

Electronic Configuration of High-Spin Imidazole-Ligated Iron(II) Octaethylporphyrinates

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The preparation and characterization of two new five-coordinate, imidazole-ligated, high-spin iron(II) octaethylporphyrinates is described. [Fe(OEP)(1,2-Me₂Im)] and [Fe(OEP)(2-MeHIm)] have been characterized by X-ray structure determinations and temperature-dependent Mössbauer spectroscopy in zero and applied magnetic fields. The distinction between imidazole-ligated and other ligands in high-spin iron(II) porphyrinates, noted for a series of tetraarylporphyrinate derivatives (Hu, C.; Roth, A.; Ellison, M. K.; An, J.; Ellis, C. M.; Schiltz, C. E.; Scheidt, W. R. *J. Am. Chem. Soc.* **2005**, *127*, 5675), is seen here as well. The sign of the quadrupole-splitting constant is again negative, which is unique to the imidazole-ligated derivatives and suggests a distinct electronic structure. The derivatives again display a remarkable temperature dependence in the quadrupole splitting, which is also seen for deoxymyoglobin and -hemoglobin. Structural features for the two new derivatives are similar to those seen earlier, although the core conformations show somewhat more doming character.

Introduction

Iron porphyrinate complexes (hemes) are the active sites in many biologically important systems. Knowledge of both the electronic and geometric structure at iron appears to be the key to understanding the diverse and complicated functions of these hemoproteins. Indeed, the electronic ground states of models of these iron(II) species have been intensively investigated both experimentally and theoretically and yet are far from being known with certainty.

The best known heme-based systems are the O₂-binding proteins myoglobin and hemoglobin, which shuttle between deoxy and oxy states. The iron of the heme remains in the 2+ formal oxidation state. In the deoxy state, iron(II) is five-coordinate and bound to the protein by the proximal histidine ligand. The heme becomes six-coordinate upon binding an O₂ molecule. The structural changes that accompany this spin-state change are essential to the mechanism of cooperative O₂ binding by hemoglobin and are the basis of the T → R transition of hemoglobin.^{1–3} In brief, the five-coordinate

deoxyheme has a structure with a significant displacement of the iron atom out of the heme plane, whereas the six-coordinate oxyheme has the iron in the plane. The signaling of the binding state between the four hemes of tetrameric hemoglobin as dioxygen is bound forms the basis of the cooperativity and is strongly coupled to the structure of the five-coordinate iron(II) porphyrin sites. The structures of several high-spin imidazole-ligated iron(II) porphyrinates have been determined by X-ray crystallography.^{4–7} Several common features are expected and observed, including an expanded porphyrinato core, large equatorial Fe–N_p⁸ bond distances, and a large out-of-plane displacement of the iron(II) atom. Perhaps somewhat unexpectedly, there are large variations in the nature of the core conformation ranging from strongly domed structures to saddled and folded cores. These lead to substantial variations (0.38–0.55 Å) in the magnitude of the out-of-plane displacements of iron from the 24-atom porphyrin core. However, the iron displacements from the four-nitrogen-atom plane are much more invariant at 0.36 Å.

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The electronic structure of iron(II) hemes is quite challenging to study because most spectroscopic probes provide little or no information about the state of the d^6 metal ion. The difficulty in understanding the electronic structure of the five-coordinate imidazole-ligated hemes is reflected in both the relatively large amount published on the issue and some changing interpretations for both experimental and theoretical studies. A number of recent density functional theory (DFT) studies for five-coordinate imidazole-ligated hemes have appeared.^{9–12} However, the conclusions reached about the electronic ground state are by no means uniform. Three of the four DFT calculations found that a triplet state was lower in energy than the experimentally observed quintet state. In all of these cases, a quintet state is predicted to be lowest in energy when the iron(II) atom is constrained to be further out of the porphyrin plane than the value obtained for the triplet state. In other words, DFT calculations suggest that large values of ΔE stabilize higher spin multiplicities. A fourth study¹¹ does predict a quintet ground state.

Iron(II) is a non-Kramers system and, except in fortuitous circumstances, is EPR silent. Fortunately, Mössbauer spectroscopy has proven to be an extremely useful spectroscopic probe for the electronic structure of iron(II). As part of a more general program of characterization of high-spin iron(II) porphyrinates, our previous study⁴ reported detailed Mössbauer spectra in an applied magnetic field for six new derivatives. The Mössbauer data measured for all high-spin iron(II) samples in both zero and applied magnetic fields, along with previously studied porphyrin derivatives, showed the same Mössbauer behavior (negative quadrupole-splitting values that are strongly temperature dependent) as that shown by deoxymyoglobin and deoxyhemoglobin, which indicates they have the same electron configuration. The electronic structure implied by the Mössbauer results shows that all of these deoxymyoglobin models are distinctly different from those of high-spin iron(II) porphyrinates ligated by all other axial ligands.

In this paper, we have examined β -substituted octaethylporphyrin derivatives rather than tetraaryl-substituted species. One of our goals was to determine if the β -substituted porphyrins display any significant differences from the tetraaryl derivatives previously characterized. We have synthesized two new five-coordinate iron(II) octaethylpor-

phyrinates using hindered imidazoles as the axial ligand. We report their molecular structures and further examine their electron configurations and the structural differences caused by the change of the porphyrin (from tetraarylporphyrins to octaethylporphyrins).

Experimental Section

General Information. All reactions and manipulations for the preparation of the iron(II) porphyrin derivatives were carried out under argon using a double-manifold vacuum line, Schlenkware, and cannula techniques. Toluene and hexanes were distilled over sodium benzophenone ketyl. Ethanethiol (Aldrich) was used as received. 2-Methylimidazole and 1,2-dimethylimidazole were purchased from Aldrich, recrystallized from toluene, and dried under vacuum. The free-base porphyrin octaethylporphyrin (H_2OEP)⁸ was purchased from Mid-Century. The metalation of the free-base porphyrin to give $[Fe(OEP)Cl]$ was done as previously described.¹³ $[Fe(OEP)]_2O$ was prepared according to a modified Fleischer preparation.¹⁴

Mössbauer measurements were performed on a constant acceleration spectrometer from 4.2 to 300 K with optional small field and in a 9 T superconducting magnet system (Knox College). Samples for Mössbauer spectroscopy were prepared by immobilization of ground crystalline material in Apiezon M grease.

Synthesis of $[Fe(OEP)(1,2-Me_2Im)]$ and $[Fe(OEP)(2-MeHIm)]$. $[Fe^{II}(OEP)]$ was prepared by reduction of $[Fe(OEP)]_2O$ (0.04 mmol) with ethanethiol (1 mL) in toluene (15 mL). The toluene solution was stirred until it turned dark red. The solvent was removed under vacuum. Excess ligand (1,2-dimethylimidazole or 2-methylimidazole) (0.4 mmol) in toluene (15 mL) was added via cannula transfer to the solid $[Fe(II)(OEP)]$ and stirred for 1 h. X-ray quality crystals were obtained in 8×250 mm sealed glass tubes by liquid diffusion using hexanes as a nonsolvent.

X-ray Structure Determinations. Single-crystal experiments were carried out on a Bruker Apex system with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystalline samples were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected at 100 K. The structures were solved by direct methods using SHELXS-97¹⁵ and refined against F^2 using SHELXL-97;^{16,17} subsequent difference Fourier syntheses led to the location of the remaining non-hydrogen atoms. For the structure refinement, all data were used including negative intensities. All non-hydrogen atoms were refined anisotropically if not otherwise stated below. For the methyl hydrogen atoms of an imidazole, a difference electron density synthesis is calculated around the circle which represents the loci of possible hydrogen positions (for a fixed C–H distance and X–C–H angle). The maximum electron density (in the case of a methyl group after local 3-fold averaging) is taken as

- (8) The following abbreviations are used in this paper: Porph, a generalized porphyrin dianion; OEP, dianion of octaethylporphyrin; $Tp-OCH_3PP$, dianion of *meso*-tetra-*p*-methoxyphenylporphyrin; TPP, dianion of *meso*-tetraphenylporphyrin; TTP, dianion of *meso*-tetratolylporphyrin; TpivPP, dianion of $\alpha,\alpha,\alpha,\alpha$ -tetrakis(*o*-pivalamidophenyl)porphyrin; Piv₂C₈P, dianion of $\alpha,\alpha,5,15$ -[2,2'-(octanediamido)-diphenyl]- $\alpha,\alpha,10$ -bis(*o*-pivalamidophenyl)porphyrin; Mb, myoglobin; Hb, hemoglobin; Im, generalized imidazole; RIm, generalized hindered imidazole; HIm, imidazole; 1-MeIm, 1-methylimidazole; 2-MeHIm, 2-methylimidazole; 1,2-Me₂Im, 1,2-dimethylimidazole; N_p, porphyrinato nitrogen; Ct, the center of four porphyrinato nitrogen atoms; EPR, electron paramagnetic resonance; *sad*, saddling; *ruf*, ruffling; *dom*, doming; *wav*, waving; *pro*, propellerling.
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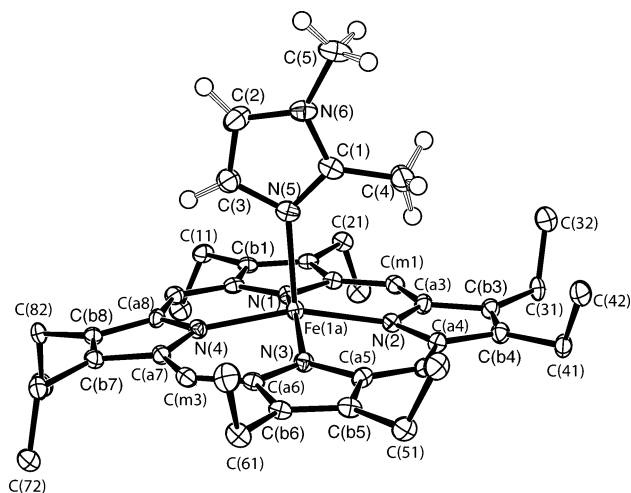
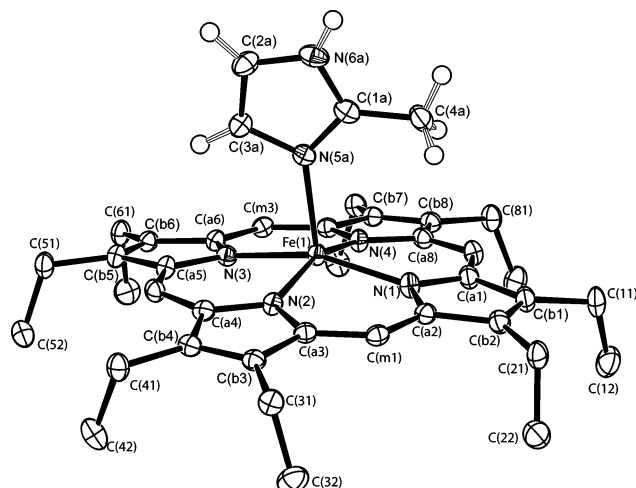
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- (17) $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4] \}^{1/2}$. The conventional R factors, R1, are based on F , with F set to zero for negative F^2 . The criterion of $F^2 > 2\sigma(F^2)$ was used only for calculating R1. R factors based on F^2 (wR2) are statistically about twice as large as those based on F , and the R factors based on ALL data will be even larger.

Table 1. Brief Crystallographic Data and Data Collection Parameters for the Two Structures

	[Fe(OEP)(1,2-Me ₂ Im)]	[Fe(OEP)(2-MeHIm)]
formula	C ₄₁ H ₅₂ FeN ₆ ·0.97C ₆ H ₅ CH ₃	C ₄₀ H ₅₀ FeN ₆ ·C ₆ H ₅ CH ₃
fw	776.87	762.84
<i>a</i> (Å)	20.2439(15)	12.6335(6)
<i>b</i> (Å)	19.7769(14)	12.9323(6)
<i>c</i> (Å)	10.1528(7)	13.5470(7)
α (deg)	90	82.285(5)
β (deg)	91.651(2)	75.039(2)
γ (deg)	90	71.063(2)
<i>V</i> (Å ³)	4063.1(5)	2019.47(17)
<i>Z</i>	4	2
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1̄
<i>D_c</i> (g/cm ³)	1.265	1.255
<i>F</i> (000)	1657	816
μ (mm ⁻¹)	0.413	0.414
cryst dimens (mm)	0.2 × 0.1 × 0.05	0.46 × 0.11 × 0.06
abs correction		SADABS
λ(Mo Kα)		0.71073 Å
<i>T</i> (K)	100(2)	100(2)
data collected	32 777	33 090
unique data	7181 (<i>R</i> _{int} = 0.0575)	8143 (<i>R</i> _{int} = 0.0330)
unique obsd	5839	6676
[<i>I</i> > 2σ(<i>I</i>)]		
refinement on <i>F</i> ²		SHELXL
final <i>R</i> indices	<i>R</i> 1 = 0.0600	<i>R</i> 1 = 0.0467
[<i>I</i> > 2σ(<i>I</i>)]	w <i>R</i> 2 = 0.1556	w <i>R</i> 2 = 0.1294
final <i>R</i> indices	<i>R</i> 1 = 0.0750	<i>R</i> 1 = 0.0590
[for all data]	w <i>R</i> 2 = 0.1174	w <i>R</i> 2 = 0.1409

the starting hydrogen position. Then the hydrogen coordinates are re-idealized and “ride” on the atoms to which they are attached with fixed thermal parameters ($u_{ij} = 1.5u_{ij}(\text{eq})$). Other hydrogen atoms were placed at idealized positions, and a riding model ($u_{ij} = 1.2u_{ij}(\text{eq})$) was used for subsequent refinements. The program SADABS¹⁸ was applied for the absorption correction. Brief crystal data for both structures are listed in Table 1. Complete crystallographic details, atomic coordinates, anisotropic thermal parameters, and fixed hydrogen atom coordinates are given in the Supporting Information for both structures.

[Fe(OEP)(1,2-Me₂Im)]·0.97C₆H₅CH₃. A red crystal with dimensions of 0.2 × 0.1 × 0.05 mm³ was used for the structure determination. The asymmetric unit contains one porphyrin complex and one partially occupied toluene molecule. During the refinement, one difference density peak at ~2.0 e/Å³, 1.1 Å away from Fe(1a) and on the opposite side of the porphyrin plane, was identified. It was refined as a disordered minor iron (Fe(1b)). Because the occupancy is very small (~3%), the 2-methylimidazole coordinated to Fe(1b) was not located. To accommodate this model, the imidazole and toluene solvent were both refined at the same occupancy as the major iron. The anisotropic displacements of both iron atoms are restrained to be the same. After the final refinement, the occupancy of the major iron, the imidazole, and the toluene solvent was found to be 97%. **[Fe(OEP)(2-MeHIm)]·C₆H₅CH₃.** A red crystal with dimensions of 0.46 × 0.11 × 0.06 mm³ was used for the structure determination. The 2-methylimidazole was found to be disordered over two positions, a major and a minor position. The minor 2-methylimidazole was refined as a rigid group; the thermal displacement parameters of N(5b) and N(6b) were each constrained to be equal to the anisotropic displacement parameters of the corresponding atoms N(5a) and N(6a) of the major imidazole orientation. After the final refinement, the occupancy of the major imidazole orientation was found to be 75%. The asymmetric unit also contains one fully occupied toluene molecule.

**Figure 1.** ORTEP diagram of [Fe(OEP)(1,2-Me₂Im)]. The single orientation of the (ordered) imidazole ligand is shown. The hydrogen atoms of the porphyrin ligand have been omitted for clarity, and 50% probability ellipsoids are depicted.**Figure 2.** ORTEP diagram of [Fe(OEP)(2-MeHIm)]. The major orientation (75%) of the imidazole ligand is shown. The hydrogen atoms of the porphyrin ligand have been omitted for clarity; the hydrogen atoms of the imidazole ligand are shown, and 50% probability ellipsoids are depicted.

Results

An ORTEP diagram of [Fe(OEP)(1,2-Me₂Im)] is illustrated in Figure 1. The major iron and 2-methylimidazole (97% occupancy) are shown. The dihedral angle, ϕ , between the imidazole plane and the plane defined by N(4), Fe(1a), and N(5) is 10.5°. The dihedral angle between the imidazole ligand and the 24-atom mean porphyrin plane is 89.5°. An ORTEP diagram showing both positions of the iron atom is provided in Figure S1.

An ORTEP diagram of [Fe(OEP)(2-MeHIm)] is given in Figure 2. The imidazole ligand is disordered over two positions with a major and a minor orientation. The diagram shows the major orientation (75% occupancy) of the axial ligand. An ORTEP diagram showing both orientations of the axial ligand is provided in Figure S2. The labeling scheme is consistent with all of the diagrams and tables. The dihedral angle between the two orientations of the imidazole ligand is 6.6°. Although the imidazole ligand of this structure is disordered, the major orientation of the ligand dominates the

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Table 2. Selected Bond Distances (Å) and Angles (deg) for [Fe(OEP)(Im)] and Related Species^a

complex ^b	Fe–N _p ^{c,d}	Fe–L _{ax} ^d	ΔN ₄ ^e	Δ ^{d,f}	Ct···Nd	Fe–N–C ^{g,h}	Fe–N–C ^{g,i}	θ ^{g,j}	φ ^{g,k}	ref
[Fe(OEP)(1,2-Me ₂ Im)]	2.080(6)	2.171(3)	0.37	0.45	2.047	132.7(3)	121.4(2)	3.8	10.5	this work
[Fe(OEP)(2-MeHIm)]	2.077(7)	2.135(3)	0.34	0.46	2.049	131.3(3)	122.4(3)	6.9	19.5	this work
average of the two	2.078(2)	2.153(25)	0.36	0.46	2.048(1)	132.0(10)	121.9(7)	5.4(22)		
[Fe(TPP)(1,2-Me ₂ Im)]	2.079(8)	2.158(2) ^l	0.36	0.42	2.048	129.3(2)	124.9(2)	11.4	20.9	4
[Fe(TTP)(2-MeHIm)]	2.076(3)	2.144(1)	0.32	0.39	2.050	132.8(1)	121.4(1)	6.6	35.8	4
[Fe(Tp–OCH ₃ PP)(2-MeHIm)]	2.087(7)	2.155(2) ^l	0.39	0.51	2.049	130.4(2)	123.4(2)	8.6	44.5	4
[Fe(Tp–OCH ₃ PP)(1,2-Me ₂ Im)]	2.077(6)	2.137(4)	0.35	0.38	2.046	131.9(3)	122.7(3)	6.1	20.7	4
[Fe(TPP)(2-MeHIm)](2-fold)	2.086(8)	2.161(5)	0.42	0.55	2.044	131.4(4)	122.6(4)	10.3	8.6	19
[Fe(TPP)(2-MeHIm)]·1.5C ₆ H ₅ Cl	2.073(9)	2.127(3) ^l	0.32	0.38	2.049	131.1(2)	122.9(2)	8.3	24.0	5
average of the six (tetraaryls)	2.080(6)	2.147(13)	0.36(4)	0.44(7)	2.048(2)	131.2(10)	123.0(11)	8.6(20)		
average of the eight (all)	2.080(5)	2.147(16)	0.36(3)	0.44(6)	2.048(2)	131.4(12)	122.7(11)	7.8(24)		
[Fe(TpivPP)(2-MeHIm)]	2.072(6)	2.095(6)	0.40	0.43	2.033	132.1(8)	126.3(7)	9.6	22.8	6
[Fe(Piv ₂ C ₈ P)(1-MeIm)]	2.075(20)	2.13(2)	0.31	0.34	2.051	126.5	120.4	5.0	34.1	7
[K(222)][Fe(OEP)(2-MeIm [−])]	2.113(4)	2.060(2)	0.56	0.65	2.036	136.6(2)	120.0(2)	3.6	37.4	20
[K(222)][Fe(TPP)(2-MeIm [−])]	2.118(13)	1.999(5)	0.56	0.66	2.044	129.6(3)	126.7(3)	9.8	23.4	20
		2.114(5)				133.6(4)	121.9(4)	6.5	21.6	
[Fe(TpivPP)(2-MeIm [−])] [−]	2.11(2)	2.002(15)	0.52	0.65	2.045	NR ^m	NR	5.1	14.7	21
[Fe(TpivPP)Cl] [−]	2.108(15)	2.301(2) ⁿ	0.53	0.59	2.040					22
[Fe(TpivPP)(O ₂ CCH ₃)] [−]	2.107(2)	2.034(3) ^o	0.55	0.64	2.033					23
[Fe(TpivPP)(OC ₆ H ₅)] [−]	2.114(2)	1.937(4) ^o	0.56	0.62	2.037					23
[Fe(TpivPP)(SC ₆ HF ₄)] [−]	2.076(20)	2.370(3) ^p	0.42	NR	2.033					22
[Fe(TPP)(SC ₂ H ₅)] [−]	2.096(4)	2.360(2) ^p	0.52	0.62	2.030					24
[Fe(TPP)(1-MeIm) ₂] ^q	1.997(4)	2.014(5)	0.0 ^r	0.0 ^r	1.997	128.2	128.3	1.1	14.7	25
[Fe(TPP)(THF) ₂]	2.057(4)	2.351(3) ^s	0.0 ^r	0.0 ^r	2.057					26

^a Estimated standard deviations are given in parentheses. ^b Unless noted otherwise, complex is high spin. ^c Averaged value. ^d In angstroms. ^e Displacement of iron from the mean plane of the four pyrrole nitrogen atoms. ^f Displacement of iron from the 24-atom mean plane of the porphyrin core. ^g Value in degrees. ^h 2-Carbon, sometimes methyl-substituted. ⁱ Imidazole 4-carbon. ^j Off-axis tilt (deg) of the Fe–N^{Im} bond from the normal to the porphyrin plane. ^k Dihedral angle between the plane defined by the closest N_p–Fe–N_{Im} and the imidazole plane in degrees. ^l Major imidazole orientation. ^m Not reported. ⁿ Chloride. ^o Anionic oxygen donor. ^p Thiolate. ^q Low Spin. ^r Six-coordinate; required to be zero by symmetry. ^s Neutral oxygen donor.

structural features of the molecule. The dihedral angle (ϕ) between the major imidazole ligand and the plane defined by N(1), Fe, and N(5a) is 19.5°. The dihedral angle between the major imidazole ligand and the 24-atom mean porphyrin plane is 80.9°. Other selected geometric parameters involving the iron and imidazole ligand are given in Table 2 for both complexes.

Figure 3 shows formal diagrams of the porphyrin cores of the two new iron(II) imidazole-ligated structures that give the displacement of each atom from the mean plane of the 24-atom porphyrin core in units of 0.01 Å. The orientation of the imidazole ligand with respect to the core atoms is shown by the line with the circle representing the methyl group bound at the 2-carbon position. An analogous diagram showing the atomic displacements from the mean plane of the four nitrogen atoms is given in Figure S3. Also included on the diagrams of Figure 3 are the individual Fe–N_p bond lengths. The average Fe–N_p bond lengths are 2.080(6) Å for [Fe(OEP)(1,2-Me₂Im)] and 2.077(7) Å for [Fe(OEP)(2-MeHIm)]. These average values and other selected bond distances and angles are given in Table 2. A complete listing of bond distances and angles for both structures is given in the Supporting Information.

The Fe–N(imidazole) bond lengths are 2.171(3) and 2.135(3) Å, respectively, which are similar to those in iron(II) tetraarylporphyrinates. In both structures the imidazole ligand Fe–N bond vector is tilted off of the normal to the 24-atom porphyrin mean plane. The values of the tilt angle, given by θ in Table 2, are 6.9° for [Fe(OEP)(1,2-Me₂Im)] and 3.8° for [Fe(OEP)(2-MeHIm)]. Two other important angles associated with the imidazole ligands (Fe–N–C) are given in

Table 2. The displacements of the iron atoms out of the porphyrin plane are 0.37 and 0.34 Å, respectively. The radii of the porphyrin cores, given by Ct···N in Table 2, are nearly identical at 2.047 and 2.049 Å.

These crystalline species were studied with variable-temperature and variable-field Mössbauer spectroscopy. The quadrupole-splitting values show a strong temperature dependence. The quadrupole splitting values for the crystalline species [Fe(OEP)(2-MeHIm)] are 1.94 mm/s at 4.2 K and 1.34 mm/s at 298 K. The isomer shifts at these respective temperatures are 0.93 and 0.82 mm/s. At 4.2 K, the quadrupole splitting for [Fe(OEP)(1,2-Me₂Im)] is 2.19 mm/s, and the isomer shift is 0.92 mm/s. These values at 298 K are 1.59 and 0.80 mm/s, respectively. Mössbauer parameters at various temperatures between 4.2 and 298 K are given in Table S13 of the Supporting Information.

Discussion

As noted in the Introduction, we have previously investigated the molecular structures and electron configuration of five-coordinate high-spin imidazole-ligated iron(II) tetraarylporphyrinates as deoxyheme model compounds.^{4,5} These complexes have several common features including an expanded porphyrinato core, large equatorial Fe–N_p bond distances, and a significant out-of-plane displacement of the iron(II) atom. But they also show much variation in core conformation, as well as differences in the orientation of imidazole plane with respect to the porphyrin core. Mössbauer spectra show a negative sign for the quadrupole splitting and a strong temperature dependence that suggests that they all have the same unusual electronic ground state

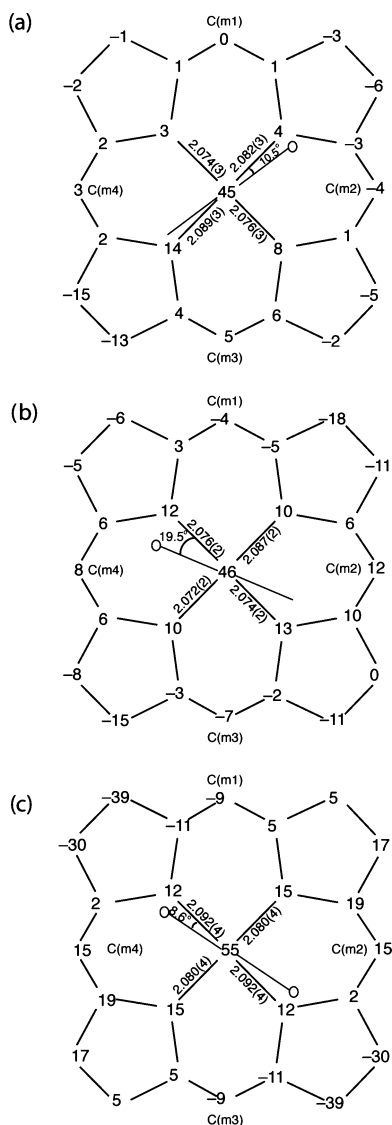


Figure 3. Formal diagrams of the porphyrinato cores of (top to bottom) (a) [Fe(OEP)(1,2-Me₂Im)], (b) [Fe(OEP)(2-MeHIm)], and (c) [Fe(TPP)(2-MeHIm)].¹⁹ The displacements of each atom from the mean plane of the 24-atom core in units of 0.01 Å are illustrated. Positive values of displacement are toward the imidazole ligand. The diagrams also show the orientation of the imidazole ligand with respect to the atoms of the porphyrin core. The location of the methyl group at the 2-carbon position is represented by the circle.

as deoxyhemoglobin and deoxymyoglobin. In this paper, we explore the possible effects of different substituents of the porphyrin core (β -pyrrole substituents vs *meso*-aryls) on the electron configuration and on any structural differences, especially core conformations. Accordingly, we have synthesized two new five-coordinate iron(II) octaethylporphyrinates with sterically hindered 2-methylimidazole and 1,2-dimethylimidazole as ligands²⁷ and characterized them by X-ray crystallography and Mössbauer spectroscopy.

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Molecular Structures. The overall structural features of [Fe(OEP)(1,2-Me₂Im)] and [Fe(OEP)(2-MeHIm)] are those expected for high-spin iron(II) porphyrinates.^{4,28} Selected structural data for these two complexes are given in Table 2, and full structural information is given in the Supporting Information. Also given in Table 2 are the values found for a number of previously characterized high-spin iron(II) systems. The average Fe–N_p bond distances for [Fe(OEP)(1,2-Me₂Im)] (2.080(6) Å) and [Fe(OEP)(2-MeHIm)] (2.077(7) Å) are well within the range for the other imidazole-ligated porphyrinates (2.073–2.087 Å). The axial Fe–N_{Im} bond lengths are 2.171(3) Å in [Fe(OEP)(1,2-Me₂Im)] and 2.135(3) Å in [Fe(OEP)(2-MeHIm)], which is in the range for those of the tetraarylporphyrinates. The Fe–N_{Im} bond lengths for the imidazole-ligated structures show a small but significant variation. The small variation is no doubt a consequence of the hindering methyl group, the differences in the relative orientation of the axial ligand, and the differing core conformations.

Similarly, the displacement of the iron atom from the plane of the four nitrogen atoms (Δ N₄) is 0.37 Å for [Fe(OEP)(1,2-Me₂Im)] and 0.34 Å for [Fe(OEP)(2-MeHIm)], values that bracket the average for the tetraaryl derivatives (Table 2). The displacements of iron from the 24-atom porphyrin plane (Δ) are 0.45 and 0.46 Å, respectively. The difference between the two values (note that Δ is larger than Δ N₄) is a measure of porphyrin core doming. The two complexes both have a moderate (0.08 and 0.12 Å) domed conformation. Porphyrin core doming is frequently observed for metalloporphyrin derivatives with metal ions that are too large to fit into the central hole of the porphyrin ring,²⁹ but doming is not as prevalent as might have been expected in the imidazole-ligated iron(II) species.

The large iron(II) ion is accommodated in the central hole of the porphyrin ring not only by the large iron atom displacements and long Fe–N_p bond distances but also by a radial expansion of the core (an increase in the size of the central hole).³⁰ The radius of the central hole is 2.047 or 2.049 Å for these two new imidazole-ligated porphyrinates, values similar to those of the tetraarylporphyrinates.

The steric bulk of the 2-methyl group leads to, in all derivatives examined to date, an off-axis tilt of the axial Fe–N_{Im} bond and a rotation of the imidazole ligand that leads

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to unequal Fe–N_{Im}–C_{Im} angles. Values for iron(II) imidazole-ligated species are given in Table 2. These angles have average values of 131.4° on the methyl side and 122.7° on the other side. The off-axis tilt and imidazole rotation are correlated to maximize the distance between the 2-methyl group and porphyrin core atoms. The ORTEP drawings of Figures 1 and 2 clearly show that the axial Fe–N_{Im} bond vector is tilted from the heme normal. The tilt angles are 3.8 and 6.9°. As can be seen in Table 2, the small differences in ligand tilting does not appear to be correlated with any other structural feature, showing no apparent relationship to the varying core conformation or to the orientation of the axial ligand plane with respect to the Fe–N_p directions. There is an interesting pattern in Figure 3, which compares [Fe(OEP)(1,2-Me₂Im)] with [Fe(TPP)(2-MeHIm)] (2-fold). Both have small dihedral angles (ϕ) which are around 10°. The corresponding Fe–N_p distances close to the imidazole plane are longer than the other pair as shown in Figure 3, and the corresponding Fe–N_{Im} distances (2.171(3) and 2.161(5) Å) are also longer than those in other porphyrinates with larger dihedral angles (ϕ). The longer Fe–N_p and Fe–N_{Im} distances are related to the smaller ϕ probably because of the interaction between the imidazole ligand and the porphyrin core.

Although most structural features including average Fe–N_p lengths and displacements of iron from the N₄ and 24-atom planes are similar (Table 2), there is significant variation in core conformation. Core conformations of the nine five-coordinate high-spin iron(II) porphyrinates are illustrated in Figure 4. Displayed in linear fashion are the displacements of the iron atom and the 24 atoms of the porphyrin core from the four pyrrole nitrogen mean plane. The two OEP structures are at the top; the remaining structures are grouped by similar overall conformation, and the hybrid porphyrin structure is shown last. The orientation of the imidazole ligand with respect to the porphyrin core is also shown: the vertical line represents the position of the imidazole shown with the pyrrole closest to the 2-methyl group. When there is a minor orientation this is illustrated with a second vertical line; the major orientation is always shown to the left. With the exception of the [Fe(TPP)(2-MeHIm)] (2-fold) structure, which has two equivalent orientations of the axial ligand, it is expected that the major ligand orientation dominates the observed structure. The results summarized in Figure 4 make evident that there is not a *single* preferred conformation for imidazole-ligated high-spin iron(II) complexes. There are some similarities in the tetraaryl complexes as we discussed in a previous study.⁴ Both of the OEP complexes have an obvious domed conformation, which is similar to that of [Fe(TPP)(2-MeHIm)]¹⁹ and [Fe(TTP)(2-MeHIm)].⁴

The core conformations have also been analyzed by the normal structural decomposition (NSD) method provided by Shelnutz et al.^{31,32} Table 3 lists the out-of-plane displacements of the minimal basis for the nine five-coordinate high-spin

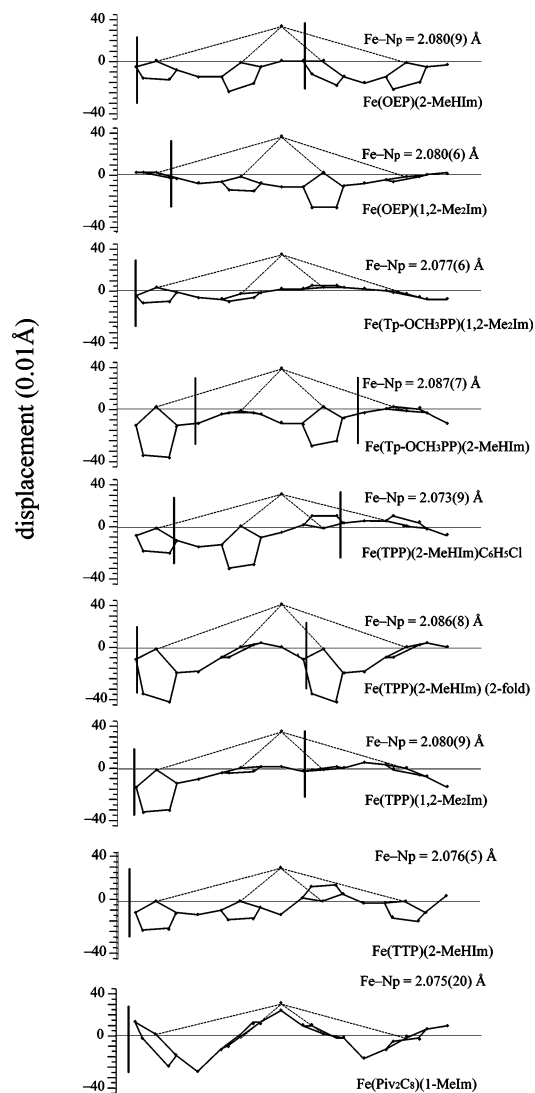


Figure 4. Diagrams illustrating the core conformation and iron displacement for nine known imidazole-ligated high-spin iron(II) porphyrinates. The displacement of the iron and the atoms of the porphyrin core from the mean plane defined by the four pyrrole nitrogen atoms is given. The position of the imidazole ligand with respect to directions defined by the Fe–N_p directions is shown.

iron(II) porphyrinates. NSD also shows wide variation of the core conformations from saddling to doming to waving. The doming deformation is the largest component for the two OEP complexes as shown in Table 3. Although a number of the tetraaryl derivatives also have a substantial doming deformation, it is not as prominent as those of the two OEP derivatives. The doming displacements in the 1,2-dimethylimidazole-ligated complexes are smaller than those in the corresponding 2-methylimidazole complexes and may be a result of the (small) steric differences between two ligands. However, the TPP complexes do not fit this pattern. The different core conformations for different crystalline forms of the TPP complexes suggest that solid-state packing and solvates in solid state will also influence the core conformation. Other weak interactions in the solid state, such as π – π interactions and hydrogen bonding, are also possible factors.

Electronic Structure. The electronic structure of these two new complexes has also been studied by Mössbauer

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Table 3. Out-of-Plane Displacements (Å) of the Minimal Basis for the X-ray Crystal Structures of Five-Coordinate High-Spin Iron(II) Porphyrinates

porphyrin	D_{oop}^a	δ_{oop}^b	<i>sad</i>	<i>ruf</i>	<i>dom</i>	<i>wav(x)</i>	<i>wav(y)</i>	<i>pro</i>	ΔN_4^c	Δ^d	ref
[Fe(OEP)(2-MeHIm)]	0.437	0.012	0.112	0.216	-0.356	0.066	-0.004	-0.018	0.34	0.46	this work
[Fe(OEP)(1,2-Me ₂ Im)]	0.282	0.013	-0.085	-0.052	-0.225	0.014	0.137	-0.006	0.37	0.45	this work
[Fe(TPP)(2-MeHIm) (2-fold)]	0.872	0.018	-0.672	0.336	-0.444	-0.000	-0.000	-0.024	0.42	0.55	19
[Fe(Tp-OCH ₃ PP)(2-MeHIm)]	0.652	0.024	-0.546	0.057	0.350	-0.039	0.014	-0.004	0.39	0.51	4
[Fe(TPP)(2-MeHIm)]	0.310	0.020	-0.119	0.012	0.180	0.200	-0.095	0.012	0.32	0.38	19
[Fe(TTP)(2-MeHIm)]	0.302	0.014	0.155	0.055	0.204	0.147	-0.024	0.006	0.32	0.39	4
[Fe(TPP)(1,2-Me ₂ Im)]	0.362	0.019	0.265	-0.077	-0.202	-0.116	-0.005	0.008	0.36	0.42	4
[Fe(Tp-OCH ₃ PP)(1,2-Me ₂ Im)]	0.116	0.014	-0.070	-0.018	0.082	-0.038	0.007	-0.004	0.35	0.38	4
[Fe(Piv ₂ C ₈ P)(1-MeIm)]	0.607	0.036	-0.026	-0.594	-0.077	-0.086	-0.017	-0.040	0.31	0.34	7

^a Observed total distortion. ^b The mean deviation as a measure of the goodness of fit. ^c Displacement of iron from the mean plane of the four pyrrole nitrogen atoms. ^d Displacement of iron from the 24-atom mean plane.

Table 4. Mössbauer Parameters for Five-Coordinate High-Spin Imidazole-Ligated Iron(II) Porphyrinates and Hb and Mb

complex	ΔE_Q^a	δ_{Fe}^a	η	Γ^b	T (K)	ref
[Fe(OEP)(1,2-Me ₂ Im)]	-2.19	0.92	0.43	0.38	4.2	this work
[Fe(OEP)(2-MeHIm)]	-1.94	0.93	0.26	0.42	4.2	this work
[Fe(Tp-OCH ₃ PP)(1,2-Me ₂ Im)]	-2.44	0.95	0.65	0.46	4.2	4
[Fe(Tp-OCH ₃ PP)(2-MeHIm)]	-2.18	0.94	0.58	0.53	4.2	4
[Fe(TPP)(1,2-Me ₂ Im)]	-1.93	0.92	0.2	0.44	4.2	4
[Fe(TPP)(2-MeHIm)]	-1.96	0.86	0.55	0.6	4.2	4
[Fe(TTP)(2-MeHIm)]	-1.95	0.85	0.1	0.42	4.2	4
[Fe(TTP)(1,2-Me ₂ Im)]	-2.06	0.86	0.04	0.43	4.2	4
[Fe(TPP)(2-MeHIm)]	-2.40	0.92	0.8	0.50	4.2	5
[Fe(TPP)(2-MeHIm)(2-fold)]	-2.28	0.93	0.8	0.31	4.2	33
[Fe(TPP)(1,2-Me ₂ Im)]	-2.16	0.92	0.7	0.25	4.2	33
[Fe((Piv ₂ C ₈ P)(1-MeIm)]	-2.3c	0.88		0.40	4.2	7
Hb	-2.40	0.92	0.7	0.30	4.2	33
Mb	-2.22	0.92	0.7	0.34	4.2	33
[Fe(OEP)(2-MeIm ⁻)]	+3.71	1.00	0.22	0.29	4.2	20
[Fe(TPP)(2-MeIm ⁻)]	+3.60	1.00	0.02	0.33	4.2	20
[Fe(TpivPP)(SC ₂ H ₅) ⁻]	+2.18	0.83	0.80	0.30	4.2	35
[Fe(TPP)(OC ₆ H ₅) ⁻]	+4.01	1.03	0	0.25	4.2	36
[Fe(TpivPP)(O ₂ CCH ₃) ⁻]	+4.25	1.05	0	0.30	4.2	37
[Fe(TpivPP)(OCH ₃) ⁻]	+3.67d	1.03		0.40	4.2	23
[Fe(TpivPP)(OC ₆ H ₅) ⁻]	+3.90d	1.06		0.38	4.2	23
[Fe(TpivPP)(2-MeIm) ⁻]	+3.51 ^d	0.97			77	21
[Fe(TpivPP)(SC ₆ HF ₄)] [NaC ₁₂ H ₂₄ O ₆]	+2.38 ^d	0.84		0.28	4.2	35
[Fe(TpivPP)(SC ₆ HF ₄)] [Na(222)]	+2.38 ^d	0.83		0.32	4.2	35
[Fe(TpivPP)Cl] ⁻	+4.36 ^d	1.01		0.31	77	22

^a In millimeters per second. ^b Line width, fwhm. ^c Sign not determined experimentally, presumed negative. ^d Sign not determined experimentally, presumed positive.

spectroscopy. Mössbauer isomer shifts (δ) and quadrupole-splitting (ΔE_Q) values have been measured from room temperature to 4.2 K. The values of ΔE_Q observed at 4.2 K are 1.94 and 2.19 mm/s, for [Fe(OEP)(1,2-Me₂Im)] and [Fe(OEP)(2-MeHIm)], respectively. These are within the range of previously reported high-spin iron(II) species;^{4,33} the large value of the isomer shift (~ 0.9 mm/s) is consistent with high-spin iron(II).³⁴ For comparison, the Mössbauer data for these two complexes and related species are listed in Table 4. From these data, as outlined below, it is almost certain that all of these five-coordinate imidazole-ligated species share many common electronic structure features.

There is a substantial temperature variation of the quadrupole-splitting values; complete values of δ and ΔE_Q versus T are given in Table S13. A plot of the data for these two complexes and related species is given in Figure S6. The value of ΔE_Q decreases significantly as the temperature is increased. The observed temperature dependence of ΔE_Q for

these two new porphyrinates is similar to the variation seen (over a smaller temperature range) for deoxymyoglobin and -hemoglobin samples^{33,39-41} and for those of the tetra-arylporphyrinate derivatives.^{4,20} As discussed previously,⁴ the explanation for this temperature variation is that there are close-lying excited states. The excited states could have the same or differing spin multiplicity relative to the ground state.

The application of applied magnetic field Mössbauer spectroscopy provides more detailed information concerning the electronic ground states. The Mössbauer data in strong

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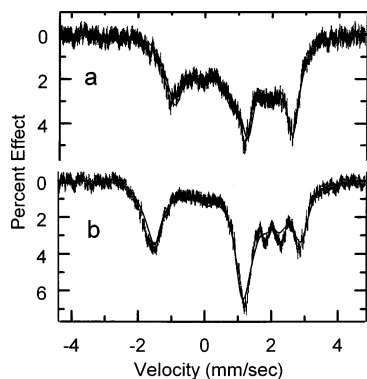


Figure 5. Figure illustrating the fits to the Mössbauer data obtained at 9 T. The spectra are (a) the one obtained for [Fe(OEP)(2-MeHIm)], and (b) the one for [Fe(OEP)(1,2-Me₂Im)].

magnetic fields shown in Figure 5 were fit with the spin Hamiltonian model used by Kent et al.³³

$$H = D[S_z^2 - 1/3S(S + 1)] + E(S_x^2 - S_y^2) + \vec{H} \vec{g} \vec{S} + H^Q - g_N^* \beta_N \vec{H} \cdot \vec{I} + \vec{S} \cdot \vec{A}^* \cdot \vec{I}$$

where D and E are the axial and rhombic zero-field splitting parameters that describe the fine structure of the $S = 2$ multiplet, \vec{A}^* is the magnetic hyperfine tensor, H^Q gives the nuclear quadrupole interaction

$$H^Q = \frac{eQV_{zz}}{12} [3I_z^2 - I(I + 1) + \eta(I_x^2 - I_y^2)]$$

Q is the quadrupole moment of the ⁵⁷Fe nucleus, and $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{ii} are components of the electric field gradient. The quadrupole splitting and isomer shift were constrained to the values determined from the zero-field data.

An analysis of the spectra showed the largest component of the electric field gradient, V_{zz} , to have a negative value and hence the sign of the quadrupole splitting value is also negative. The asymmetry parameters for two new complexes are relatively large, 0.43 and 0.26, which are consistent with other related imidazole-ligated species.^{4,33,39–41} The large asymmetry parameter indicates the low symmetry of the electric-field gradient (EFG), which is also reflected in the solid-state structures of these complexes.

As shown in Table 4, there are a number of five-coordinate high-spin iron(II) porphyrinate derivatives definitely known^{35–37} to have a positive value for the quadrupole splitting, while the positive value of a number of others must be regarded as highly probable.^{21–23,35} These derivatives are listed in Table 4 with a “+” sign. As shown in the table, all of these complexes have an anionic species as the axial ligand. For iron porphyrinate complexes, it is reasonable to assume that the EFG at the nucleus is dominated by contributions from the d electrons.³⁸ Following the discussion of Debrunner,³⁴ a large positive quadrupole splitting with a small asymmetry parameter is consistent only with the doubly occupied d orbital being in the heme plane (i.e., the orbital must be either d_{xy} or $d_{x^2-y^2}$). The $(d_{xy})^2(d_{xz})^1(d_{yz})^1(d_z)^2(d_{x^2-y^2})^1$ ground state has also been assigned for [Fe(TPP)(OPh)]^{–36} and Na(222)[Fe(TpivPP)(OAc)].³⁷ Indeed, we believe that the

$(d_{xy})^2(d_{xz})^1(d_{yz})^1(d_z)^2(d_{x^2-y^2})^1$ state is the usual one for high-spin iron(II) porphyrinates; the “unusually large” quadrupole split doublet signal from high-spin iron(II) should be regarded as normal.

The negative sign for the quadrupole splitting value usually indicates that the more negative charge is along the heme normal, which led to the conclusion that the doubly occupied d orbital for the imidazole-ligated complexes is a d_{π} orbital (i.e., the doubly occupied orbital is perpendicular to the heme plane). The d_{xz} and d_{yz} orbitals have an EFG with a negative component V_{zz} along the heme normal. This straightforward d-orbital occupancy is consistent with a simple crystal-field model. But in these imidazole-ligated complexes, the negative quadrupole splitting is also associated with large asymmetry parameters and makes this simple model unsatisfying. The doubly occupied d orbital must reflect a low-symmetry ligand field and thus a mixture of the d_{xz} , d_{yz} , and d_{xy} orbitals, which can give a negative sign to ΔE_Q , and the asymmetry parameter can be relatively large (although simply mixing the orbitals will not affect the magnitude of ΔE_Q).

In addition to a negative ΔE_Q , the imidazole-ligated complexes also have a much smaller magnitude of ΔE_Q than those systems shown in Table 4 with positive quadrupole splittings. Such a change in magnitude requires either (i) a significantly different configuration of charges on the ligands or (ii) a significant difference in the radial wave functions of the d electrons. We can easily discount the first case: a negatively charged ligand along the z axis will make a negative contribution to V_{zz} , presumably along the heme normal for the more symmetric doubly occupied d_{xy} systems. If one could remove that charge and maintain the d electron configuration, an even larger positive quadrupole splitting would be expected. We argue that covalency effects are in fact likely to be larger for the doubly occupied d_{π} systems, as those doubly occupied orbitals are oriented in a direction much more likely to involve them in hybridization than is a d_{xy} orbital. Radially expanded d_{π} orbitals would then result in smaller contributions of those wave functions to the EFG and thus a smaller observed quadrupole splitting. The Fe–N_{ax} bond length differences in the imidazole-ligated (longer) versus imidazolate-ligated (shorter) species are consistent with this.

In this model, when ΔE_Q is negative, the largest component of the EFG will no longer lie near the heme normal. Indeed, single-crystal Mössbauer data have shown that, for deoxymyoglobin, V_{zz} is negative and far from the heme normal, within 22° of the heme plane.³⁹ So, the Mössbauer properties are better described by a hybrid orbital composed of the two axial d_{π} orbitals, along with a significant d_{xy} contribution. Such mixing of d_{xy} with the d_{π} orbitals will occur in any ligand field of sufficiently low symmetry. For example, an axial potential rotated off an octahedral symmetry axis will mix the states. Such a field would be expected for 5-coordinate hemes with the axial ligand displaced from the heme normal. A detailed analysis of the Mössbauer spectra of all high-spin iron(II) porphyrinates is in progress and will be published subsequently.⁴²

We believe that it is the low-symmetry mixed d-orbital configuration with a ΔE_Q that is smaller and negative, as found for deoxymyoglobin, deoxyhemoglobin, and the imidazole-ligated iron(II) porphyrinates that is the unusual electronic state for high-spin iron(II) porphyrinates. Thus, high-spin iron(II) porphyrinates can be divided into two different electronic configurations. As can be seen from a comparison of structural data (Table 2) with the signed quadrupole derivatives of Table 4, this division into two groups is also manifested in the structures. The complexes, anionic ligand-coordinated species, with a known $(d_{xz})^1(d_{yz})^1(d_{xy})^2(d_z)^1(d_{x^2-y^2})^1$ configuration, have significantly larger iron atom displacements and equatorial Fe–N_p bonds.⁴ It can be explained that, with more d_{xy} character, spin–orbit coupling will mix $d_{x^2-y^2}$ character more strongly into the doubly occupied orbital for these other iron(II) species than for the imidazole derivatives. The electrostatic repulsion of the in-plane orbital by the negative charge of the pyrrole nitrogens is thus expected to increase the magnitude of the iron atom displacement from the porphyrin plane with a concomitant increase in the value of the Fe–N_p bond distances in comparison to the imidazole-ligated systems.

Although the quadrupole splitting is in principle directly correlated with the detailed structure of the complex,⁴³ a comparison of the ΔE_Q values with the respective structure does not yet suggest a general correlation. A comparison of the values for the 1,2-dimethylimidazole complexes with the 2-methylimidazole complexes suggests that the latter have smaller absolute values for OEP, TTP, and Tp–OCH₃PP derivatives. There may thus be a weak correlation between conformations and quadrupole-splitting values.

Summary. Structural studies of two new high-spin iron(II) octaethylporphyrinates undertaken in this investigation show that they have features common to those in tetraarylporphyrinates, such as an expanded porphyrinato core, large equatorial Fe–N_p bond distances, and a significant out-of-plane displacement of the iron(II) atom. Both OEP complexes have core doming as the dominant deformation. But there

are a number of differing core conformations observed for all discussed structures, which indicates that there is not a *single* preferred conformation for imidazole-ligated high-spin iron(II) complexes. The different core conformations for different crystalline forms of TPP complexes suggest that solid-state packing and solvents in the solid state will also influence the core conformation. Other weak interactions in the solid state, such as π – π interactions and hydrogen bonding, are other possible factors. Mössbauer studies reveal that the two OEP derivatives have the same behavior as those of tetraaryl derivatives, negative quadrupole splitting values and relative large asymmetry parameters. Both the structures and Mössbauer spectroscopy suggest high-spin iron(II) porphyrinates can be divided into two classes of electron configurations with significantly different geometric structures. The anionic ligand-coordinated species have the $(d_{xy})^2(d_{xz})^1(d_{yz})^1(d_z)^1(d_{x^2-y^2})^1$ ground state, while these imidazole-ligated porphyrinates have a ground state with a hybrid orbital composed of the two axial d_π orbitals with a significant d_{xy} contribution. These features could be important for the biological function of heme proteins, such as reversible O₂ binding.

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Supporting Information Available: Figures S1 and S2 showing ORTEP diagrams of [Fe(OEP)(1,2-Me₂Im)] and [Fe(OEP)(2-MeHIm)], Figure S3 displaying the displacements from the N₄ plane, Figures S4 and S5 showing the simultaneous fits to the variable field Mössbauer data, Figure S6 showing the *T* dependence of the ΔE_q values, Tables S13 and S14 giving full details on the observed data and the fits, Tables S1–S12 giving complete crystallographic details, atomic coordinates, bond distances and angles, anisotropic temperature factors, and fixed hydrogen atom positions for [Fe(OEP)(1,2-Me₂Im)] and [Fe(OEP)(2-MeHIm)] (PDF), and crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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