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Iron Porphyrins with Different Imidazole Ligands. A Theoretical Comparative Study

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Abstract

A theoretical comparative study of a series of five- and six-coordinate iron porphyrins, FeP(L) and FeP(L)(O₂), has been carried out using DFT methods, where P = porphine and L = imidazole (Im), 1-methylimidazole (1-MeIm), 2-methylimidazole (2-MeIm), 1,2-dimethylimidazole (1,2-Me₂Im), 4-ethylimidazole (4-EtIm), or histidine (His). Two ligated “picket fence” iron porphyrins, FeTpivPP(2-MeIm) and FeTpivPP(2-MeIm)(O₂), were also included in the study for comparison. A number of density functionals were employed in the computations in order to obtain reliable results. The performance of functionals and basis set effects were investigated in detail on FeP, FeP(Im), and FeP(Im)(O₂), for which certain experimental information is available and there are some previous calculations in the literature for comparison. Many subtle distinctions in the effects of the different imidazole ligands on the structures and energetics of the deoxy- and oxy iron porphyrins are revealed. While FeP(2-MeIm) is identified to be high spin ($S = 2$), the ground state of FeP(1-MeIm) may be an admixture of a high-spin ($S = 2$) and an intermediate-spin ($S = 1$) state. The ground state of FeP(L)(O₂) may be different with different L. A weaker Fe-L bond more likely leads to an open-shell singlet ground state for the oxy complex. The 2-methyl group in 2-MeIm, which increases steric contact between the ligand and the porphyrinato skeleton, weakens the Fe-O₂ bond, and thus iron porphyrins with 2-MeIm mimic T-state (low affinity) hemoglobin. The calculated FeP(2-MeIm)-O₂ bonding energy is comparable to the FeTpivPP(2-MeIm)-O₂ one, in agreement with the fact that the “picket-fence” iron porphyrin binds O₂ with affinity similar to that of myoglobin, but different from the result obtained by the CPMD scheme. Im and 4-EtIm closely resemble His, the biologically axial base, and so future computations on hemoprotein models can be simplified safely by using Im.

1. Introduction

Metal porphyrins (MPors),¹ most notably the iron porphyrins, are one of the most important groups of organometallic compounds.^{2,3} They occur in many proteins and enzymes which are responsible for three major activities: electron transfer, oxygen transfer, and photosynthesis. Iron porphyrins serve as the prosthetic group in hemoglobin (Hb) and myoglobin (Mb), as well as other heme proteins such as peroxidases, catalases, and cytochromes. One of the most important properties of iron porphyrins is the strong attraction of the central Fe to molecules in addition to the porphyrin. This extra coordination is responsible for attachment of the active iron porphyrin to carrier proteins. The active center of Hb and Mb consists of iron protoporphyrin IX (FePPIX) complex bound through a single,

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Supporting Information Calculated relative energies for selected states of FeP, FeP(Im), and FeP(Im)(O₂) at different functionals' optimized structures and with different basis sets. Calculated relative energies for selected states of FeP, FeP(Im) and FeP(Im)(O₂) with various recently developed functionals. Calculated FeP-Im bonding energies in FeP(Im) and FeP(Im)-O₂ bonding energies in FeP(Im)(O₂) with various functionals in the non-SCF and SCF procedures. Non-relativistic relative energies for selected states of FeP, FeP(Im), and FeP(Im)(O₂). This information is available free of charge via the internet at <http://pubs.acs.org>.

‘proximal’, axial histidine (His) to the protein; the deoxy forms of both Hb and Mb, deoxyheme, give rise to a five-coordinate, high-spin ($S = 2$) Fe^{II} .⁴ Upon oxygenation at the opposite ‘distal’ face, a diamagnetic $\text{Fe}^{\text{III}}\text{O}_2^-$ complex forms reversibly.^{5,6} Figure 1 illustrates the familiar four-coordinate FePPIX of heme *b* and the heme group bound to dioxygen (O_2) within the Mb unit.

The electronic structure of the iron ion in iron porphyrin complexes is very interesting and has been the focus of much experimental and theoretical work. For the transition metal Fe, the partial occupancy of the 3d-shell can yield a number of low-lying electronic states that are within a narrow energy range; the reaction processes of hemoproteins are suggested to depend essentially on changes in the oxidation number or spin state of the iron ion.⁷ Controversies once existed in the literature regarding the ground-state configuration of four-coordinate iron^{II} (i.e. ferrous) porphyrins without axial ligands. It is now generally accepted that the ground state is intermediate spin ($S = 1$): only the $^3\text{A}_{2g}$ state arising from the $(d_z^2)^2(d_{xy})^2(d_{\pi})^2$ configuration is compatible with Mössbauer,^{8,9} magnetic moment,¹⁰ and proton NMR^{11,12} data.

There have been many theoretical studies of iron porphyrins and related compounds. A simple, un-substituted iron porphine (FeP) was often adopted to model the basic iron porphyrins. FeP(Py) (Py = pyridine), FeP(NH_3), and FeP(Im) (Im = imidazole) complexes were used to mimic the active center of both Hb and Mb. Their O_2 complexes were therefore used as models for oxyHb or oxyMb. A simple MP is indeed able to mimic the essential properties of the more complicated FePPIX;¹³ the peripheral substituents on the porphyrin ring and their conformation are shown not to affect the electronic and structural properties of the central iron porphyrin. Histidine (His) is a substituted imidazole and so the simple, un-substituted imidazole (Im) may be considered as a well simplified model for the histidine residue attached to the FePPIX in Hb/Mb. But Py and NH_3 are questionable models of the imidazole ligand. FeP(Py) was shown to be a poor model for high-spin deoxyheme.¹⁴ On the other hand, some previous density functional theory (DFT) calculations^{15,16} on the relaxed structure of FeP(Im) predicted a triplet ($S = 1$) state as the ground state for this complex, at odds with the situation for deoxyheme. Later, Scherlis and Estrin¹⁷ reported *ab initio* and DFT calculations on simplified FeP(Im) and FeP(Im)(O_2) model complexes, where the porphine macrocycle was replaced by two amidinato ligands. Those calculations on the simplified models are not of much relevance to the present calculations on full porphyrin models. Recently, a DFT + U approach was applied by Scherlis et al.¹⁸ to describe the low-lying states of iron porphyrins. In this approach, there is an adjustable parameter U. Different values of U will yield rather different results, and for different systems, the U values may also be different. The reliability of the DFT + U results, which strongly depend on U, is hard to judge here. More recently, Radon and Pierloot^{19a} performed both DFT and *ab initio* calculations on FeP(Im) and FeP(Im)(O_2); the “experimental” heme- O_2 binding energy is well reproduced by the CASPT2 method with a large basis set. The high-level *ab initio* calculated result can thus be used here to examine how well our present DFT methods treat the various iron heme complexes.

In this paper, we will perform a theoretical comparative study of iron porphyrins with a number of different imidazole ligands that include imidazole (Im), 1-methylimidazole (1-MeIm), 2-methylimidazole (2-MeIm), 1,2-dimethylimidazole (1,2-Me₂Im), 4-ethylimidazole (4-EtIm), and histidine (His). Iron porphyrins with different imidazole ligands have been synthesized and characterized; they include FeTPP(2-MeIm),²⁰ FeTpivPP(1-MeIm),²¹ FeTpivPP(2-MeIm),²² and FeTpivPP(1,2-Me₂Im),²² where TPP is tetraphenylporphine and TpivPP stands for tetra($\alpha,\alpha,\alpha,\alpha$ - orthopivalamide)phenylporphine. These model porphyrins, which are known to be high-spin complexes, have been used experimentally to gain more knowledge about the properties and functioning of heme groups.²⁰⁻²³ FeTpivPP is an

interesting “picket-fence” compound, having steric shielding on one side of the porphyrin and reversibly oxygenating in solution. The 1-MeIm and 2-MeIm complexes are taken as models for the R-form (high ligand affinity) and T-form (low ligand affinity) Hbs, respectively;²⁴ 2-MeIm lowers the O₂-bonding affinity by a power of 10 with respect to the analogous 1-MeIm.²² Using the CPMD (Car-Parrinello Molecular Dynamics) program, Rovira and Parrinello¹³ reported DFT/BP calculations on five-coordinate FeTpivPP(2-MeIm) and six-coordinate FeTpivPP(2-MeIm)(O₂), where FeTpivPP(2-MeIm) was predicted to be triplet ($S = 1$), again in disagreement with experiment. On the other hand, these authors showed a very large increase in the ligand bonding energy [$E_{\text{bond}}(\text{Fe-L})$] to Fe in the presence of the bulky TpivP substituents; for example, the calculated E_{bond} for Fe-O₂ in FeTpivPP(2-MeIm)(O₂) is as large as 47 kcal/mol (2.04 eV), which may be too large for the compound to release O₂ after the ligand molecule is adsorbed by the compound. According to experiment,²¹⁻²³ FeTpivPP(L), as the deoxyHb or deoxyMb model, reversibly binds molecular oxygen and has an oxygen affinity similar to the values measured for hemoproteins.²⁴ The Fe-O₂ bonding in FeTpivPP(2-MeIm)(O₂) may need to be re-investigated. 4-EtIm resembles His very much (see Figure 2) and has been used to model the proximal His384 in the model of the cytochrome oxidase active site.²⁵ A comparison among the various imidazole ligands would be of interest so as to determine the sensitivity of the electronic structure and bonding in FePor(L) and FePor(L)(O₂) to the precise nature of the imidazole ligand. To examine the effects of the TpivP substituents on the Fe-O₂ bonding, FeTpivPP is included in our calculations in addition to FeP. This work has two main aims:

1. To examine the effects of different imidazole ligands on the structures and energetics of various spin states of the deoxy- and oxy iron porphyrins.
2. To verify whether the TpivP substituents have considerable influence on the coordinated molecular oxygen O₂.

With the existence of a number of low-lying states, the electronic structure of iron porphyrins has proven to be difficult to describe theoretically. Previous *ab initio* calculations on FeP based on Hartree-Fock (HF),²⁶ configuration interaction (CI),²⁷ MRMP,²⁸ and CASPT2^{28,29} methods, all predicted a high-spin ($S = 2$) quintet as the ground state for this complex, in disagreement with experiment. This failure was ascribed to the fact that the stability of the high-spin state is always exaggerated in the HF-type theories since they contain only Fermi correlation, but not Coulomb correlation.³⁰ The correlation calculations mentioned above apparently did not include sufficient correlation effects to overcome the deficiency of the underlying HF-type treatment.

Naturally, density functional theory (DFT) has been applied to iron porphyrins and appears to be a good choice in this respect. Calculations on FeP by Kozłowski *et al.*³¹ using the BP and B3LYP functionals predicted the ground state to be $^3A_{2g}$, in agreement with the experiments on FeTPP (iron tetraphenylporphine).⁸⁻¹² However, it is known that the ability of DFT to calculate the relative spin-state energies is sensitive to the type of functionals;³¹ the mentioned BP functional in fact fails to give the correct ground state for high-spin systems,³² although it provides a “correct” intermediate-spin ground state for FeP. We once investigated the behaviors of a large variety of density functionals in describing the energetics for iron porphyrins and related compounds and found that several functionals, namely B3LYP, B97, B97-1, and τ -HCTH-hyb, were able to yield satisfactory results for the systems considered.³² To obtain reliable results, tests are needed for different functionals. We therefore examined the performance of various density functionals for calculating the structures and energetics of the heme model complexes considered here. In addition, the influence of basis-set size on the calculated properties was also examined.

2. Computational Details

All calculations used the Amsterdam Density Functional (ADF) program package – ADF2009.01.^{33,34} To obtain reliable results and for the sake of comparison, a number of density functionals^{30,35–47} were used in the calculations; they include: (1) GGA functionals (BP, PBE, revPBE, OPBE, OPerdew, OLYP, HCTH/407) that contain a generalized gradient approximation (GGA) correction; (2) meta-GGA functionals (Becke00, τ -HCTH) that contain the electron kinetic energy density $\tau [= \Sigma(\Sigma\phi_i)^2]$ (in addition to GGA); and (3) hybrid-GGA functionals (B3LYP, B3LYP*, PBE0, B97, τ -HCTH-hyb) that contain a fraction of the HF (or exact) exchange. A brief description of their formulation is given in Table 1. The various functionals have their own specific advantages and disadvantages.³²

In the present version of ADF, certain GGA (here HCTH/407), meta-GGA (here Becke00, τ -HCTH) and hybrid GGA (here B97, τ -HCTH-hyb) functionals included in the program are treated in a non-self-consistent (non-SCF) manner. That is, the SCF calculation is performed with a different specific functional; the obtained electron densities are then used as input for energy evaluation with the GGA, meta-GGA or hybrid meta-GGA functional. It has been shown that for calculations of the relative energies (E^{relative}) of spin states in a molecule, the non-SCF and SCF procedures yield very close results.⁴⁸ Since the evaluation of the exchange-correlation (XC) potential has not been implemented in ADF for these functionals, geometry optimization cannot be efficiently performed with them. In this case, the molecular structures used were those optimized with the BP functional, which gives an excellent description of molecular structure for the systems.

The STO (Slater-type orbital) basis set used is the standard ADF-TZP, which is triple- ζ for valence orbitals plus one polarization function. To assess the adequacy of TZP, different basis sets (DZP, TZ2P, TZ2P+) have been tested by performing calculations on FeP, FeP(Im), and FeP(Im)(O₂). The definitions of these basis sets are given in Table 1. Large basis-set effects were once found in previous calculations by other authors.¹⁹ To obtain reliable results, no frozen-core approximation (FCA) was used; instead, all-electron calculations were carried out here. It is stated that for the present version of ADF, hybrid functionals cannot be used in combination with frozen cores (ADF2009.01 User's Guide). In fact, a number of meta-GGA functionals implemented also cannot be used with FCA in the current version of ADF.

Relativistic corrections for the valence electrons were calculated by the quasi-relativistic (QR) method.⁴⁹ In this scalar, one-component approach, spin-orbit (SO) coupling is not taken into account. Because SO effects are mainly atomic in nature (in molecules, SO coupling is mostly quenched by the non-spherically symmetric molecular field), they are not expected to have significant influence on molecular properties, except metal-ligand binding energies. Here we concentrate on the bonding interaction between an iron porphyrin and an axial ligand. The SO coupling is much smaller in a large molecule (iron porphyrin) than in an atom (Fe, where the d-shell SO coupling is already small). The effects of relativity are supposed to be non-negligible for Fe. To check the magnitude of these effects on the spin-state energetics, additional non-relativistic calculations were performed on FeP, FeP(Im), and FeP(Im)(O₂), and the results are provided in the Supporting Information. The calculations for open-shell states were spin unrestricted. Spin contamination in the unrestricted calculations was found to be small, as is shown in other calculations on comparable compounds.^{30,50} So, the energetics obtained from the DFT calculations can be expected to be meaningful.

3. Results and Discussion

Figure 2 illustrates the molecular structures of FeP, FeTpivPP, and various imidazole ligands. When only a single axial ligand (L) is added to the system, significant out-of-plane distortions are expected and in fact observed. The structural parameters of particular interest for a FePor(L) complex are $R_{\text{Ct}(\text{N4})\cdots\text{N}(\text{eq})}$ (distance between the center of the ring and the equatorial, porphinato nitrogen), $R_{\text{Ct}(\text{N4})\cdots\text{Fe}}$ (distance between the center of the ring and Fe), and $R_{\text{Fe-L}}$ (here $R_{\text{Fe-N}(\text{ax})}$) (axial Fe-L bond length). $R_{\text{Ct}(\text{N4})\cdots\text{N}(\text{eq})}$ is a measure of the porphinato core size and $R_{\text{Ct}(\text{N4})\cdots\text{Fe}}$ represents the displacement of Fe out of the N4-plane toward the L ligand. Bonding an O_2 to the five coordinate complex moves the Fe back into the plane. But $R_{\text{Ct}(\text{N4})\cdots\text{Fe}}$ in FePor(L)(O_2), though small, is not zero experimentally and may be different in different compounds.²² For example, the Fe in crystalline FeTpivPP(2-MeIm)(O_2) remains 0.086 Å out of the porphyrin N4 plane toward the 2-MeIm ligand, in marked contrast to that observed in FeTpivPP(1-MeIm)(O_2), where the displacement is −0.02 Å out of the plane toward the dioxygen ligand (here a negative value denotes an out-of-plane displacement toward the O_2 ligand). Hence, we have also presented the calculated $R_{\text{Ct}(\text{N4})\cdots\text{Fe}}$ values for each FePor(L)(O_2). To better examine the effects of the axial ligand on the properties of the iron porphyrins, the results on the unligated FeP and FeTpivPP are also presented. For the planar FeP, the structural parameters of interest are mainly the equatorial Fe-N bond length $R_{\text{Fe-N}(\text{eq})}$, which is different for different spin states. The $d^6 \text{Fe}^{\text{II}}$ ion in the iron porphyrin can exhibit three spin states, namely $S = 0$ (low spin, singlet), $S = 1$ (intermediate spin, triplet), and $S = 2$ (high spin, quintet). Each of the $S = 1$ and 2 spinors may correspond to several possible electronic configurations. In this paper, only the results for the lowest-energy configuration of each spinor are presented. The optimized structural parameters given for FeTpivPP include $R_{\text{Ct}(\text{N4})\cdots\text{Fe}}$. Figure 3 illustrates the molecular structures of FeP(Im) and FeP(Im)(O_2); the imidazole ligand uses its N_ϵ nitrogen to attach Fe. The calculated FeP-L bonding energies [$E_{\text{bond}}(\text{FeP-L})$] in FeP(L) and FeP(L)- O_2 bonding energies in FeP(L)(O_2) are defined as:

$$\begin{aligned} -E_{\text{bond}}(\text{FeP} - \text{L}) &= E[\text{FeP}(\text{L})] - \{E(\text{FeP}) + E(\text{L})\} \\ -E_{\text{bond}}[\text{FeP}(\text{L}) - \text{O}_2] &= E[\text{FeP}(\text{L})(\text{O}_2)] - \{E[\text{FeP}(\text{L})] + E(\text{O}_2)\} \end{aligned}$$

Here $E[\text{FeP}(\text{L})]$, $E(\text{FeP})$, $E(\text{L})$, $E[\text{FeP}(\text{L})(\text{O}_2)]$, $E[\text{FeP}(\text{L})]$, and $E(\text{O}_2)$ are total energies of the indicated species, which are optimized independently.

3.1. FeP, FeP(Im), and FeP(Im)(O_2): Performance of Functionals and Basis Set Effects

We performed an extensive test of different functionals and basis sets on FeP, FeP(Im), and FeP(Im)(O_2) in order to ensure the functional and basis set used for other larger systems are adequate, since there exists certain experimental information and several calculations with different methods have been reported in the literature. Our geometry optimizations for the three systems have been performed with five functionals (BP, PBE, OLYP, B3LYP, PBE0) and four basis sets (DZP, TZP, TZ2P, TZ2P+). The calculated structural parameters of the four-, five-, and six-coordinate iron porphyrin complexes are presented in Tables 2, 3, and 4, respectively, together with available experimental data^{51,52} and calculated results from other authors.^{19a,53} On the basis of the optimized structures, the spin-state energetics and FeP-Im bonding energies in FeP(Im) and FeP(Im)- O_2 bonding energies in FeP(Im)(O_2) were then calculated.

3.1.1. Structures—The BP/TZP optimized Fe-N(eq) bond lengths for the triplet, quintet, and singlet states of FeP are 1.973, 2.038, and 1.989 Å, respectively. Little changes in $R_{\text{Fe-N}(\text{eq})}$ are observed from one functional to another or from one basis set to another. This may be expected for this rigid molecule. It also is found that the structural parameters

obtained with PBE are always very close to those calculated with BP for every molecule. Therefore, the structural parameters for FeP(Im) and FeP(Im)(O₂) obtained with PBE are no longer listed in the tables. In the high-spin state, there is one electron occupying the anti-bonding $d_{x^2-y^2}$ orbital, thereby resulting in an elongated Fe-N(eq) bond (by 0.05 – 0.07 Å). The calculated bond lengths of FeP for the triplet states agree very well with the X-ray crystal structure data on FeTPP ($R_{\text{Fe-N(eq)}} = 1.972$ Å).

Attaching a single axial ligand (L) to FeP pulls Fe out of the porphyrin plane. The calculated $\text{Ct(N4)} \cdots \text{Fe}$ distance depends on the spin multiplicity in addition to $R_{\text{Fe-N(eq)}}$ (or the core size $R_{\text{Ct(N4)} \cdots \text{N(eq)}}$). That is, the high spin state has a considerably larger Fe displacement than do the lower-spin states. $R_{\text{Fe-N(ax)}}$ is sensitive to spin state as well, as the triplet has a larger Fe-N(ax) bond length than do the quintet and singlet. For the singlet with a $(d_{xy})^2(d_{\pi})^4$ configuration, the absence of an electron in the Fe- d_{z^2} orbital leads to a rather short Fe-N(ax) bond.

For the triplet and quintet, the porphyrin core is slightly expanded by ca. 0.02 Å upon the axial-ligand attachment, whereas the core size remains the same for the singlet. The BP/TZP values for the Fe out-of-plane displacement in FeP(Im) are 0.16, 0.29, and 0.15 Å for the triplet, quintet, and singlet, respectively. Examining the results obtained with the other functionals, the structural parameters $R_{\text{Ct(N4)} \cdots \text{N(eq)}}$ and $R_{\text{Fe-N(ax)}}$ that relate to the rigid FeP portion change only slightly (at most 0.02 Å) with a change of functional, similar to the case of FeP. But the situation for the axial Fe-N(ax) bond length appears to be different. In the extreme case, $R_{\text{Fe-N(ax)}}$ obtained with OLYP in the $S = 1$ state is 0.12 Å larger than that with BP. But the difference is less than 0.02 Å in the $S = 0$ state when the same functional is used. The Fe-N(ax) distances obtained with the hybrid functionals B3LYP and PBE0, which agree with each other, are more or less (0.01 – 0.06 Å) larger than that with BP, depending on state. Concerning the basis-set effects, the structural parameters obtained with DZP are systematically smaller by 0.01 – 0.02 Å than those with TZP. Then, nearly no changes (<0.01 Å) in the R values are found from TZP to TZ2P to TZ2P+.

A comparison is made between our results and those from previous DFT calculations on FeP(Im) by other authors using different programs – CPMD,¹⁵ Gaussian94 (G94),¹⁶ and Jaguar.⁵³ The CPMD-BP calculations gave a rather small porphyrin-core size (2.01 Å) for the high-spin state and showed that the $R_{\text{Ct(N4)} \cdots \text{N(eq)}}$ values for the three spin states are comparable. According to our results, the core size in the high-spin state (2.06 Å) is 0.06 – 0.07 Å larger than those in the lower-spin states; this trend is in agreement with experiments.^{8,20} The axial Fe-N(ax) bond lengths calculated with CPMD-BP are also somewhat different from ours. Owing to the presence of one electron in the d_{z^2} orbital, $R_{\text{Fe-N(ax)}}$ for the triplet is predicted by us to be ca. 0.30 Å larger than that of the singlet. The CPMD-BP calculations gave a relatively small $R_{\text{Fe-N(ax)}}$ for the triplet but a relatively large $R_{\text{Fe-N(ax)}}$ for the singlet, where the difference in $R_{\text{Fe-N(ax)}}$ for the two spin states is only 0.15 Å. It is seen that the G94-B3LYP calculations¹⁶, as well as the recent Jaguar-BP and Jaguar-B3LYP calculations,⁵³ on the different spin states of FeP(Im) yielded structural parameters and trends that are in good agreement with our results. The G94-B3LYP calculated core sizes are consistently larger than the present BP calculated ones by 0.03 Å. No X-ray crystal structural data are available in the literature for a comparable, five-coordinate, synthetic FePor(Im) compound. The experimental structural parameters given in Table 3 are those measured for deoxy-Mb,^{51,52} which are seen to be in good agreement with our calculated results in the high-spin ($S = 2$) state, particularly the BP calculated ones. Deoxy-Mb is known to have a quintet ground state.⁴

The O₂ binding to FeP(L) restores the planarity of the FeN4 moiety and also changes the electronic structure of FeP(L). The geometry of the O₂ molecule attached to Fe in FeP(L)

(O₂) is in an angular, end-on fashion, as shown in Figure 3. This geometry has been well established by both experiment^{21,22} and calculation.¹⁵ Figure 4 illustrates the change of the orbital energy level diagram from FeP (in ³A_{2g} state) to FeP(Im) (in ⁵A state) to FeP(Im)(O₂) (in ³A state). The HOMO (highest occupied molecular orbital) in FeP(Im)(O₂) is of mainly O₂-π_g* character (72%), admixed by some Fe-d_{yz} orbital (24%). The same is true for the other O₂ adducts. FeP(L)(O₂) has no longer a high-spin ground state. The possible spin states for the six-coordinate, oxy iron porphyrin are now S = 0(C) (closed-shell singlet), S = 1 (triplet), and S = 0(O) (open-shell singlet); they correspond to the (d_{xy})²(d_{xz})²(d_{yz})², (d_{xy})²(d_{xz})²(d_{yz}α)¹(O₂-π_g*α)¹, and (d_{xy})²(d_{xz})²(d_{yz}α)¹(O₂-π_g*β)¹ electronic configurations, respectively. Therefore, the Fe–O₂ bond can be formally described as Fe^{III}–O₂[−] for both the triplet and open-shell singlet, where electron charge is transferred from FeP to O₂. The following structural features are revealed for FeP(Im)(O₂) (see Table 4):

1. The transition from the five-coordinate, *high-spin*, deoxy form to the six-coordinate, lower-spin, oxy form leads to a contraction in the porphyrin core size as well as in the Fe–N(ax) bond length.
2. The Fe–N(eq) distances (core sizes) (which are about 2.00 – 2.03 Å) depend little on the selected spin state.
3. One electron in O₂-π_g* leads to a longer Fe–O bond as compared to that in the closed-shell singlet.

The experimental structural parameters given in Table 4 are those measured for oxy-Mb,⁵¹ which is thought to be open-shell singlet. Several other DFT calculations (CPMD-BP,¹⁵ Turbo-BP,^{19a} Turbo-OLYP,^{19a} Turbo-B3LYP,^{19a} Jaguar-BP,⁵³ and Jaguar-B3LYP⁵³) on FeP(ImP)(O₂) from the literature are listed here for comparison; they were performed, however, just for the S = 0(O) state.

The Fe–N(eq) distance in oxy-Mb is 2.01 Å, which represents about 0.04 Å core-size expansion as compared to FeTPP (1.97 Å). This trend is well reproduced by our calculations on FeP and FeP(Im)(O₂). On the other hand, good quantitative agreement is found between the experimental data and the BP optimized structures in the S = 1 and S = 0(O) states. Again, the calculated R_{Fe–N(eq)} is insensitive to the choice of functional. But a large change in R_{Fe–N(ax)} or R_{Fe–O} may occur from one functional to another. Particularly, large Fe–N(ax) bond lengths are obtained with OLYP. Similar results are also obtained by the other calculations^{19a} with the same functional. The B3LYP and PBE0 calculated R_{Fe–N(ax)} values are generally comparable to the BP ones, except for the B3LYP value in the S = 0(O) state, which is ca. 0.08 Å larger than the BP one. Similarly, comparable, relatively large Fe–N(ax) distances are also obtained in the Turbo^{19a} and Jaguar⁵³ calculations with the same B3LYP functional. Concerning the Fe–O distance, the various functionals give similar results for the S = 0(C) and S = 1 states. But for the S = 0(O) state, the OLYP, B3LYP, and PBE0 functionals all predict much longer Fe–O distances than BP. In the other calculations,^{19a,53} the OLYP and B3LYP calculated Fe–O distances in the S = 0(O) state are also larger than the BP one, but the trend there seems to be less pronounced than that in our results. The Fe–O distances calculated with BP in the S = 0(O) state are all in reasonable agreement with experiment.

There are no notable changes in the various R values from one basis set to another.

3.1.2. Spin-state energetics—We then calculated the spin-state energetics (i.e. relative energies E_{relative} for selected states) of the systems at the various functionals' optimized structures and with the different basis sets. The spin-state energetics of FeP, FeP(Im), and FeP(Im)(O₂) calculated with the various functionals at the BP/TZP optimized structure are

collected in Table 5. The results calculated at different functionals' optimized structures and with different basis sets are provided in Supporting Information.

For FeP, there are little changes in the calculated structure from one functional to another (see Table 2). Therefore, little changes are found in the spin-state energetics with a choice of structures optimized by different functionals (see Table S1). Similar cases occur for FeP(Im) and for FeP(Im)(O₂) in the $S = 0$ (C) and $S = 1$ states, although the Fe-N(ax) distance may be rather different for different functionals. It is shown that only a change of the Fe-O distance may affect the relative energies of the spin states. This is just the case for FeP(Im)(O₂) in the $S = 0$ (O) state, and we will discuss this issue later. As to the effects of basis sets, little changes in the spin-state energetics are observed from TZP to TZ2P to TZ2P+ for every system (Supporting Information), indicating that the TZP basis set is good or reliable enough in the calculations. Some changes in the energetics may occur from DZP to TZP. For example, the DZP calculated relative energies for the $S = 0$ state of FeP are systematically smaller by ca. 0.1 eV than those obtained with TZP.

Magnetic measurements^{8,10} have established that the unligated, four-coordinate iron porphyrin is intermediate spin ($\mu = 4.4 \mu_B$). Previous calculations^{31,32} using the BP and other functionals show that the ground state of FeP is $^3A_{2g}$ arising from the $(d_{xy})^2(d_{z^2})^2(d_{xz}, d_{yz})^2$ configuration, in agreement with various experimental assignments.⁸⁻¹² Based on previous studies,³² a reliable energy gap between the quintet and triplet states of FeP was estimated to be 0.1 – 0.2 eV. According to this criterion, the BP and PBE functionals overestimate the relative energy (E^{relative}) of the high-spin state by about 0.5 eV. A revised PBE (revPBE) shows some improvement over PBE in calculating the energetics of the high-spin state. The PBE0 functional, however, predicts the quintet to be the ground state, in disagreement with experiment. HCTH/40 indicates nearly degenerate triplet and quintet states. From Table 5, the functionals that are able to provide a satisfactory description of the energetics of FeP, are OPBE, OPerdew, OLYP, τ -HCTH, B3LYP, B97, and τ -HCTH-hyb.

It has been shown^{30,32} that the inclusion of some HF exchange in the GGA has a large effect on the energetics of the high-spin states. In general, the more the HF exchange admixture is, the lower the resulting E^{relative} for the high-spin state. Thus, the B3LYP* functional, where the HF exchange admixture is reduced from 20% (in original B3LYP) to 15%, yields a more positive E^{relative} for the quintet than does B3LYP. In contrast, PBE0, which includes 25% HF exchange, gives a slightly negative E^{relative} for the quintet and so underestimates the relative energy for the high-spin state. For the unligated, four-coordinate iron porphyrins, the singlet is much higher in energy than either the triplet or quintet.

The attachment of L to FeP reduces significantly the energy differences among the spin states. While the calculations with BP show the triplet and singlet to be nearly degenerate, the PBE calculations give a clear energetic preference of ca. 0.1 eV for the singlet over the triplet. Then revPBE yields results similar to BP. However, all other functionals show the energy of the singlet to be notably higher than that of the triplet. For FeP(Im), nearly the same energetics of the triplet and quintet are obtained with OPBE, OPerdew, and OLYP; the three functionals that use the OPTX correction for exchange give results which are very close. The same is true for any other complexes. In contrast, the meta-GGA and most hybrid functionals favor the quintet over the triplet by a clear amount of energy. The results that show a high-spin ground state for FeP(Im) can be considered as reliable. The calculation with B3LYP* that contains only 15% HF exchange, still predicts a triplet ground state for FeP(Im).

Previous CPMD calculations¹⁵ on FeP(Im) used only the BP functional in evaluating the energetics of the spin states. Their results for E^{relative} are somewhat different from ours calculated with the same functional. CPMD-BP predicted a clear trend in the E^{relative} : $S = 1 < S = 2 < S = 0$, while our results vary in the order $S = 1 \approx S = 0 < S = 2$. A triplet ground state was also obtained in the G94-B3LYP calculations.¹⁶ Our B3LYP results, which give a high-spin ground state for FeP(Im), may be considered to be more accurate.

For FeP(Im)(O₂), the calculated energetics of the spin states are again sensitive to the DFT method employed. We first examine the results obtained at the structure optimized with the BP functional, which are given in Table 5. As mentioned above, BP gives an excellent description of molecular structure for FeP(Im)(O₂). In general, all the GGA functionals except HCTH/407 predict the closed-shell singlet [$S = 0(\text{C})$] and the triplet ($S = 1$) to be nearly degenerate; the open-shell singlet [$S = 0(\text{O})$] lies 0.1 – 0.3 eV higher in energy. For the calculations with the other functionals, the ground state of the complex is a triplet. HCTH/407 and the meta-GGA functionals give a order of E^{relative} as $S = 1 < S = 0(\text{C}) < S(\text{O})$, while the hybrid functionals yield an opposite order between $S = 0(\text{C})$ and $S = 0(\text{O})$, namely $S = 1 < S = 0(\text{O}) < S(\text{C})$. Examining the energetics obtained by the OLYP, B3LYP, or PBE0 functional at its own optimized structure, which gives a rather long Fe-O bond distance in the $S = 0(\text{O})$ state, we can see a significant reduction in the relative energy of the $S = 0(\text{O})$ state for the hybrid functionals, so that the triplet and open-shell singlet energies are virtually degenerate. But the Fe-O bond distances optimized by these functionals are probably greatly overestimated.

Experimental results on the oxy forms of Hb/Mb and synthetic models have been interpreted in term of a $\text{Fe}^{\text{III}}\text{-O}_2^-$ bonding picture⁵⁴ and these iron superoxide complexes were shown to be diamagnetic ($\mu = 0$).²¹ Our calculations with the hybrid functionals clearly support the electron-transfer superoxide $\text{Fe}^{\text{III}}\text{-O}_2^-$ model for FeP(L)(O₂); a diamagnetic FeP(Im)(O₂) complex is then obtained at the structures optimized by the hybrid functionals.

3.1.3. FeP–Im and FeP(Im)–O₂ bonding energies—The Heme–O₂ bonding energy has been studied intensively because of its importance in the understanding of the hemoprotein functions. There are no direct measurements of E_{bond} for O₂ bound to a natural heme or a synthetic FePor(L) model. The experimental datum cited here (Table 6) refers to the dissociation barrier for Mb, corrected for the absence of the protein environment;^{19a} it is 0.44 eV. Accurate prediction of bonding energies for diatomic ligands to heme is a difficult issue in theoretical computations;^{18,19a,53} where pure DFT functionals overestimate the binding of O₂, while hybrid functionals underbind the ligand. The high-level *ab initio* CASPT2 calculations^{19a} on FeP(Im)(O₂) with a large basis set are seen to give result that agrees well with “experiment”.

Here, the FeP(Im)–O₂ bonding energy has been evaluated with five functionals (BP, PBE, OLYP, B3LYP, PBE0) and with different basis sets. The results are provided in Table 6. It should be pointed out that the E_{bond} 's obtained at different functionals' optimized structures are almost the same.

Compared with the experimental and CASPT2 data, our BP/TZP calculated FeP(Im)–O₂ bonding energy (0.81 eV) is about 0.4 eV too large. An even larger E_{bond} value (1.19 eV) was obtained in a recent calculation with BP.^{19a} However, the B3LYP functional underestimates the E_{bond} by a same amount (~0.4 eV). OLYP shows some improvement over B3LYP, whereas PBE is inferior to BP. PBE0 gives a negative value for E_{bond} , thereby severely underbinding the ligand. A similar case was also found in other calculations with PBE0.⁵³ A DFT + U calculation with the optimal parameter $U = 4.0$ eV gave an E_{bond} of 1 kcal/mol (0.04 eV),¹⁸ which is comparable to our B3LYP value (0.05 eV). A further test of

the other functionals indicates that revPBE and Becke00 predict FeP(Im)–O₂ bonding energies (0.51 and 0.31 eV respectively) which are quite close to experiment (see Supporting Information). Again, no significant discrepancies among the TZP, TZ2P, and TZ2P+ basis sets are found for the bonding energy prediction. But there is some change in E_{bond} from DZP to TZP.

An alternative argument suggests that the binding of O₂ to a free iron porphyrin without a distal cavity should be very weak.¹⁸ This argument is based on the fact there has been experimental difficulty to isolate an oxygenated species; the O₂ molecule in hemoproteins is stabilized by a second interaction of the distal side (hydrogen bond, trapping effect, etc.). Therefore, a very small FeP(Im)–O₂ bonding energy (0.04 eV) obtained with the DFT + U method was claimed to be reasonable.¹⁸ But it should be pointed out that the experimental difficulty to isolate oxygenated iron porphyrins in solution is probably due to the fact that Fe^{II} is easily oxidized to Fe^{III} and not to the fact that the bond is extremely weak.

Table 6 also lists the calculated FeP–Im bonding energies in FeP(Im). They range from 0.13 eV (B3LYP) to 0.66 eV (PBE). No experiment or other calculations are available to compare with these results.

In the next sections, our calculations on the other FeP(L) and FeP(L)(O₂) systems with the various density functionals are performed at the BP optimized structures and with the TZP basis sets only. As is shown above, the BP functional performs very well with respect to the experimental structure in each case and the chosen basis set is also reliable enough in these calculations. In most cases, the changes in the calculated molecular structure by using different functionals are in fact small.

3.2. The Other FeP(L) Complexes

The calculated structural parameters for the various FeP(L) complexes (including FeP(Im) for comparison) are presented in Table 7, together with the FeP–L bonding energies evaluated by BP and B3LYP in their respective calculated ground states. The relative energies for selected states calculated with various functionals are collected in Tables 8 and 9.

3.2.1. FeP(1-MeIm)—According to the E_{bond} values, 1-MeIm is slightly more tightly bound to FeP than Im; the -CH₃ group in 1-MeIm acts as a σ -donor, which favors the coordination of the ligand L to Fe. BP and B3LYP give the same increase of 0.04 eV in E_{bond} from L = Im to L = 1-MeIm. The structural parameters of FeP(1-MeIm) do not show notable difference from those of FeP(Im).

The -CH₃ group in 1-MeIm is shown to have a notable influence on the calculated relative energy of the high-spin state. From L = Im to L = 1-MeIm, the E^{relative} values for S = 2 are increased by 0.03 eV with BP and 0.06 – 0.11 eV with the other functionals. Therefore, certain meta-GGA and hybrid functionals (Becke00, B3LYP, and τ -HCTH-hyb) that give a negative E^{relative} of S = 2 for FeP(Im), now yield a slightly positive value for FeP(1-MeIm) (the E^{relative} of S = 1 is set to zero). A comparable complex FeTpivPP(1-MeIm) (no X-ray structure data are available) was suggested to be high spin based on a measured magnetic moment of $\mu = 4.8 \mu_{\text{B}}$.²¹ But the relatively small μ value may imply that the high-spin state is not fully populated in FeTpivPP(1-MeIm). The expected μ value for a pure S = 2 spin state is as large as $4.9 \mu_{\text{B}}$. A measured magnetic moment is usually larger than the expected μ value. Based on this analysis, FeTpivPP(1-MeIm) may have only partial population of the high-spin state, which is admixed with the intermediate-spin state. In fact, our calculations with reliable DFT methods do not clearly yield a high-spin ground state for FeP(1-MeIm); instead, here a high-spin and an intermediate-spin state are nearly degenerate.

3.2.2. FeP(2-MeIm) and FeP(1,2-Me₂Im)—The effect of 2-MeIm on FeP is shown to be rather different from that of 1-MeIm. The -CH₃ group in 2-MeIm makes a short contact with the porphyrin and hence leads to a repulsive steric interaction with the porphyrin ring. Therefore, there is a significant increase in the Ct(N4)···Fe and Fe-N(ax) separations in FeP(2-MeIm) as compared to those in FeP(Im). The steric repulsion between -CH₃ and the porphyrin ring also makes the Fe-N(ax) bond weaker, particularly for the singlet. But no change is found in the porphyrin core size from FeP(Im) to FeP(2-MeIm). There are X-ray crystal structural data available for an analogous system FeTPP(2-MeIm)·EtOH,²⁰ so that a straightforward comparison with experiment can be made here. The molecular structure of FeTPP(2-MeIm) in the crystal is characterized by the Fe atom being out of plane by 0.42 Å from the mean plane defined by the 4 porphyrin nitrogens (N4). The calculated critical structural parameters for FeP(2-MeIm) in *S* = 2 agree very well with the experimental ones. This further confirms the fact that the real FeTPP(2-MeIm) complex is high spin.

The increase in both $R_{\text{Ct(N4)}\cdots\text{Fe}}$ and $R_{\text{Fe-N(ax)}}$ from FeP(Im) to FeP(2-MeIm) gives rise to a change in the relative energies of the spin states. There is a notable increase in E^{relative} for the singlet, while the quintet is stabilized slightly; the trends in E^{relative} are opposite to those from FeP(Im) to FeP(1-MeIm). While FeP(1-MeIm) is thought by us to be a spin-admixed (*S* = 2, 1) system, the FeP(2-MeIm) species has a clear preference for a high-spin state as the ground state according to both calculation and experiment. The measured magnetic moment for FeTPP(2-MeIm) is 5.3 μ_{B} ,²¹ significantly larger than that for FeTpivPP(1-MeIm) (4.8 μ_{B}),²¹ and also larger than the expected value (4.9 μ_{B}) of a pure *S* = 2 state.

Upon introducing a sterically unhindered 1-methyl group on the imidazole, the electron-donating property of -CH₃ always makes the axial ligand coordinate slightly more strongly with the iron ion according to the BP results in the singlet. In the high-spin state, the B3LYP functional does not yield the same trend in E^{relative} . The relative energy of the high-spin state is increased somewhat from FeP(2-MeIm) to FeP(1,2-Me₂Im), which seems to indicate that the Fe-N(ax) bond is slightly stronger in FeP(1,2-Me₂Im) than in FeP(2-MeIm). Nevertheless, a high-spin ground state is still expected for the former system.

3.2.3. FeP(4-EtIm) and FeP(His)—The calculated structural parameters and FeP-L bonding energy in FeP(4-EtIm) are very close to those obtained in FeP(1-MeIm), as are the calculated relative energies for the singlet. However, a notable difference between FeP(4-EtIm) and FeP(1-MeIm) is found in the relative energy of the quintet, which is lower for the former than for the latter. Therefore, FeP(4-EtIm) clearly has a high-spin ground state according to the calculations with the reliable DFT methods. This is somewhat different from the situation of FeP(1-MeIm). When 4-EtIm is replaced by His, the Fe-L bond is slightly strengthened and as a result, the quintet of FeP(His) is slightly destabilized as compared to that of FeP(4-EtIm). The relative energies of the high-spin state of FeP(His) are then found to be comparable to those of FeP(Im).

3.3. The Other FeP(L)(O₂) Complexes (L = 1-MeIm, 2-MeIm, 1,2-Me₂Im, 4-EtIm, and His)

The BP calculated structural parameters for the various FeP(L)(O₂) complexes (including FeP(Im)(O₂) as well as FeP(O₂) for comparison) are presented in Table 10, together with available X-ray crystal structural data²² on analogous, synthetic systems and with the FeP(L)-O₂ bonding energies evaluated by BP and B3LYP in their respective calculated ground states. The relative energies for selected states calculated with various functionals are collected in Tables 11 and 12.

The structural features revealed for FeP(Im)(O₂) (see Section 3.1.1) are also possessed by the other FeP(L)(O₂) complexes. The Fe-N(eq) distances or core sizes (2.00 – 2.03 Å) in FeP(Im)(O₂) depend little on the selected state. Here from Table 10, they also depend little

on the system. From $L = \text{Im}$ to $L = 1\text{-MeIm}$, nearly no changes in the structural parameters are observed, as for the five-coordinate systems. The situation may be different when L is another ligand.

In the open-shell singlet $S = 0(\text{O})$, the bulky 2-methyl group on the 2-MeIm ligand results in lengthened Fe-O bond relative to the sterically less demanding 1-MeIm; the trend is in agreement with the X-ray structural data²² on FeTpivPP(1-MeIm)(O₂) and FeTpivPP(2-MeIm)(O₂), but different from the CPMD-BP calculated results¹³ on FeP(Im)(O₂) and FeTpivPP(2-MeIm)(O₂) in the same state, where the obtained $R_{\text{Fe-O}}$ values for the two complexes are very close. [Note that there is no difference in $R_{\text{Fe-O}}$ between FeP(Im)(O₂) and FeP(1-MeIm)(O₂)]. The structure of the triplet also corresponds to a larger Fe-O-O angle. The O-O bond lengths for different spin states and different systems are very similar, 1.28 – 1.30 Å, which represents a bond expansion of 0.04 – 0.06 Å from the bond length of free O₂ (1.24 Å).

Fe is not entirely in the porphyrin N4 plane in the six-coordinate iron porphyrin with two axial hetero ligands and a slight out-of-plane displacement of Fe occurs in every FeP(L)(O₂); $R_{\text{Cl(N4)}\cdots\text{Fe}}$ is negative with $L = \text{Im}$, 1-MeIm, 4-EtIm, and His, denoting that Fe is on the same side of the porphyrin-N4 plane as O₂, while it is positive with $L = 2\text{-MeIm}$ and 1,2-Me₂Im. The subtle change in $R_{\text{Cl(N4)}\cdots\text{Fe}}$ from $L = 1\text{-MeIm}$ to $L = 2\text{-MeIm}$ is consistent with the available X-ray structural data²² on FeTpivPP(1-MeIm)(O₂) and FeTpivPP(2-MeIm)(O₂).

Concerning the calculated energetics of the spin states, all the GGA functionals except HCTH/407 predict the closed-shell singlet [$S = 0(\text{C})$] and the triplet ($S = 1$) to be nearly degenerate for every FeP(L)(O₂); the open-shell singlet [$S = 0(\text{O})$] lies 0.1 – 0.3 eV higher in energy. For the calculations with the other functionals, the ground state of the complex is either a triplet or an open-shell singlet, depending on the ligand L . A clear triplet ground state is obtained with $L = \text{Im}$, 1-MeIm, or 4-EtIm. With $L = 2\text{-MeIm}$ or 1,2-Me₂Im, there is a large relative stabilization of the open-shell singlet and according to the B3LYP and PBE0 results, this state is favored over the triplet by 0.03 – 0.05 eV. In fact, all the hybrid functionals are seen to yield a rather small energy difference between the open-shell singlet and the triplet, as do the HCTH/407 and τ -HCTH functionals. We failed to obtain results for the open-shell singlet of FeP(His)(O₂), as we encountered SCF convergence problems with this state for this complex. But we may see that the calculated relative energies of the triplet of FeP(His)(O₂) are all surprisingly very similar to those of FeTpivPP(2-MeIm)(O₂), which has an open-shell singlet ground state according to the calculations with B3LYP, B3LYP*, PBE0, and B97 (see next Section). A great similarity is found among the state relative energies of FeP(Im)(O₂), FeP(1-MeIm)(O₂), and FeP(4-EtIm)(O₂) or between the state relative energies of FeP(2-MeIm)(O₂) and FeP(1,2-Me₂Im)(O₂). Without a ligand L , the FePO₂ species clearly has an open-shell singlet according to our calculations with the hybrid functionals.

Our calculations seem to indicate that the weaker the Fe-L bond in FeP(L), the more likely the ground state of FeP(L)(O₂) is an open-shell singlet. A variation of the calculated $E_{\text{bond}}(\text{FeP-L})$ with various L is schematically illustrated in Figure 5. The ligation with the ligand which lies under the dashed line (i.e. 2-MeIm, 1,2-Me₂Im) gives a preferred open-shell singlet. The B3LYP calculated $E_{\text{bond}}(\text{FeP-L})$ shows similar variation with L to BP, although the two functionals yield rather different absolute $E_{\text{bond}}(\text{FeP-L})$ values for a given system.

A large difference is also found between the BP and B3LYP calculated FeP(L)-O₂ bonding energies $E_{\text{bond}}[\text{FeP(L)-O}_2]$, but they show a similar trend, as illustrated in Figure 6. Our BP

value of $E_{\text{bond}} = 0.81$ eV for $L = \text{Im}$ is comparable to a previous CPMD-BP result (0.65 eV) (see Section 3.1.3 above for a detailed discussion of the $\text{FeP}(\text{Im})\text{--O}_2$ bonding energy). The E_{bond} values obtained with B3LYP are all very small, at most 0.05 eV. But the $\text{FeP}(\text{L})\text{--O}_2$ bonding energy is expected to be small in view of the (experimental) fact that O_2 molecule is bound only weakly to Fe.

According to the B3LYP results, the Fe- O_2 bond strength is always enhanced in the presence of the axial L; $E_{\text{bond}}(\text{Fe-O}_2)$ is increased by 0.26 eV from $\text{FeP}(\text{O}_2)$ to $\text{FeP}(\text{Im})(\text{O}_2)$. This increase is less pronounced in the BP results. A significant decrease in $E_{\text{bond}}(\text{Fe-O}_2)$ is then found on going from $L = 1\text{-MeIm}$ to $L = 2\text{-MeIm}$. According to experiments,²² the change in L from 1-MeIm to 2-MeIm produces a ten-fold decrease in the O_2 affinity to Fe. The trend in the calculated E_{bond} values is at least in qualitative agreement with the experimental results. There is nearly no change in $E_{\text{bond}}(\text{Fe-O}_2)$ from $L = 2\text{-MeIm}$ to $L = 1,2\text{-Me}_2\text{Im}$.⁵⁵ The calculated Fe- O_2 bonding energy for $L = 4\text{-EtIm}$ is the same as that for $L = \text{Im}$, but smaller than that for $L = \text{His}$.

There are two different structural forms of Hb, the low-affinity “T” state and the high-affinity “R” state.^{4,24} Since 2-MeIm or 1,2-Me₂Im lowers the O_2 affinity to Fe, its complex has been used as model for the T-form of Hb.²⁴ According to experimental studies,²⁴ iron porphyrins with 2-MeIm at least mimic (if not model) T-state Hb; on the other hand, iron porphyrins with 1-MeIm could be taken as models for Hb in the R state.

3.6. FeTpivPP, FeTpivPP(2-MeIm) and FeTpivPP(2-MeIm)(O_2)

Finally, we report our calculations on FeTpivPP, FeTpivPP(2-MeIm), and FeTpivPP(2-MeIm)(O_2). Table 13 displays the calculated relative energies for selected states of the three systems. The optimized structural parameters have been reported in Tables 2, 7, and 10, respectively. The five-coordinate ‘picket-fence’ iron porphyrin is the first synthetic heme model system and has oxygen affinities similar to the values measured for hemoproteins.²⁴ Its O_2 adduct has thus attracted much interest as a model for oxyHb and oxyMb.

For FeTpivPP, there are no notable differences in both the calculated bond lengths and spin-state energetics as compared with the results for FeP. The magnetic moment of this complex was early reported to be $5.0 \mu_{\text{B}}$,^{21b} suggesting a high-spin ground state with $S = 2$. This seems to be at variance with the theoretical results obtained through the various functionals. No X-ray crystal structural determinations have been reported for four-coordinate FeTpivPP. Since there is an apparent correlation between the Fe-N(eq) bond length and the spin state of the iron ion, only crystal structural data are able to provide the most convincing evidence as to whether FeTpivPP is intermediate- or high spin.

A high-spin ground state is definitely established for FeTpivPP(2-MeIm) on the basis of the X-ray crystal structural data,²². Previous CPMD-BP calculations¹³ on this complex at its relaxed structure predicted its ground state to be triplet, in disagreement with experiment. In contrast, our calculations with HCTH/407, $\tau\text{-HCTH}$, B3LYP, PBE0, and B97 clearly show the ground state of the complex to be high spin. While no notable differences in electronic structure are found between FeTpivPP and FeP (see Table 5), the high-spin state of FeTpivPP(2-MeIm) is less stabilized as compared to that of FeP(2-MeIm). Therefore, the $\tau\text{-HCTH-hyb}$ functional, which yields a high-spin ground state for FeP(2-MeIm), now gives a preference of the triplet over the quintet by 0.03 eV for FeTpivPP(2-MeIm).

The open-shell singlet of FeTpivPP(2-MeIm)(O_2) seems to be somewhat more stabilized as compared to that of FeP(2-MeIm)(O_2); this state is never higher in energy than the triplet according to the calculations with every hybrid functional here. The B3LYP results show the

open-shell singlet to be energetically favored over the triplet by as much as 0.1 eV, which is in agreement with the diamagnetism of the complex.^{21,22}

Our BP calculated Fe–O₂ bonding energy in FeTpivPP(2-MeIm)(O₂) is 0.71 eV, nearly the same as that (0.70 eV) in FeP(2-MeIm)(O₂); the $E_{\text{bond}}(\text{Fe-O}_2)$ is not affected by this particular peripheral substitution. This is in agreement with the experimental fact that the “picket-fence” iron porphyrin binds O₂ with an affinity similar to that of Mb, but in contrast to the CPMD-BP calculations which show the picket-fence environment considerably stabilizes the binding of O₂ to Fe (by 1.39 eV). The CPMD-BP calculated E_{bond} in FeTpivPP(2-MeIm)(O₂) is as large as 2.04 eV, which may be too large for the O₂ molecule to be released from the compound once it is adsorbed. Our B3LYP calculations show an increase of 0.06 eV in $E_{\text{bond}}(\text{Fe-O}_2)$ from FeP(2-MeIm)(O₂) to FeTpivPP(2-MeIm)(O₂); the trend is also much weaker than that from the CPMD calculations. Although the tertiary butyl and amide N-H groups of the “picket-fence” are turned inward toward coordinated O₂ (see Figure 2), the distances between the protons and the terminal O atom are large, which were thought to preclude any possibility of hydrogen bonding.²¹

4. Conclusions and Remarks

The computations on all the complexes studied here provide a detailed and comprehensive comparison of the effects of the various axial imidazole ligands on the structures and energetics of the various spin states of the deoxy- and oxy iron porphyrins. An extensive test of several functionals and basis sets were performed on FeP, FeP(Im), and FeP(Im)(O₂). The BP functional performs very well with respect to the experimental structure in each case. The other functionals yield somewhat longer axial bond distances in certain states. But in most cases, the changes in the calculated molecular structure by using different functionals are small. The basis set effects are insignificant within the ADF framework, presumably because of the use of Slater-type orbitals (STOs), in contrast to the other previous calculations.^{19a} The chosen TZP basis set is adequate in the present calculations. The results for the energetics obtained with the different functionals are, however, considerably different, which indicates that the choice of functional is crucial.

Upon introducing a methyl group on the imidazole ring, the electron-donating property of –CH₃ makes the 1-MeIm ligand coordinate a little more strongly with FeP than does Im. The 2-methyl group in 2-MeIm, however, increases steric contact between the ligand and the porphyrinato skeleton, thereby weakening the FeP–L bond significantly. The calculations with the reliable DFT methods correctly predict a high-spin ground state for FeP(2-MeIm) and FeTpivPP(2-MeIm). But the ground state of FeP(1-MeIm) may be an admixture of a high-spin ($S = 2$) and an intermediate-spin ($S = 1$) state. Experiments have indicated a difference in the effects of 1-MeIm and 2-MeIm on the electronic structure of their iron porphyrin complexes. The measured magnetic moment of FeTPP(2-MeIm) ($\mu = 5.3 \mu_B$)²¹ is significantly larger than that of FeTpivPP(1-MeIm) ($\mu = 4.8 \mu_B$).²¹ The trend in the calculated relative energies of the high-spin state from L = 1-MeIm to L = 2-MeIm is qualitatively consistent with experiment. The FeP(L) complexes with the other imidazole ligands are predicted to be high spin as well by the calculations with the reliable DFT methods. While there is a significant bond lengthening of the Fe–N(ax) bond from L = 1-MeIm to L = 2-MeIm, no notable change in the structural parameters is found from L = Im to L = 1-MeIm or from L = 2-MeIm to L = 1,2-Me₂Im.

Concerning FeP(L)(O₂), our calculations with the hybrid functionals clearly support the electron-transfer superoxide Fe^{III}–O₂[–], but the spin multiplicity of the complex may be different for different L; the weaker the Fe–L bond in FeP(L) is, the more likely the ground state is an open-shell singlet. Therefore, at the BP optimized structures, which are in good

agreement with experiment, the $\text{FeP(L)(O}_2\text{)}$ complexes with $\text{L} = 2\text{-MeIm}$ and $1,2\text{-Me}_2\text{Im}$ are predicted to be in an open-shell singlet, while those with $\text{L} = \text{Im}$, 1-MeIm , and 4-EtIm are calculated to be triplet. According to the extended calculations on $\text{FeP(Im)(O}_2\text{)}$, the hybrid functionals (B3LYP, PBE0) give a rather long Fe–O bond distance in the $S = 0(\text{O})$ state, and so they (nearly) yield an open-shell singlet ground state for this system at these hybrid functionals' optimized structures. But the Fe–O distances obtained with these hybrid functionals are probably significantly overestimated.

In addition to the electronic structure, the calculations also show how the Fe– O_2 bonding in $\text{FeP(L)(O}_2\text{)}$ is affected by changes in L. The strength of the O_2 bonding to Fe is decreased notably from $\text{L} = 1\text{-MeIm}$ to $\text{L} = 2\text{-MeIm}$. Therefore, iron porphyrins with 2-MeIm mimic T-state (low-affinity) Hb and those with 1-MeIm could be taken as models for R-state (high-affinity) Hb. The Tpivot groups surrounding the central iron porphyrin in FeTpivotPP are not shown to have a notable influence on the Fe– O_2 bond strength. This is in agreement with experiment, but differs from the CPMD-BP calculated results which show the “picket-fence” environment considerably stabilizes the O_2 bonding to Fe.

According to the calculations, the Im and 4-EtIm ligands closely resemble histidine (His), the biologically axial base. Future computations on the hemoprotein models can be simplified safely by using Im; there are no notable differences in the electronic structure and bonding between the complexes with $\text{L} = \text{Im}$ and 4-EtIm.

So far, no one has found a universally “best” functional for accurate prediction of geometries and energies of varieties of systems. In the present work, the BP functional gives an excellent molecular structure in each case, but fails to predict the high-spin nature of the system. The hybrid functionals (B3LYP, PBE0) predict a good level of accuracy for the spin-state energetics, but they probably overestimate the $\text{FeP(L)}\text{--}\text{O}_2$ bond length in the $S = 0(\text{O})$ state and underestimate this bond strength.

In recent years, Truhlar's group proposed various new functionals, called M05,⁵⁶ M05-2X,⁵⁷ M06,⁵⁸ M06-2X,⁵⁸ and M06-L.⁵⁹ They belong to the fourth rung of Jacob's ladder and are claimed to perform well for kinetics, thermochemistry, and non-covalent interactions. These functionals have been implemented in the updated computational program used here. The updated program has also included several very recently developed functionals: revTPSS,⁶⁰ PBEsol,⁶¹ RGE2,⁶² and SSB-D.⁶³ It would be of interest to see how well these functionals perform for the iron porphyrins. We have thus carried out some additional test calculations on the spin-state energetics of FeP, FeP(Im) , $\text{FeP(Im)(O}_2\text{)}$ at the BP optimized structures. The results are reported in Supporting Information (Table S7), and they show that only the SSB-D and M06-L functionals yield reasonable results for both FeP and FeP(Im) . Furthermore, we have also tried to evaluate, at the BP optimized structures, the FeP–Im and $\text{FeP(Im)}\text{--}\text{O}_2$ bonding energies with the various functionals that include all the functionals given in Table 1. The results are presented in Supporting Information as well (Table S8). As mentioned in Section 2, certain GGA, meta-GGA and hybrid GGA functionals included in the program are treated in a non-SCF manner and for calculations of the relative energies (E^{relative}) of spin states in a molecule, the non-SCF and SCF procedures yield very close results. But for calculations of E_{bond} , the non-SCF procedure could produce a large error. This is because E_{bond} is the difference of energies among different species ($\text{AB} \rightarrow \text{A} + \text{B}$) while the E^{relative} values of different spin states are calculated on a same species; there are error cancellations in the non-SCF calculation of E^{relative} , but not in E_{bond} when the non-SCF procedure is adopted. However, the mentioned error in E_{bond} can be reduced greatly when the accuracy of the numerical integration is increased. Thus we set a high level of integration accuracy (accint = 7.0) in the non-SCF calculations of E_{bond} . For the sake of comparison, the SCF results of E_{bond} obtained with a number of functionals are provided in

Table S8. (For the M05/M06 series of functionals, high integration accuracy is always required even for calculations in the SCF manner.) We can see that the non-SCF and SCF procedures give very close E_{bond} results for all the GGA functionals. A large difference between the non-SCF and SCF E_{bond} results is usually found for a hybrid functional, particularly M06-2X. Among the recently developed functionals, TPSSH appears to give the best $E_{\text{bond}}[\text{FeP}(\text{Im})-\text{O}_2]$ result (non-SCF: 0.41 eV, SCF: 0.44 eV) as compared to the estimated experimental value (0.44 eV), whereas the E_{bond} values obtained the GGA and meta-GGA functionals are more or less overestimated (by 0.1 – 0.7 eV). None of the M05/M06 functionals yields a reasonable $E_{\text{bond}}[\text{FeP}(\text{Im})-\text{O}_2]$ value (Negative values of –2.0 eV to –0.3 eV are obtained by these functionals).

Finally we examined the effects of relativity on the spin-state energetics; they are supposed to be non-negligible for Fe. Thus, a set of additional non-relativistic calculations were carried out on FeP, FeP(Im), and FeP(Im)(O₂). The results are provided in Supporting Information. It is shown that the relativistic effects amount to about 0.05 eV.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References and Notes

- (1). We use Por to refer to any porphyrin, regardless of substituents.
- (2). Berezin, BD. Coordination Compounds of Porphyrins and Phthalocyanines. John Wiley & Sons Ltd; New York: 1981.
- (3). Lever, ABP.; Gray, HB., editors. Iron Porphyrins. Addison-Wesley publishing company Inc.; Massachusetts: 1983.
- (4). Scheidt WR, Reed CR. Chem. Rev. 1981; 81:543.
- (5). Collman JP, Brauman JI, Halbert TR, Suslick. K. Proc. Natl. Acad. Sci. USA. 1976; 73:3333.
- (6). Collman JP, Fu L, Zingg A, Diederich F. J. Chem. Soc., Chem. Commun. 1997:193.
- (7). Poulos TL. Adv. Inorg. Biochem. 1988; 7:1. [PubMed: 2821744]
- (8). Collman JP, Hoard JL, Kim N, Lang G, Reed CA. J. Am. Chem. Soc. 1975; 97:2676. [PubMed: 166106]
- (9). Lang G, Spartalian K, Reed CA, Collman JP. J. Chem. Phys. 1978; 69:5424.
- (10). Boyd PDW, Buckingham DA, McMeeking RF, Mitra S. Inorg. Chem. 1979; 18:3585.
- (11). Goff H, La Mar GN, Reed CA. J. Am. Chem. Soc. 1977; 99:3641. [PubMed: 858871]
- (12). Mispelter J, Momenteau M, Lhoste JM. J. Chem. Phys. 1980; 72:1003.
- (13). Rovira C, Parrinello M. Chem. Eur. J. 1999; 5:250.
- (14). Liao MS, Scheiner S. J. Chem. Phys. 2002; 116:3635.
- (15). Rovira C, Kunc K, Hutter J, Ballone P, Parrinello M. J. Phys. Chem. A. 1997; 101:8914.
- (16). Kozłowski PM, Spiro TG, Zgierski MZ. J. Phys. Chem. B. 2000; 104:10659.
- (17). Scherlis DA, Estrin DA. Intl. J. Quantum Chem. 2002; 87:158.
- (18). Scherlis DA, Cococcioni M, Sit P, Marzari N. J. Phys. Chem. B. 2007; 111:7384. [PubMed: 17547444]
- (19) (a). Radon M, Pierloot K. J. Phys. Chem. A. 2008; 112:11824. [PubMed: 18942804] (b) Zhao Y, Truhlar DG. J. Chem. Theory Comput. 2010; 6:1104.

- (20). Jameson GB, Molinaro FS, Ibers JA, Collman JP, Brauman JI, Rose E, Suslick KS. *J. Am. Chem. Soc.* 1978; 100:6769.
- (21) (a). Collman JP, Gagne RR, Reed CA. *J. Am. Chem. Soc.* 1974; 96:2629. [PubMed: 4833715] (b) Collman JP, Gagne RR, Reed CA, Halbert TR, Lang G, Robinson WT. *J. Am. Chem. Soc.* 1975; 97:1427. [PubMed: 1133392]
- (22). Jameson GB, Molinaro FS, Ibers JA, Collman JP, Brauman JI, Rose E, Suslick KS. *J. Am. Chem. Soc.* 1980; 102:3224.
- (23). Collman JP, Gagne RR, Halbert TR, Marchon J-C, Reed CA. *J. Am. Chem. Soc.* 1973; 95:7868. [PubMed: 4759037]
- (24) (a). Collman JP. *Acc. Chem. Res.* 1977; 10:265. (b) Collman JP. *Inorg. Chem.* 1997; 36:5145.
- (25). Blomberg LM, Blomberg MRA, Siegbahn PEM. *J. Inorg. Biochem.* 2005; 99:949. [PubMed: 15811512]
- (26). Dedieu A, Rohmer M-M, Veillard A. *Adv. Quantum Chem.* 1982; 16:43.
- (27). Rawlings DC, Gouterman M, Davidson ER, Feller D. *Intl. J. Quantum Chem.* 1985; 28:773.
- (28). Choe Y-K, Nakajima T, Hirao K. *J. Chem. Phys.* 1999; 111:3837.
- (29). Pierloot K. *Mol. Phys.* 2003; 101:2083.
- (30). Reiher M, Salomon O, Hess A. *Theor. Chem. Acc.* 2001; 107:48.
- (31). Kozłowski PM, Spiro TG, Berces A, Zgierski Z. *J. Phys. Chem. B.* 1998; 102:2603.
- (32). Liao M-S, Watts JD, Huang M-J. *J. Comput. Chem.* 2006; 27:1577. [PubMed: 16868988]
- (33). te Velde G, Bickelhaupt FM, van Gisbergen SJA, Fonseca-Guerra C, Baerends EJ, Snijders JG, Ziegler T. *J. Comput. Chem.* 2001; 22:931.
- (34). ADF2009. 1; SCM: Theoretical Chemistry. Vrije Universiteit; Amsterdam, The Netherlands: also <<http://www.scm.com>>
- (35). Becke AD. *Phys. Rev. A.* 1988; 38:3098. [PubMed: 9900728]
- (36). Perdew JP. *Phys. Rev. B.* 1986; 33:8822.
- (37). Perdew JP, Burke K, Ernzerhof M. *Phys. Rev. Lett.* 1996; 77:3865. [PubMed: 10062328]
- (38). Zhang Y-K, Yang W-T. *Phys. Rev. Lett.* 1998; 80:890.
- (39). Handy NC, Cohen AJ. *Mol. Phys.* 2001; 99:403.
- (40). Lee C, Yang W-T, Parr RG. *Phys. Rev. B.* 1988; 37:785.
- (41). Hamprecht FA, Cohen AJ, Tozer DJ, Handy NC. *J. Chem. Phys.* 1998; 109:6264.
- (42). Boese AD, Handy NC. *J. Chem. Phys.* 2001; 114:5497.
- (43). Becke AD. *J. Chem. Phys.* 2000; 112:4020.
- (44). Boese AD, Handy NC. *J. Chem. Phys.* 2002; 116:9559.
- (45). Becke AD. *J. Chem. Phys.* 1993; 98:5648.
- (46). Adamo C, Barone V. *J. Chem. Phys.* 1999; 110:6158.
- (47). Becke AD. *J. Chem. Phys.* 1997; 107:8554.
- (48). Liao M-S, Watts JD, Huang M-J. *J. Phys. Chem. A.* 2005; 109:11996. [PubMed: 16366654]
- (49). Ziegler T, Tschinke V, Baerends EJ, Snijders JG, Ravenek W. *J. Phys. Chem.* 1989; 93:3050.
- (50). Groenhof AR, Swart M, Ehlers AW, Lammertsma K. *J. Phys. Chem. A.* 2005; 109:3411. [PubMed: 16833677]
- (51). Vojtechovsky J, Chu K, Berendzen J, Sweet RM, Schlichting I. *Biophys. J.* 1999; 77:2153. [PubMed: 10512835]
- (52). Kachalova GS, Popov AN, Bartunik HD. *Science.* 1999; 284:473. [PubMed: 10205052]
- (53). Strickland N, Harvey JN. *J. Phys. Chem. B.* 2007; 111:841. [PubMed: 17249828]
- (54). Momenteau M, Reed CA. *Chem. Rev.* 1994; 94:659.
- (55). It is stated in ref. ²² that the change in L from 1-MeIm to 2-MeIm produces a ten-fold decrease in O₂ affinity to Fe; another ten-fold decrease occurs on replacing 2-MeIm with 1,2-Me₂Im as the axial base. The latter trend is not supported by our calculations. In a more recent paper published by one of the same authors (ref. ^{24b}), a figure shows a ten-fold decrease in the O₂-bonding affinity from L = 1-MeIm to L = 1,2-Me₂Im. This seems to indicate no change in E_{bond}(Fe-O₂) from L = 2-MeIm to L = 1,2-Me₂Im.

- (56). Zhao Y, Schultz NE, Truhlar DG. J. Chem. Phys. 2005; 123:161103. [PubMed: 16268672]
- (57). Zhao Y, Schultz NE, Truhlar DG. J. Chem. Theory Comput. 2006; 2:364.
- (58). Zhao Y, Truhlar DG. Theor. Chem. Acc. 2008; 120:215.
- (59). Zhao Y, Truhlar DG. J. Chem. Phys. 2006; 125:194101. [PubMed: 17129083]
- (60). Perdew JP, Ruzsinszky A, Csonka GI, Constantin LA, Sun J. Phys. Rev. Lett. 2009; 103:026403. [PubMed: 19659225]
- (61). Perdew JP, Ruzsinszky A, Csonka GI, Vydrov OA, Scuseria GE, Constantin LA, Zhou X, Burke K. Phys. Rev. Lett. 2008; 100:136406. [PubMed: 18517979]
- (62). Ruzsinszky A, Csonka GI, Scuseria GE. J. Chem. Theory Comput. 2009; 5:763.
- (63). Swart M, Sola M, Bickelhaupt FM. J. Chem. Phys. 2009; 131:094103. [PubMed: 19739845]

Figure 1.

(a) Iron protoporphyrin IX (FePPIX, heme group) of hemoproteins. (b) The heme group bound to O₂ and in the presence of the distal (His64) and proximal histidines (His93) within the myoglobin (Mb) (*code 1A6M*).

Figure 2.
Molecular structures of FeP, FeTpivPP, and various imidazole ligands.

Figure 3.
Molecular structures of FeP(Im) and FeP(Im)(O₂).

Figure 4.
Orbital energy level diagrams of FeP, FeP(Im), and FeP(Im)(O₂).

Figure 5. Schematic illustration of the calculated FeP–L bonding energies in FeP(L) with the BP and B3LYP functionals.

Figure 6. Schematic illustration of the calculated $\text{FeP(L)}-\text{O}_2$ bonding energies in $\text{FeP(L)}(\text{O}_2)$ with the BP and B3LYP functionals.

Table 1

Density functionals and basis sets used in the Calculations

Functional	Formulation
BP	Becke's 1988 gradient correction for exchange (ref. ³⁵) plus Perdew's 1986 gradient correction for correlation (ref. ³⁶).
PBE	Perdew-Burke-Ernzerhof's 1996 corrections for both exchange and correlation (ref. ³⁷).
revPBE	Revised PBE functional proposed in 1998 by Zhang and Yang (ref. ³⁸).
OPBE	Handy-Cohen's 2001 OPTX correction for exchange (ref. ³⁹) plus PBE correction for correlation.
OPerdew	OPTX correction for exchange plus Perdew's 1986 gradient correction for correlation.
OLYP	OPTX correction for exchange plus Lee-Yang-Parr's 1988 correlation functional (ref. ⁴⁰).
HCTH/407	Hamprecht-Cohen-Tozer-Handy 1998 correction for both exchange and correlation (ref. ⁴¹), containing 15 parameters refined against data from a training set of 407 atomic and molecular systems (ref. ⁴²).
Becke00	Becke's 2000 correction for both exchange and correlation, where the kinetic-energy density $\tau = \sum (\nabla \phi_i)^2$ is included (ref. ⁴³).
τ -HCTH	The kinetic-energy density τ is included in the HCTH/407 form (ref. ⁴⁴).
B3LYP	Becke's 1993 three-parameter hybrid functional (ref. ⁴⁵) using LYP correlation functional.
B3LYP*	The Hartree-Fock (HF) exchange admixture is reduced from 20% (in original B3LYP) to 15% (ref. ³⁰).
PBE0	Parameter-free hybrid functional using the PBE model (ref. ⁴⁶).
B97	Becke's 1997 hybrid functional that contains 10 adjustable parameters (ref. ⁴⁷).
τ -HCTH-hyb	HF exchange is introduced into the τ -HCTH functional (ref. ⁴⁴).

Basis set ^a	Description
DZP	Double- ζ for valence orbitals plus one polarization function.
TZP	Triple- ζ for valence orbitals plus one polarization function.
TZ2P	Triple- ζ for valence orbitals plus two polarization function.
TZ2P+	With one extra d-diffuse function on TZ2P for Fe.

^aThe basis sets and their notations can be found in the following references: (a) van Lenthe, E.; Baerends, E. J. *J. Comput. Chem.* **2003**, *24*, 1142. (b) Chong, D. P.; van Lenthe, E.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Comput. Chem.* **2004**, *25*, 1030. (c) Chong, D. P. *Mol. Phys.* **2005**, *103*, 749. (d) Jensen, L.; Swart, M.; van Duijnen, P. Th.; Snijders, J. G. *J. Chem. Phys.* **2002**, *117*, 3316.

Table 2

Calculated structural parameters (distance R in Å) for selected states of FeP and FeTpivPP (with different functionals and basis sets for FeP)

State	FeP [R _{Fe-N(eq)}]								FeTpivPP	
	TZP				BP				BP/TZP	
	BP	PBE	OLYP	B3LYP	PBE0	DZP	TZ2P	TZ2P+	R _{Fe-N(eq)}	R _{Cu(N4)-Fe}
S = 1 ^a	1.973	1.972	1.979	1.977	1.963	1.968	1.968	1.968	1.967	0.012
S = 2 ^b	2.038	2.039	2.048	2.041	2.029	2.036	2.037	2.037	2.035	0.020
S = 0 ^c	1.989	1.988	1.992	2.007	1.992	1.987	1.988	1.988	1.986	0.057
Exptl ^d	1.972									

^a Configuration: (d_{xy})²(d_z²)²(d_π)².

^b Configuration: (d_{xy})¹(d_z²)²(d_π)²(d_x²-y²)¹.

^c Configuration: (d_{xy})²(d_π)⁴.

^d X-ray crystal structural data on FeTPP (ref. 8).

Table 3

Calculated structural parameters (distance R in Å) for selected states of FeP(Im) with different functionals and basis sets

	$R_{\text{Ct(ND)}\cdots\text{N(eq)}}$			$R_{\text{Ct(ND)}\cdots\text{Fe}}$			$R_{\text{Fe-N(ax)}}$		
	S = 1	S = 2	S = 0	S = 1	S = 2	S = 0	S = 1	S = 2	S = 0
BP/TZP	1.994	2.058	1.984	0.157	0.291	0.150	2.201	2.143	1.906
OLYP/TZP	2.002	2.067	1.992	0.157	0.305	0.186	2.324	2.210	1.922
B3LYP/TZP	2.017	2.074	2.012	0.151	0.316	0.137	2.250	2.179	1.965
PBE0/TZP	2.006	2.066	1.998	0.132	0.296	0.119	2.211	2.151	1.947
BP/DZP	1.988	2.053	1.980	0.133	0.267	0.128	2.180	2.131	1.903
BP/TZ2P	1.990	2.055	1.982	0.156	0.290	0.147	2.198	2.141	1.904
BP/TZ2P+	1.993	2.055	1.982	0.156	0.291	0.147	2.199	2.141	1.904
BP (CPMD) ^a	1.99	2.01	1.98	0.15	0.33	0.24	2.14	2.10	1.99
B3LYP (G94) ^b	2.021	2.088	2.016	0.13	0.23	0.15	2.233	2.147	1.923
BP (Jaguar) ^c	2.071				0.272			2.168	
B3LYP (Jaguar)	2.018	2.075	2.012	0.128	0.287	0.142	2.306	2.214	1.964
Exptl: Mb (1BZN) ^d	2.036				0.290			2.15	
Exptl: Mb (1A6N) ^e	2.038				0.363			2.14	

^a Calculations using the CPMD program (ref. 15).

^b Calculations using the Gaussian94 program (ref. 16).

^c Calculations using the Jaguar 6.0 program (ref. 53).

^d X-ray structural data on deoxy-Mb (code 1BZN) (ref. 51).

^e X-ray structural data on deoxy-Mb (code 1A6N) (ref. 52).

Table 4

Calculated structural parameters (distance R in Å, angle $\angle$ in degree) for selected states of FeP(Im)(O₂) with different functionals and basis sets

	$R_{\text{Fe-N(eq)}}$				$R_{\text{Fe-N(ax)}}$				$R_{\text{C(Im4)---Fe}}$			
	S = 0 (C) ^a	S = 1	S = 0 (O) ^b	S = 0 (C)	S = 0 (C)	S = 1	S = 0 (O)	S = 0 (C)	S = 0 (C)	S = 1	S = 0 (O)	S = 0 (O)
BP/TZP	2.012	2.008	2.006	2.110	2.045	2.073	2.317	2.034	2.008	2.017		
OLYP/TZP	2.018	2.016	2.011	2.214	2.137	2.317	2.317	2.034	2.008	2.017		
B3LYP/TZP	2.025	2.009	2.008	2.093	2.037	2.148	2.148	2.049	0.007	2.008		
PBE0/TZP	2.010	2.002	1.997	2.043	2.021	2.079	2.079	2.041	0.030	0.076		
BP/DZP	2.005	2.002	1.999	2.092	2.024	2.052	2.052	2.054	2.008	2.009		
BP/TZ2P	2.009	2.005	2.003	2.106	2.040	2.064	2.064	2.050	2.007	2.007		
BP/TZ2P+	2.009	2.006	2.005	2.105	2.039	2.062	2.062	2.049	2.006	2.006		
BP (CPMD) ^c			2.015			2.08						
BP (Jaguar) ^d			2.015			2.080				2.024		
B3LYP (Jaguar)			2.020			2.119				2.017		
BP (Turbo) ^e			2.010			2.104						
OLYP (Turbo)			2.028			2.294						
B3LYP (Turbo)			2.018			2.135						
Exptl: Mb (1A6M) ^f			2.01			2.06						

	$R_{\text{Fe-O}}$				$R_{\text{O-O}}$				$\angle_{\text{FeOO}}$			
	S = 0 (C)	S = 1	S = 0 (O)	S = 0 (C)	S = 0 (C)	S = 1	S = 0 (O)	S = 0 (C)	S = 0 (C)	S = 1	S = 0 (O)	S = 0 (O)
BP/TZP	1.754	1.845	1.858	1.289	1.287	1.290	1.290	1.24.8	134.0	130.6		
OLYP/TZP	1.753	1.854	2.079	1.279	1.278	1.265	1.265	126.0	135.4	122.7		
B3LYP/TZP	1.761	1.857	2.038	1.271	1.273	1.267	1.267	124.8	134.2	117.2		
PBE0/TZP	1.753	1.881	2.136	1.252	1.233	1.238	1.238	124.8	134.8	116.4		
BP/DZP	1.753	1.854	1.863	1.286	1.283	1.286	1.286	123.6	132.4	129.6		
BP/TZ2P	1.749	1.837	1.849	1.278	1.276	1.279	1.279	125.2	134.9	131.7		
BP/TZ2P+	1.750	1.840	1.853	1.278	1.275	1.279	1.279	125.2	135.0	131.9		
BP (CPMD) ^c			1.77			1.30				121		

	R_{Fe-O}			R_{O-O}			$\angle_{FeOO}$		
	$S=0$ (C)	$S=1$ (O)	$S=0$ (O)	$S=0$ (C)	$S=1$ (O)	$S=0$ (O)	$S=0$ (C)	$S=1$ (O)	$S=0$ (O)
BP (Turbo) ^d			1.811			1.281			121.0
OLYP (Turbo)			1.861			1.264			122.3
B3LYP (Turbo)			1.868			1.279			119.2
BP (Jaguar) ^e			1.839						119.9
B3LYP (Jaguar)			1.899						118.5
Exptl: Mb (1A6M) ^f			1.81						122

^d Closed-shell singlet.

^b Open-shell singlet.

^c Calculations using the CPMD program (ref. 15).

^d Calculations using the Turbomole v5.9 program (ref. 19).

^e Calculations using the Jaguar 6.0 program (ref. 53).

^f X-ray structural data on oxy-Mb (code 1A6M) (ref. 51).

Table 5

Calculated relative energies (E_{relative} in eV) for selected states of FeP, FeP(Im) and FeP(Im)(O₂) at the BP/TZP optimized structure

		FeP			FeP(Im)			FeP(Im)(O ₂)		
		S=1	S=2	S=0	S=1	S=2	S=0	S=0 (C) ^a	S=1	S=0 (O) ^b
GGA	BP	0	0.69	1.48	0	0.49	-0.02	0	0.01	0.20
	PBE	0	0.69	1.48	0	0.44	-0.10	0	0.03	0.21
	revPBE	0	0.55	1.43	0	0.30	0.02	0	0.00	0.18
	OPBE	0	0.19	1.39	0	-0.02	0.14	0	0.01	0.26
	OPerdew	0	0.20	1.45	0	-0.01	0.14	0	0.01	0.26
	OLYP	0	0.24	1.40	0	0.01	0.18	0	-0.01 (0.00) ^c	0.23 (0.17) ^c
	HCTH/407	0	0.03	1.57	0	-0.20	0.26	0	-0.06	0.20
Meta-GGA	Becke00	0	0.34	1.50	0	-0.05	0.11	0	-0.19	0.06
	τ -HCTH	0	0.07	1.50	0	-0.14	0.27	0	-0.05	0.22
Hybrid-GGA	B3LYP	0	0.19	1.50	0	-0.10	0.40	0	-0.42 (-0.39)	-0.17 (-0.39)
	B3LYP*	0	0.35	1.49	0	0.07	0.26	0	-0.30	-0.07
	PBE0	0	-0.01	1.56	0	-0.29	0.46	0	-0.51 (-0.49)	-0.25 (-0.48)
	B97	0	0.09	1.41	0	-0.20	0.32	0	-0.37	-0.12
	τ -HCTH-hyb	0	0.21	1.46	0	-0.07	0.20	0	-0.32	-0.07

^aClosed-shell singlet.

^bOpen-shell singlet.

^cThe value in parentheses is result calculated at the structure optimized by the corresponding functional in the row.

Table 6

Calculated FeP–Im bonding energies in FeP(Im) and FeP(Im)–O₂ bonding energies in FeP(Im)(O₂) with different functionals and basis sets (E_{bond} in eV)

	TZP				BP			CASPT2 ^a	Exptl ^b
	BP	PBE	OLYP	B3LYP	PBE0	DZP	TZ2P	TZ2P+	
$E_{\text{bond}}(\text{FeP–Im})$	0.52	0.66	0.26	0.13	0.53	0.82	0.53	0.51	
$E_{\text{bond}}[\text{FeP(Im)–O}_2]$	0.81	0.88	0.10	0.05	–0.24	0.70	0.80	0.75	0.44

^aCASPT2 calculations with large basis sets (ref. 19).

^bDissociation barrier for Mb, corrected for the absence of the protein environment (ref. 19).

Table 7

Calculated structural parameters (distance R in Å) and FeP–L bonding energies (E_{bond} in eV) for selected states of various FeP(L) complexes with the BP functional

System	State	$R_{\text{C1(N4)}\cdots\text{N(eq)}}$	$R_{\text{C1(N4)}\cdots\text{Fe}}$	$R_{\text{Fe-N(ax)}}$	$E_{\text{bond}}(\text{FeP-L})^a$
FeP(Im)	S = 1	1.994	0.157	2.201	
	S = 2	2.058	0.291	2.143	0.13 (B3LYP) ^b
	S = 0	1.984	0.150	1.906	0.52 (BP) ^c
FeP(1-MeIm)	S = 1	1.993	0.163	2.196	
	S = 2	2.060	0.289	2.145	0.17 (B3LYP)
	S = 0	1.984	0.151	1.908	0.56 (BP)
FeP(2-MeIm)	S = 1	1.995	0.176	2.269	
	S = 2	2.057	0.343	2.172	0.10 (B3LYP)
	S = 0	1.980	0.190	1.944	0.37 (BP)
FeP(1,2-Me ₂ Im)	Exptl ^d	2.043	0.42	2.161	
	S = 1	1.995	0.182	2.264	
	S = 2	2.057	0.331	2.162	0.09 (B3LYP)
FeP(4-EtIm)	S = 0	1.980	0.197	1.949	0.40 (BP)
	S = 1	1.994	0.163	2.193	
	S = 2	2.057	0.300	2.134	0.16 (B3LYP)
FeP(His)	S = 0	1.984	0.152	1.908	0.56 (BP)
	S = 1	1.994	0.159	2.187	
	S = 2	2.058	0.303	2.131	0.17 (B3LYP)
FeTpvPP(2-MeIm)	S = 0	1.984	0.148	1.909	0.58 (BP)
	S = 1	1.988	0.156	2.238	
	S = 2	2.048	0.356	2.171	0.15 (B3LYP)
Exptl ^e	S = 0	1.975	0.198	1.950	0.40 (BP)
		2.033	0.399	2.095	

^a See text for the definition of E_{bond} .

^b Bonding energy calculated with B3LYP in the S = 2 state.

^c Bonding energy calculated with BP in the S = 0 state, as this state is the ground state or nearly the ground state obtained with BP.

^dX-ray crystal structural data on FeTPP(2-Melm) (ref. 20),
^eX-ray crystal structural data on FeTpivPP(2-Melm) (ref. 22).

Table 8

Calculated relative energies (E_{relative} in eV) for the intermediate- ($S = 1$), high- ($S = 2$), and low-spin ($S = 0$) states of FeP(Im) and FeP(1-MeIm)

		FeP(1-MeIm)			FeP(2-MeIm)			FeP(1,2-Me ₂ Im)		
		S = 1	S = 2	S = 0	S = 1	S = 2	S = 0	S = 1	S = 2	S = 0
GGA	BP	0	0.52	-0.04	0	0.46	0.06	0	0.47	0.06
	PBE	0	0.52	-0.08	0	0.42	0.01	0	0.44	0.03
	revPBE	0	0.38	0.04	0	0.28	0.15	0	0.32	0.17
	OPBE	0	0.05	0.15	0	-0.04	0.29	0	0.01	0.33
	OPerdew	0	0.06	0.15	0	-0.03	0.28	0	0.01	0.31
Meta-GGA	OLYP	0	0.07	0.20	0	-0.01	0.34	0	0.05	0.35
	HCTH/407	0	-0.12	0.28	0	-0.20	0.46	0	-0.16	0.48
	Becke00	0	0.02	0.14	0	-0.08	0.24	0	-0.04	0.25
	τ -HCTH	0	-0.07	0.28	0	-0.16	0.39	0	-0.12	0.35
	B3LYP	0	0.01	0.41	0	-0.12	0.53	0	-0.08	0.51
Hybrid-GGA	B3LYP*	0	0.17	0.28	0	0.05	0.38	0	0.08	0.37
	PBE0	0	-0.17	0.48	0	-0.31	0.59	0	-0.29	0.61
	B97	0	-0.09	0.34	0	-0.23	0.45	0	-0.18	0.51
	τ -HCTH-hyb	0	0.04	0.21	0	-0.11	0.29	0	-0.06	0.35

Table 9

Calculated relative energies (E_{relative} in eV) for the intermediate- ($S = 1$), high- ($S = 2$), and low-spin ($S = 0$) states of FeP(4-EtIm) and FeP(His)

		FeP(4-EtIm)			FeP(His)		
		S = 1	S = 2	S = 0	S = 1	S = 2	S = 0
GGA	BP	0	0.48	-0.04	0	0.48	-0.04
	PBE	0	0.43	-0.10	0	0.46	-0.12
	revPBE	0	0.29	0.02	0	0.32	0.00
	OPBE	0	-0.03	0.14	0	0.01	0.12
	OPerdew	0	-0.02	0.14	0	0.01	0.12
Meta-GGA	OLYP	0	0.00	0.19	0	0.03	0.16
	HCTH/407	0	-0.21	0.27	0	-0.17	0.24
	Becke00	0	-0.06	0.12	0	0.00	0.11
	τ -HCTH	0	-0.15	0.27	0	-0.12	0.25
	B3LYP	0	-0.11	0.40	0	-0.08	0.38
Hybrid-GGA	B3LYP*	0	0.06	0.26	0	0.09	0.24
	PBE0	0	-0.30	0.47	0	-0.26	0.45
	B97	0	-0.20	0.32	0	-0.18	0.29
	τ -HCTH-hyb	0	-0.07	0.20	0	-0.05	0.17

Table 10

Calculated structural parameters (distance R in Å, angle $\angle$ in degree) and FeP(L)-O₂ bonding energies (E_{bond} in eV) for selected states of various FeP(L)(O₂) complexes with the BP functional

System	State	R _{Fe-N(eq)}	R _{Fe-N(ax)}	R _{C(N4)-Fe} ^a	R _{Fe-O}	R _{O-O}	$\angle$ FeOO	E _{bond} [FeP(L)-O ₂] ^b
FeP(O ₂)	S = 0 (C) ^c	2.002		-0.181	1.719	1.285	125.5	0.70 (BP)
	S = 1	1.999		-0.239	1.811	1.290	129.0	
	S = 0 (O) ^d	1.996		-0.233	1.889	1.281	122.2	-0.21 (B3LYP)
FeP(Im)(O ₂)	S = 0 (C)	2.012	2.110	-0.034	1.754	1.289	124.8	0.81 (BP)
	S = 1	2.008	2.045	-0.008	1.845	1.287	134.0	0.05 (B3LYP)
	S = 0 (O)	2.006	2.073	-0.017	1.858	1.290	130.6	
[BP (CPMD)] ^e	S = 0 (C)							0.52
	S = 0 (O)	2.015	2.08		1.77	1.30	121	0.65
	S = 0 (C)	2.012	2.104	-0.031	1.755	1.283	125.6	0.78 (BP)
FeP(1-MeIm)(O ₂)	S = 1	2.009	2.042	-0.006	1.844	1.287	134.4	0.05 (B3LYP)
	S = 0 (O)	2.007	2.071	-0.010	1.859	1.291	130.8	
	Exptl ^f	1.98	2.07	-0.02	1.75	>1.16	<131	
FeP(2-MeIm)(O ₂)	S = 0 (C)	2.010	2.207	0.021	1.753	1.288	125.4	0.70 (BP)
	S = 1	2.007	2.132	0.048	1.844	1.288	133.4	
	S = 0 (O)	2.003	2.230	0.044	1.935	1.288	123.8	-0.01 (B3LYP)
FeP(1,2-Me ₂ Im)(O ₂)	Exptl ^g	1.996	2.107	0.086	1.898	>1.22	<129	
	S = 0 (C)	2.010	2.203	0.032	1.754	1.288	125.5	0.69 (BP)
	S = 1	2.008	2.137	0.058	1.844	1.288	133.5	
FeP(4-EtIm)(O ₂)	S = 0 (O)	2.004	2.239	0.051	1.940	1.288	123.6	0.02 (B3LYP)
	S = 0 (C)	2.011	2.101	-0.029	1.755	1.290	124.9	0.81 (BP)
	S = 1	2.008	2.040	-0.010	1.844	1.288	134.4	0.05 (B3LYP)
FeP(His)(O ₂)	S = 0 (O)	2.007	2.064	-0.011	1.856	1.290	131.0	
	S = 0 (C)	2.011	2.105	-0.038	1.757	1.292	122.4	0.87 (BP)
	S = 1	2.009	2.033	-0.006	1.847	1.288	133.2	0.07 (B3LYP)
FeTpvPP(2-MeIm)(O ₂)	S = 0 (C)	2.003	2.202	0.010	1.751	1.296	125.2	0.71 (BP)
	S = 1	2.001	2.150	0.045	1.831	1.297	133.2	0.04 (B3LYP)
	S = 0 (O)	1.996	2.217	0.048	1.921	1.298	123.0	

System	State	R _{Fe-N(eq)}	R _{Fe-N(ax)}	R _{C1(N4)···Fe^a}	R _{Fe-O}	R _{O-O}	∠ _{FeOO}	E _{bond} [FeP(L)-O ₂] ^b
[BP (CPMD)] ^e	S = 0 (C)							1.98
	S = 1							1.91
	S = 0 (O)	2.01	2.11		1.78	1.30	121.0	2.04
	Exptl ^g	1.996	2.107	0.086	1.898	>1.22	<129	

^aA negative value denotes an out-of-plane displacement toward the oxygen ligand.

^bSee text for the definition of E_{bond}; here BP and B3LYP represent the bonding energies calculated with the two functionals respectively in the indicated states.

^cClosed-shell singlet.

^dOpen-shell singlet.

^eCalculations with the BP functional using the CPMD program (ref. 13).

^fX-ray crystal structural data on FeTpivPP(1-Melm)(O₂) (ref. 22).

^gX-ray crystal structural data on FeTpivPP(2-Melm)(O₂) (ref. 22).

Table 11

Calculated relative energies (E_{relative} in eV) for the closed-shell ($S = 0$), triplet- ($S = 1$), and low-spin ($S = 0$), open-shell states of $\text{FeP}(\text{O}_2)$, $\text{FeP}(1\text{-MeIm})$ (O_2), and $\text{FeP}(2\text{-MeIm})(\text{O}_2)$

		$\text{FeP}(\text{O}_2)$			$\text{FeP}(1\text{-MeIm})(\text{O}_2)$			$\text{FeP}(2\text{-MeIm})(\text{O}_2)$		
		$S = 0$ (C) ^a	$S = 1$	$S = 0$ (O) ^b	$S = 0$ (C)	$S = 1$	$S = 0$ (O)	$S = 0$ (C)	$S = 1$	$S = 0$ (O)
GGA	BP	0	0.09	0.18	0	0.01	0.20	0	0.03	0.18
	PBE	0	0.10	0.20	0	0.02	0.19	0	0.02	0.18
	revPBE	0	0.06	0.13	0	-0.01	0.16	0	0.00	0.09
	OPBE	0	0.07	0.14	0	-0.01	0.24	0	0.02	0.12
	OPerdew	0	0.08	0.15	0	0.00	0.25	0	0.02	0.12
	OLYP	0	0.05	0.11	0	-0.02	0.21	0	0.00	0.06
	HCTH/407	0	-0.02	0.01	0	-0.08	0.18	0	-0.06	-0.05
Meta-GGA	Becke00	0	-0.13	-0.10	0	-0.20	0.04	0	-0.19	-0.12
	τ -HCTH	0	0.02	0.06	0	-0.06	0.21	0	-0.04	0.01
Hybrid-GGA	B3LYP	0	-0.35	-0.48	0	-0.42	-0.19	0	-0.42	-0.45
	B3LYP*	0	-0.23	-0.30	0	-0.31	-0.08	0	-0.31	-0.28
	PBE0	0	-0.45	-0.64	0	-0.51	-0.26	0	-0.52	-0.56
	B97	0	-0.31	-0.42	0	-0.38	-0.13	0	-0.38	-0.39
	τ -HCTH-hyb	0	-0.24	-0.31	0	-0.33	-0.08	0	-0.33	-0.29

^a Closed-shell singlet.

^b Open-shell singlet.

Table 12

Calculated relative energies (E_{relative} in eV) for the closed-shell ($S = 0$), triplet- ($S = 1$), and low-spin ($S = 0$), open-shell states of $\text{FeP}(1,2\text{-Me}_2\text{Im})(\text{O}_2)$, $\text{FeP}(4\text{-EtIm})(\text{O}_2)$, and $\text{FeP}(\text{His})(\text{O}_2)$

		FeP(1,2-Me2Im)(O2)				FeP(4-EtIm)(O2)				FeP(His)(O2)			
		S = 0 (C) ^a	S = 1	S = 0 (O) ^b	S = 0 (C)	S = 1	S = 0 (O)	S = 0 (C)	S = 1	S = 0 (C)	S = 1		
GGA	BP	0	0.03	0.18	0	0.01	0.20	0	0.05				
	PBE	0	0.04	0.19	0	0.02	0.21	0	0.06				
	revPBE	0	0.01	0.10	0	-0.01	0.18	0	0.04				
	OPBE	0	0.03	0.12	0	0.00	0.26	0	0.03				
	OPerdew	0	0.03	0.13	0	0.00	0.26	0	0.04				
Meta-GGA	OLYP	0	0.01	0.06	0	-0.02	0.23	0	0.02				
	HCTH/407	0	-0.06	-0.06	0	-0.08	0.20	0	-0.03				
	Becke00	0	-0.18	-0.11	0	-0.21	0.04	0	-0.14				
	τ-HCTH	0	-0.03	0.01	0	-0.05	0.23	0	-0.02				
	B3LYP	0	-0.41	-0.45	0	-0.42	-0.17	0	-0.35				
Hybrid-GGA	B3LYP*	0	-0.29	-0.28	0	-0.31	-0.07	0	-0.24				
	PBE0	0	-0.50	-0.55	0	-0.52	-0.24	0	-0.45				
	B97	0	-0.36	-0.37	0	-0.39	-0.11	0	-0.31				
	τ-HCTH-hyb	0	-0.30	-0.26	0	-0.34	-0.05	0	-0.26				

^a Closed-shell singlet.

^b Open-shell singlet.

Table 13

Calculated relative energies (E_{relative} in eV) for selected states of FeTpivPP, FeTpivPP(2-MeIm), and FeTpivPP(2-MeIm)(O₂)

		FeTpivPP			FeTpivPP(2-MeIm)			FeTpivPP(2-MeIm)(O ₂)		
		S = 1	S = 2	S = 0	S = 1	S = 2	S = 0	S = 0 (C) ^a	S = 1	S = 0 (O) ^b
GGA	BP	0	0.72	1.49	0	0.48	0.08	0	0.01	0.15
	PBE	0	0.71	1.48	0	0.53	0.07	0	0.07	0.19
	revPBE	0	0.58	1.44	0	0.35	0.19	0	0.03	0.10
	OPBE	0	0.22	1.41	0	0.03	0.35	0	0.04	0.12
	OPerdew	0	0.23	1.46	0	0.05	0.34	0	0.05	0.14
	OLYP	0	0.27	1.41	0	0.04	0.35	0	0.02	0.07
	HCTH/407	0	0.05	1.55	0	-0.17	0.47	0	-0.04	-0.01
Meta-GGA	Becke00	0	0.35	1.56	0	-0.02	0.25	0	-0.15	-0.11
	τ -HCTH	0	0.09	1.51	0	-0.08	0.36	0	-0.01	0.05
Hybrid-GGA	B3LYP	0	0.20	1.69	0	-0.05	0.52	0	-0.35	-0.42
	B3LYP*	0	0.37	1.63	0	0.13	0.39	0	-0.24	-0.26
	PBE0	0	0.00	1.80	0	-0.21	0.64	0	-0.42	-0.50
	B97	0	0.11	1.62	0	-0.13	0.53	0	-0.29	-0.33
	τ -HCTH-hyb	0	0.23	1.62	0	0.03	0.39	0	-0.23	-0.23

^a Closed-shell singlet.

^b Open-shell singlet.