Fe(TPP)(NO$_2$)(NO)]	1.37	0.02	293	9
	1.36	0.13	4.2	9
	1.36	0.13	77	51
[Fe(OEP)(C$_6$H$_4$-*p*-F)(NO)]	0.56	0.05	293	7
	0.57	0.14	4.2	7
	{FeNO}^{7} complexes			
[Fe(TpivPP)(NO$_2$)(NO)]$^-$ (form 1)	1.78	0.22	200	52
[Fe(TpivPP)(NO$_2$)(NO)]$^-$ (form 2)	1.20	0.35	4.2	52
[Fe(TPP)(NO)]	1.24	0.35	4.2	52
[Fe(OEP)(NO)]	1.26	0.35	100	53

[a] In dimethylacetamide solution.

synthesize and structurally characterize [Fe(Porph)(L)(NO)]$^+$ complexes with highly distorted heme cores. The key question is whether substantial core deformations yield electronic or other effects that could lead to FeNO bending.

The porphyrin cores of the previously structurally characterized [Fe(Porph)(L)(NO)]$^+$ complexes have little to modest ruffling in three species; a fourth is slightly saddled.[20] A diagram illustrating the idealized types of porphyrin core distortions is given in Figure S2. As noted, all have linear FeNO groups. One of the ways to introduce nonplanar porphyrin core distortions is to increase the steric requirements of the axial and/or equatorial ligands. The atoms of the porphyrin core and the metal atom will generally accommodate the steric demands of the larger ligands.

A common tactic to induce porphyrin core distortion is to add bulky substituents at the porphyrin periphery. This tactic includes the complete substitution of all positions on the porphyrin ring periphery.[33] A common example of such a sterically crowded porphyrin derivative is octaethyltetraphenyl porphyrin with eight β-pyrrole ethyl substituents and four *meso*-phenyl groups. Metalloderivatives of OETPP have very distorted porphyrin cores; all known structures of this dodeca-substituted porphyrin have a porphyrin core that is severely saddled.[34−44]

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The saddled conformation is observed for four-, five-, and six-coordinate derivatives.

Aside from the obvious distortion in the porphyrin core, there are additional practical reasons for choosing OETPP derivatives to study the effects of deformation of the core on FeNO geometry. It is known that OETPP derivatives are more easily oxidized as compared to tetraphenylporphyrin derivatives. The respective reduction potentials are Fe(OETPP)Cl = −0.60 V, Fe(OEP)Cl = −0.50 V, and Fe(TPP)Cl = −0.30 V.[45] The relative ease of oxidation reflects increased porphyrin basicity which should make the OETPP $\{FeNO\}^6$ species less susceptible to reductive nitrosylation, a common unwanted reaction in the syntheses of iron(III) nitrosyl complexes.[20] Other novel properties arising from using this congested porphyrin are optical and excited-state properties.[36] Cheng et al. reported that the macrocyclic distortion led to a spin-admixed $S = {}^5/_2, {}^3/_2$ state for [Fe(OETPP)Cl] rather than the more typical high-spin state,[42] although Weiss and co-workers failed to confirm the admixed state in a polymorphic derivative with a comparable core conformation.[43] Recently, Ohgo et al.[44] reported that $[Fe(OETPP)(Py)_2]^+$ undergoes a temperature-dependent spin-state transition, possibly aided by core conformation effects originating from the use of OETPP. Thus, an $[Fe(OETPP)(L)(NO)]^+$ derivative would appear to be a strong candidate for a species with a unorthodox structure of the FeNO group, if this were to result from core distortion or modulation of electronic structure at iron.

Fortunately, we were able to obtain X-ray quality crystals of the $\{FeNO\}^6$ complex, $[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$. The structure of the complex was found to be severely saddled as expected. Figure 1 presents an edge-on view that clearly shows the saddle conformation. Figure 4 presents quantitative information on the conformation. The displacements of atoms from the mean plane of the core, although large, are typical of those previously observed for other OETPP derivatives.

The saddled core conformation leads to an average $Fe-N_p$ bond length of 1.990(9) Å, which is slightly shorter than those observed earlier for $\{FeNO\}^6$ nitrosyl derivatives.[20] The core saddling influences the orientation of the imidazole ligand with respect to the porphyrin. The dihedral angle between the imidazole plane and the nearest $Fe-N_p$ vector is very small at 14.6°. The similarly described dihedral angles of all of the other $[Fe(Porph)(L)(NO)]^+$ complexes (L = planar ligand) are greater than 25.0°.[20] The Fe−N(NO) bond length of 1.650(2) Å is within the range observed for other $\{FeNO\}^6$ complexes and is not affected by the saddled core. The Fe−N−O angle is nearly linear at 177.0(3)°, in agreement with all of the other $[Fe(Porph)(L)(NO)]^+$ complexes where L represents a neutral nitrogen-donating axial ligand. The axial Fe−N distance of 1.983 (2) Å is also a typical distance for an imidazole ligand trans to NO (see Table 2). Thus, it appears that the strongly deformed (saddled) core of $[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$ does not influence the coordination group geometry including the FeNO group. Therefore, this result does not support the idea that core deformation will lead to a bent FeNO group. However, the unusual result of a bent FeNO group in the $\{FeNO\}^6$ nitrophorin seen by Roberts et al.,[19] that led us to study $\{FeNO\}^6$ complexes with distorted hemes, may be specific to a ruffling of the core, not a saddling distortion.

We then turned to the approach of using steric crowding by a hindered axial imidazole ligand, 2-methylimidazole, trans to NO, to induce core ruffling. The success of the strategy is shown by the strongly ruffled cores in the iron(III) species $[Fe(TPP)(2\text{-}MeHIm)_2]^+$[46] and $[Fe(TMP)(1,2\text{-}Me_2Im)_2]^+$[47] that were induced by the presence of the closely approaching 2-methyl substituent of the two axial imidazoles. However, there are other ways, apart from core distortions, to alleviate the close interactions between axial ligand atoms and porphyrin core atoms. Thus, a heme core distortion is not observed in $[Fe(OEP)(2\text{-}MeHIm)_2]^+$.[48] Rather, a spin-state change, a different axial ligand plane orientation pattern, axial bond elongation, and a planar core are observed. Thus, it was not totally surprising to find in crystalline $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ that there are two independent cations in the unit cell and that each one has responded differently to the presence of the methyl group in the 2-position of the imidazole ligand.

In one cation in the asymmetric unit of the cell, the porphyrin molecule responds to the steric crowding of the 2-methyl group of the imidazole ligand by ruffling the core. We denote this conformer as $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**). In the other independent cation of the asymmetric unit, the porphyrin core is much less distorted as can be seen in the formal diagram illustrating the out-of-plane displacements for atoms of the two cations (Figure 5). We denote the second conformer as $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**), given its more nearly planar conformation, although the ring is clearly not planar.

For $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**), the porphyrin ring accommodates the steric demands of the 2-methylimidazole ligand by moving the iron atom out of the plane toward the imidazole ligand by 0.02 Å rather than toward the more dominant nitrosyl ligand as is the case for all of the other $[Fe(Porph)(L)(NO)]^+$ complexes. In addition, there is both *modest* doming and ruffling of the porphyrin core. Finally, the dihedral angle between the imidazole ligand plane and the closest $Fe-N_p$ vector is only 17.4°, as compared to the greater than 25.0° angle for the similarly described dihedral angles of all of the other $[Fe(Porph)(L)(NO)]^+$ complexes. The Fe−N(ax) bond is tipped slightly off-axis along with the usual unequal Fe−N(6)−C angles of 133.2(2) and 120.80(15)° formed with the imidazole ligand. The larger angle involves the methyl substituted carbon atom of the imidazole.

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Table 4. Solid-State Nitrosyl Stretching Frequencies for Several $\{FeNO\}^6$ Porphyrin Complexes[a]

complex	ν(NO) (cm^{-1})	∠FeNO (deg)	ref
$[Fe(OEP)(1\text{-}MeIm)(NO)]^+$	1921[b]	177.28(17)	20
$[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$	1917	175.6(2) 177.4(2)	this work
$[Fe(OEP)(4\text{-}CNPy)(NO)]^+$	1916		20
$[Fe(OEP)(Iz)(NO)]^+$	1914	177.6(3)	20
$[Fe(OEP)(PMS)(NO)]^+$	1913		20
$[Fe(OEP)(2\text{-}MePrz)(NO)]^+$	1912		20
$[Fe(OEP)(Prz)(NO)]^+$	1911		20
$[Fe(OEP)(Pz)(NO)]^+$(**2**)	1909[c]		20
$\{[Fe(OEP)(NO)]_2Prz\}^{2+}$	1899	176.5(3)	20
$[Fe(OEP)(Pz)(NO)]^+$(**1**)	1894[c]	176.9(3)	20
$[Fe(OEP)(1\text{-}MeIm)(NO)]^+$	1890[b]		20
$[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$	1871	177.0(3)	this work
$[Fe(OEP)(NO)]^+$	1862[d]	176.9(3)	30
$[Fe(OEP)(NO)]^+$	1838	173.19(13)	32
$[Fe(OEP)(C_6H_4\text{-}p\text{-}F)(NO)]$	1791	157.4(2)	7
$[Fe(TpivPP)(NO_2)(NO)]$	1893	169.3(2)	9
$[Fe(TPP)(H_2O)(NO)]^+$	1937[d]	174.4(10)	30
$[Fe(TPP)(HO\text{-}i\text{-}C_5H_{11})(NO)]^+$	1935[d]	177.1(7)	31
$[Fe(OEP)(NO)]$[e]	1666	144.4(2)	4
$[Fe(OEP)(NO)]$[f]	1673	142.74(8)	4

[a] Nujol mull. [b,c] Two crystalline modifications. [d] KBr pellet. [e] Monoclinic form. [f] Triclinic form.

In $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**), the pyrrole rings are rotated alternately around the Fe−N_p bonds; the rotation angles between a five-membered pyrrole ring and the mean plane of the four pyrrole nitrogens in $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**) are +8.0°, −8.4°, +12.4°, and −11.2°. In comparison, the rotation angles for the relatively planar $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**) are all less than ±5°. The ruffled core in $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**) allows for the shorter average Fe−N_p bond length of 2.003(7) Å as compared to 2.014(8) Å in $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**). The iron in this cation is displaced toward the nitrosyl group by 0.03 Å as is expected for the more dominant ligand. The ruffled core also allows the Fe−N(imidazole) bond length to be shorter at 2.032(2) Å as compared to 2.053(2) Å for $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**pla**). Both axial Fe−N(imidazole) distances are slightly longer than those found for the unhindered imidazole (by 0.04−0.07 Å) as a result of the 2-methyl group (Table 2). Most importantly, however, the ruffling *does not* affect the Fe−N(NO) bond length or the Fe−N−O angle. The Fe−N(NO) bond length of 1.648(2) Å is within the range seen for the previously structurally characterized $\{FeNO\}^6$ species, and the Fe−N−O angle is nearly linear, as expected, at 177.4(2)°. More convincingly, because $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$(**ruf**) possesses the same degree of ruffling as the heme core in the nitrophorin NP4-NO (the comparative rotation angles between the five-membered pyrrole ring and the mean plane of the four pyrrole nitrogens in NP4-NO are +8.5°, −8.8°, +11.0°, and −11.8°[19]), we believe that we have characterized a very close model to the heme in NP4-NO and have found no evidence for bending of the FeNO group.

The structural results thus show that neither of the two very different nonplanar core conformations has an effect on the Fe−N−O group geometry. We have also investigated whether these core distortions might have more subtle effects on the iron electronic structure observable by spectroscopic techniques. Therefore, we have measured all spectroscopic data that can be obtained from these diamagnetic complexes to ascertain whether any effect can be seen. Because this approach depends on observing differences in spectroscopic properties, the comparisons following emphasize the more commonly studied OEP derivatives.

First, the electronic spectrum of $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ in CH_2Cl_2 has a Soret band at 414 nm that is red-shifted as compared to other iron(III)(octaethylporphyrin) species and also shifted relative to the $\{FeNO\}^7$ species [Fe(OEP)(NO)]. In the visible region, the bands at 529 and 561 nm are distinctively sharp in contrast to the usual broadened α and β bands of other porphyrin complexes. These features are very similar to the *characteristic* UV−vis spectra of previously characterized $[Fe(OEP)(L)(NO)]^+$ complexes, all of which, in the solid state, are known to have linear FeNO groups.[20] In addition, although there are not many OETPP species with which to compare, the Soret band of $[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$ is also strongly red-shifted at 464 nm in CH_2Cl_2 as compared to the Soret of [Fe(OETPP)Cl] at 396 nm and the Soret of $[Fe(OETPP)(OClO_3)]$ at 437 nm.

Second, these new nitrosyl species with distorted hemes were also investigated by infrared spectroscopy. Nitrosyliron porphyrinate complexes exhibit very strong NO stretches in the infrared, and the value of the NO stretch can be diagnostic of the degree of FeNO bending. Table 4 gives nitrosyl stretching frequencies and FeNO bond angles for the structurally characterized $\{FeNO\}^6$ and $\{FeNO\}^7$ octaethylporphyrin complexes along with a few related species. We can see that all of the porphyrin species with linear FeNO geometries have NO stretching frequencies above 1838 cm^{-1}. In contrast, the two crystalline forms of the $\{FeNO\}^7$ species, [Fe(OEP)(NO)], have FeNO angles of ∼140°, and the NO stretches are below 1700 cm^{-1}. The species, $[Fe(OEP)(C_6H_4\text{-}p\text{-}F)(NO)]$, has an intermediate FeNO angle of 157.4(2)° and an intermediate ν(NO) at 1791 cm^{-1}. The solid-state ν(NO) for $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4$ appears at 1917 cm^{-1} (as a single very sharp stretch). This is at the high end of the range of the ν(NO) frequencies for previously reported $[Fe(OEP)(L)(NO)]^+$ species where L represents a neutral nitrogen-donating axial ligand.[20] Thus, the value of the nitrosyl stretching frequency for $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4$ is unaffected by core conformation and is also consistent with the observed linear Fe−N−O group. Similar conclusions appear reasonable for the $[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$ derivative as well. The work presented here makes it reasonable to suggest that the nitrosyl stretching frequency should be a good reporter of FeNO geometry, irrespective of core conformation. The one nitrosyl stretching frequency reported for a nitrophorin derivative is that for the isoform NP1-NO[49] at 1917 cm^{-1}. This is quite consistent with a linear nitrosyl group; an anomalous value for NP4-NO should be seen if a bent FeNO group exists in the NP4-NO structure.

Finally, ^{57}Fe Mössbauer spectroscopy is also very sensitive to the electronic environment at iron which again must be reflected in the coordination group geometry. Mössbauer data were collected for $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ both at zero field and at an applied 6 T magnetic field at 4.2 K. The spectra are illustrated in Figure 6. The spectrum obtained in zero field is a

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single quadrupole doublet with a quadrupole splitting constant of 1.88 mm/s. In addition, the Lorentzian line widths are as narrow as any prior $\{FeNO\}^6$ derivative. We conclude that the Mössbauer data are consistent only with a single electronic state; that is, both conformers of $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ have the same isomer shift and quadrupole splitting parameters within the line width of 0.29 mm/s. The spectrum obtained in a 6 T field is well fit by a diamagnetic ground state using the parameters given in the figure caption.

Table 3 lists the Mössbauer parameters[50−53] for several iron(nitrosyl) porphyrin complexes. We see from this table that all of the $\{FeNO\}^6$ complexes have characteristically small isomer shift values. In particular, the six-coordinate $\{FeNO\}^6$ complexes have isomer shifts less than 0.13 mm/s at 4.2 K. The isomer shifts for the $\{FeNO\}^7$ species are significantly larger. The quadrupole splitting parameters for the $\{FeNO\}^6$ species with linear FeNO groups are all greater than ∼1.3 mm/s. In $[Fe(OEP)(C_6H_4\text{-}p\text{-}F)(NO)]$, which is an $\{FeNO\}^6$ complex with a bent FeNO group, the quadrupole splitting is unusually small. This indicates a very different electronic structure at iron from other $[Fe(Porph)(L)(NO)]^+$ complexes where L is a nitrogen-donating axial ligand. The 1.88 mm/s quadrupole splitting at 4.2 K for $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ is very similar to the quadrupole splitting for the most closely related solid-state species, $[Fe(OEP)(Iz)(NO)]ClO_4$, at 1.92 mm/s. The isomer shift for $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ at 0.05 mm/s is also similar to the characteristically small isomer shifts found for $[Fe(Porph)(L)(NO)]^+$ species. Thus, the Mössbauer data for $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$ agree with the other spectroscopic results and the structural observation of a linear FeNO group.

Summary

Distortions of the porphyrin core that are comparable or greater than those found in the heme of NP4-NO, which are imposed on ferric porphyrin nitrosyl complexes by sterically demanding equatorial or axial ligands in $[Fe(OETPP)(1\text{-}MeIm)(NO)]^+$ and $[Fe(OEP)(2\text{-}MeHIm)(NO)]^+$, do not lead to bending of the FeNO group. A normal iron coordination geometry is observed. In addition, the solid-state Mössbauer parameters, nitrosyl stretching frequencies, and electronic spectra of these cations are consistent with other $[Fe(Porph)(L)(NO)]^+$ complexes which have relatively planar hemes and linear FeNO groups.

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Supporting Information Available: Tables S1−S12, giving complete crystallographic details, atomic coordinates, bond distances and angles, anisotropic temperature factors, and fixed hydrogen atom positions for $[Fe(OETPP)(1\text{-}MeIm)(NO)]ClO_4\cdot C_6H_5Cl$ and $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4\cdot 0.5CH_2Cl_2$. An ORTEP diagram illustrating the arrangement of the molecules in the unit cell of $[Fe(OEP)(2\text{-}MeHIm)(NO)]ClO_4\cdot 0.5CH_2Cl_2$ (Figure S1) and a schematic depiction of porphyrin core distortions (Figure S2) (PDF). An X-ray crystallographic file, in CIF format, is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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