

Perferryl Fe^{V} –Oxo Nonheme Complexes: Do They Have High-Spin or Low-Spin Ground States?Hui Chen,^{*,†,‡} Wenzhen Lai,[†] Jiannian Yao,[‡] and Sason Shaik^{*,†}[†]Institute of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry, Hebrew University of Jerusalem, Givat Ram Campus, 91904 Jerusalem, Israel[‡]Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China

S Supporting Information

ABSTRACT: Nonheme perferryl $\text{Fe}^{\text{V}}=\text{O}$ species are studied herein by means of coupled cluster (CCSD(T)) calculations with a complete basis set limit estimate and density functional B3LYP computations. It is shown that the high-spin/low-spin (HS/LS) energy order in these $\text{Fe}^{\text{V}}=\text{O}$ species is highly dependent on the electronic nature of the ligand sphere and the geometric position of ligands relative to the $\text{Fe}^{\text{V}}=\text{O}$ moiety. When only σ -donor amines ligate $\text{Fe}^{\text{V}}=\text{O}$, the LS state is slightly lower than the HS states. However, when a strong π -donor ligand such as hydroxyl is cis to $\text{Fe}^{\text{V}}=\text{O}$, the HS state becomes highly favored. And on the contrary, if the π -donor ligand is trans to $\text{Fe}^{\text{V}}=\text{O}$, the LS state is predicted here to be highly favored. This last type of perferryl complex has not yet been made by experimental means. Generally, our findings are consistent with the available experimental data.^{4a,6,7} Some implications of these findings on the behavior of experimental systems are discussed.

Nonheme high-valent oxoiron reagents have attracted considerable interests in bioinorganic chemistry, since these complexes mimic active oxidants of many nonheme enzymes.¹ Among the high-valent oxoiron complexes, the ferryl species have been extensively studied both experimentally² and theoretically.³ These studies have generated a great deal of knowledge about the spin-state energies and oxidative reactivity of ferryl $\text{Fe}^{\text{IV}}=\text{O}$ species. By contrast, our knowledge of perferryl $\text{Fe}^{\text{V}}=\text{O}$ species remains scant. The formation of perferryl $\text{Fe}^{\text{V}}=\text{O}$ was proposed, for some nonheme enzymes and synthetic analogues, based on indirect experimental indications.⁴ To date, the only experimentally observed perferryl species is the synthetic complex $[\text{O}=\text{Fe}^{\text{V}}(\text{TAML})]^-$ of Collins et al.,⁵ wherein TAML is a macrocyclic tetraamide ligand of the tetra anion (see Chart 3). However, there are indications that more perferryl species might have been observed, but their structures and electronic features are still not firmly established. Hence, a study of their types and their spin states is deemed timely.

Very recently, there appeared an experimental EPR study⁶ which assigned the spin-state identity of the proposed⁷ reactive $\text{Fe}^{\text{V}}=\text{O}$ species during nonheme iron catalyzed epoxidation of alkenes. Thus, Talsi et al.⁶ showed that active species of the catalyst systems based on nonheme iron complexes, tentatively assignable to be $\text{Fe}^{\text{V}}=\text{O}$, are low-spin species. However, it remains unclear whether and how the spin state ordering of perferryl $\text{Fe}^{\text{V}}=\text{O}$ is determined by the ligand sphere. In response, we present a high level ab initio coupled cluster (CC) with complete basis set (CBS) limit estimate as well as DFT computational results for electronic structures and spin state energetics of nonheme perferryl $\text{Fe}^{\text{V}}=\text{O}$ complexes.⁸ The study accounts for and rationalizes the experimental findings for the related experimental species and uncovers new features. As we shall demonstrate,

the perferryls turn out to possess a spectrum of intriguing features. The usage of CC theory further allows us to evaluate the performance of an approximate functional like B3LYP in describing all of the available electronic states of perferryls. The computational methods and details (structures, energies, tests of the CBS limit estimates, potential energy surface scan profile) are all given in the Supporting Information (SI).

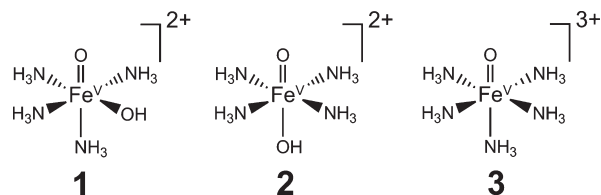
A prototype perferryl $\text{Fe}^{\text{V}}=\text{O}$ structure that has been proposed frequently in experimental systems^{4,6,7} is $[\text{O}=\text{Fe}^{\text{V}}-\text{OH}(\text{L})]^{2+}$, wherein the hydroxyl group is at the cis position to the $\text{Fe}=\text{O}$ unit, and L is the remaining neutral polydentate ligand made usually of amine/pyridine moieties. Alternatively, there could also exist perferryl complexes devoid of an OH ligand, i.e., $[\text{O}=\text{Fe}^{\text{V}}(\text{L})]^{3+}$, wherein only a neutral polydentate ligand, or maybe one additional solvent molecule, is wrapped around $\text{Fe}^{\text{V}}=\text{O}$. Moreover, changing the cis-OH to trans-OH will generate a third complex, with electronic structure features that are not known from experiments. As such, we designed the three hexa-coordinate model complexes shown in Chart 1, for which high-level CCSD(T) calculations with a CBS limit extrapolation⁹ estimate can be applied to serve as our reference for DFT calculations.

The various electronic configurations of perferryl complexes are depicted in Scheme 1. Generally, the high-spin (HS) quartet (Q) states (Q_{xy} , Q_{pO} , and Q_{xy-pO}) are all characterized by triradicaloid configurations, while the LS doublet (D) states can be classified as either a monoradicaloid configuration (D_{π}) with one unpaired electron or triradicaloid doublet configurations (D_{pO} and D_{xy-pO}) with three unpaired electrons coupled

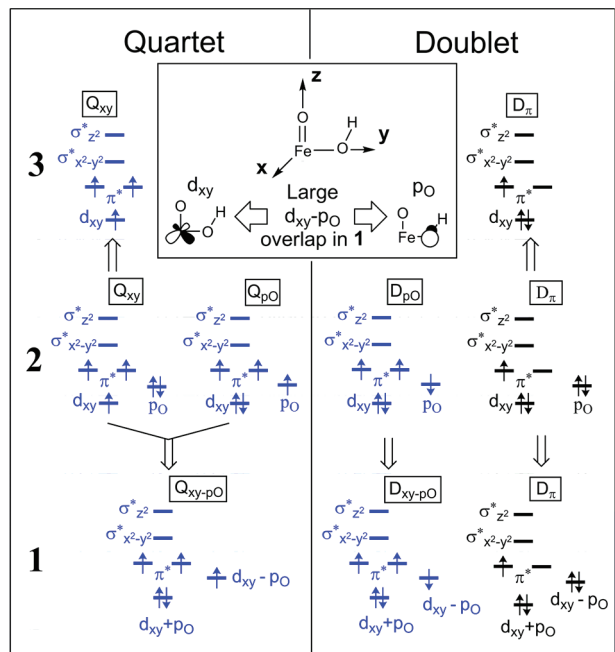
Received: August 31, 2011

Published: September 09, 2011

Chart 1. The Three Used Model Perferryl Complexes



Scheme 1. Potential Triradicaloid (blue) and Monoradicaloid (black) Configurations for 1–3 and Their Connections



antiferromagnetically. Previous DFT calculations focused mostly on the triradicaloid LS states.^{10a} One exception is the study by Neese et al. for **2**, wherein the monoradicaloid LS state was calculated while the triradicaloid LS state was not reported.¹¹

The configurations in Scheme 1 are system-dependent and fall into two classes: One class is labeled Q_{pO} , Q_{xy-pO} , D_{pO} , and D_{xy-pO} , wherein the subscripts indicate that OH acts as a noninnocent ligand. This arises because the short Fe–OH bond (1.8 Å) creates a large overlap between the $p(OH)$ orbital, perpendicular to the Fe–O–H plane, and the π^* or d_{xy} type Fe=O orbital, whereby the OH ligand acquires also significant spin density. The other class is labeled as Q_{xy} , D_{π} , which means that the open shell part of these configurations involves only the orbitals of the Fe^V=O moiety (d_{xy} or π^* FeO type, respectively). This latter class is also called “genuine” or sometimes “true” Fe^VO,¹² to distinguish it from the cases with noninnocent ligands, e.g., in the extreme case of compound **1** (Cpd I) in heme enzymes like P450, which possess a ferryl Fe^{IV}O unit and a porphyrin cation radical.¹³ Due to the absence of the π -donor hydroxyl ligand in **3**, the space separation of the unpaired electrons by ligand noninnocence is not possible anymore, and hence, the triradicaloid states must have their three unpaired electrons localized on the Fe^VO center. As such, the LS

Table 1. The Calculated Adiabatic Q–D Gaps (kcal/mol) for 1–3^a

complex	state	UB3LYP/def2-QZVP ^b	CCSD(T)/CBS
1	Q_{xy-pO}	0.0 (0.0) [0.0]	0.0
	D_{π}	10.9 (15.8) [9.7]	12.4
	D_{xy-pO}	16.3 (10.9) [15.9]	— ^c
2	Q_{xy}	0.0 (0.0) [0.0]	0.0
	Q_{pO}	−4.0 [−3.4]	1.5
	D_{π} ^d	−4.3 [−3.4]	−15.8
	D_{pO}	−7.5 (−5.9) [−7.1]	— ^c
	D_{π}	−0.8 (4.7) [−0.8]	−3.1
3	Q_{xy}	0.0 (0.0) [0.0]	0.0
	D_{π}	−0.8 (4.7) [−0.8]	−3.1

^aThe structures used in CCSD(T) calculation are from UB3LYP/def2-TZVP geometry optimization for the corresponding states. ^bValues outside/inside parentheses are with/without spin-projection for spin contamination; values in brackets also include zero point energy (ZPE) correction for the spin-projected energies. ^cSymmetry-broken states for which the RCCSD(T) method cannot be applied. ^dNot spin contaminated.

triradicaloid states of **3** will be destabilized relative to the HS states by a loss of exchange energy.¹⁴ Consequently, in the absence of the π -donor OH ligand, the favored LS state in **3** will be the monoradicaloid LS state. Indeed, the only LS state which we could locate herein for **3** using B3LYP calculations is D_{π} .

Table 1 summarizes the calculated adiabatic Q–D gaps for 1–3 at the CCSD(T)/CBS estimate and the B3LYP/def2-QZVP levels. Inspection of the CCSD(T) results for **1**, for which the π -donor hydroxyl group is at the cis position to the perferryl Fe=O unit, shows that the ground state is HS and is preferred by 12.4 kcal/mol over the LS D_{π} state. By contrast to **1**, for **2**, wherein the π -donor hydroxyl ligand is trans to the perferryl Fe=O moiety, the LS D_{π} state is favored over the two HS states by 15.8 and 17.3 kcal/mol. Finally, for species **3**, in which only σ -donor amine ligands bind iron, and which may be considered as a model for nitrogenous-ligated nonheme complexes,¹ the HS and LS states are close in energy, with the latter being 3.1 kcal/mol lower. We note that this result for **3** is quite similar to our recent multireference CASPT2^{15a} computational results for the “true” Fe^VO electromers of Cpd I in heme systems, which has been subsequently confirmed also by RASPT2^{15b} computations. This, and other tests of the basis sets (see SI), show that the CCSD(T)/CBS estimates are solid.

For **1** and **3**, in Table 1, B3LYP performs in agreement with CCSD(T), especially after correction of the spin-contamination.¹⁶ Thus, complex **1** exhibits in spin-contamination corrected-B3LYP a monoradicaloid D_{π} state, which is 10.9 kcal/mol higher than the triradicaloid HS ground state,¹⁷ in reasonable agreement with the CCSD(T) datum of 12.4 kcal/mol. Similarly, for **3**, spin-contamination corrected B3LYP predicts a D_{π} ground state in agreement with CCSD(T). For **2**, the B3LYP predicts correctly the preference for a LS state. But the B3LYP energy gap relative to the HS state Q_{xy} is significantly smaller than the corresponding CCSD(T) gap. That this gap is large is supported by independent multireference SORCI calculation of the vertical gap (12.9 kcal/mol).^{11,18} This indicates that the performance of an approximate functional tends to be system-dependent. In addition, we note that the ZPE correction in Table 1 does not change our results much.

Since **1** and **2** are structural isomers, their relative energy is chemically relevant. Figure 1 shows this comparison, using as a

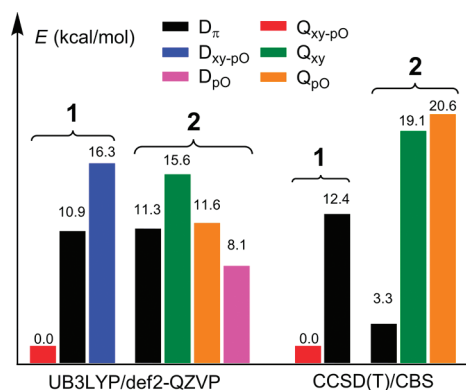
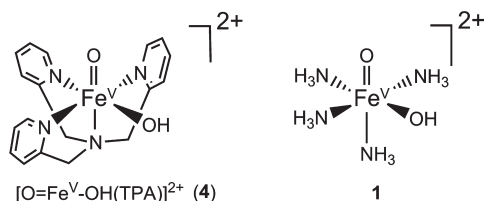


Figure 1. Relative UB3LYP/def2-QZVP and CCSD(T)/CBS estimate energies of various spin states for the isomeric perferryls, **1** and **2**, relative to the lowest state Q_{xy-pO} of **1**. Whenever necessary, the relative DFT energies of doublet states given are after spin-contamination correction.

Chart 2. Complex $[O=Fe^V-OH(TPA)]^{2+}$ (**4**) and Its Model, **1**



reference the most stable state, Q_{xy-pO} for **1**, and depicts the relative energies of the other states. The computed stability of $1-Q_{xy-pO}$ is in agreement with the fact that all of the so far proposed nonheme $HO-Fe^V=O$ complexes under experimental conditions contain a cis hydroxyl ligand but never a trans OH ligand. Additionally, as shown in Figure 1, the difference between B3LYP and CCSD(T) for **2** is quite large. This large difference owes its origins to the following factors: one is the underestimation by B3LYP of the stability of 2-LS; the other is overestimation of the stability of 2-HS states. With CCSD(T), the 2- D_{π} is only 3.3 kcal/mol higher than $1-Q_{xy-pO}$. As such, **2** may be thermodynamically accessible, although in small quantities. Furthermore, the conversion of $1-Q_{xy-pO}$ to 2- D_{π} may represent a new spin crossover system but for a high-valent iron, wherein the spin state interchanges as the OH ligand flips between the cis and trans positions.

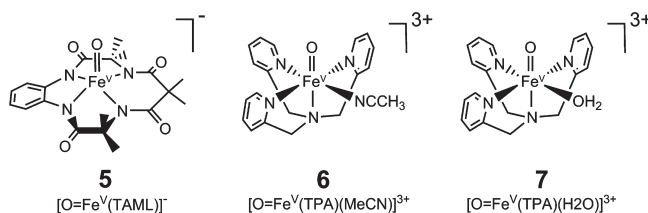
Having shown the key findings of the three perferryl model systems, one may wonder how relevant these findings are to the more realistic synthetic nonheme complexes. To answer this concern, we compare the predictions for **1** to a related experimentally proposed^{4a,10a–10c} complex, $[O=Fe^V-OH(TPA)]^{2+}$ (TPA = tris(2-pyridylmethyl)amine), **4**, shown in Chart 2. Table 2 shows the relative spin-state energies for **1** and **4**.¹⁹ The computed triradicaloid $Q_{xy-pO}-D_{xy-pO}$ gap for **4** (18.4 kcal/mol) is close to the previous B3LYP calculation (20.5 kcal/mol) using a smaller basis set,^{10a} and $Q_{xy-pO}-D_{\pi}$ gaps of both **1** and **4** in Table 2 are on par with the CCSD(T)/CBS gap for **1** in Table 1. Furthermore, it is apparent from Table 2 that the spin-contamination corrected gaps, $Q_{xy-pO}-D_{xy-pO}$ and $Q_{xy-pO}-D_{\pi}$, for **1** and **4** are very similar. As such, we may conclude that the simplified complex **1** is a

Table 2. The B3LYP Calculated Adiabatic Q–D Gaps (kcal/mol) for **1** and **4**^a

	state	4	1
UB3LYP/def2-TZVPP ^b	Q_{xy-pO}	0.0 (0.0) [0.0]	0.0 (0.0)
	D_{π}	16.0 (20.5) [16.3]	11.1 (16.0)
	D_{xy-pO}	18.4 (12.2) [19.1]	16.1 (10.7)

^aThe structures in all calculations are optimized by UB3LYP/def2-TZVP for the corresponding states. ^bValues outside/inside parentheses are with/without spin-projection for spin contamination; values in brackets are from the SMD solvation model calculation with spin-projection for spin contamination.

Chart 3. Perferryl Complexes **5–7**



fairly reliable model of **4** as far as the spin-state ordering is concerned. Furthermore, since the experiments with **4** were carried out^{4a} in acetonitrile, we tested these spin-state gaps for **4** using the SMD continuum solvation model.²⁰ The results, which are shown in brackets in Table 2, demonstrate that the Q–D gaps are intrinsic properties of **4** and are almost unaffected by solvation. Generally, our consistent DFT and CCSD(T) calculations for **4** and **1** imply that **4** is not likely to have a LS ground state, which does not support the recent tentative proposal from Talsi et al.²¹ Their assignment may refer to a different structure than **4**.

Having shown our results for **1–4** including both model and experimental systems, we may now compare our CCSD(T) results to experimental findings.^{5,6} Thus, our results for **3** (in Table 1) indicate that whenever the ligand sphere of the perferryl moiety involves only σ -donor amine ligands, the corresponding $Fe^V=O$ complex is likely to be LS, with a very close HS state of the Q_{xy} type. The first part of this prediction is consistent with the proven LS identity of $[O=Fe^V(TAML)]^-$ found by Collins et al. and is depicted in **5** in Chart 3, albeit having a ligand arrangement different from that of **3**.⁵ Furthermore, Talsi et al.⁶ assigned, based on EPR spectra, a LS ground state, for complexes of the $[O=Fe^V-(L)(S)]^{3+}$ type, wherein L is an amine/pyridine ligand and S is acetonitrile or a water molecule, as in **6** and **7**.²² However, the second part of the prediction regarding the accessibility of the HS state has not been addressed yet by experimentation. This HS state may well affect the EPR or Mössbauer spectra of these complexes,^{24,25} and furthermore, being so low in energy, it is likely that this state will be involved in the reactivity of these perferryl reagents.

Our result of **2** further suggests that if an –OH or –OR ligand can be placed trans to the $Fe^V=O$ moiety, then the LS state will be strongly preferred over the HS (Table 1). This prediction awaits future experimental tests.

In conclusion, using coupled cluster and DFT calculations, we demonstrated here that the spin-state energetics of perferryl $Fe^V=O$ species is highly dependent on the ligand sphere and its arrangement in space. When there are no π -donor ligands such as

a –OH or –OR group but only σ -donor amine/pyridine ligands, the HS and LS perferferryl states are close in energy with a slight preference for LS. When a π -donor ligand is at the cis position of perferferryl $\text{Fe}^{\text{V}}=\text{O}$, the HS ground state is highly preferred, and on the contrary, when π -donor ligands are at the trans position of perferferryl $\text{Fe}^{\text{V}}=\text{O}$, a LS ground state is highly preferred. The solvent has a minor influence on these spin state energetics of perferferryl species. These theoretical findings can be used as fingerprints for probing perferferryl complexes, which may or may not be present in a given medium.^{6,21} At present, the predictions are consistent with the previous observations which propose perferferryl $\text{Fe}^{\text{V}}=\text{O}$ as an active species in those nonheme systems.⁷ Furthermore, the different spin states of these complexes may result in different reactivity patterns and may be worthy of experimental exploration.

■ ASSOCIATED CONTENT

S Supporting Information. Cartesian coordinates, computational details, and full set of computational results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This work was supported by the Chinese Academy of Sciences (to H.C.) and ISF Grant 53/09 (to S.S.).

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- (16) Due to the higher energy of D_{π} compared to D_{xy-pO} before spin-contamination correction, DFT calculation may meet with a convergence problem without utilizing molecular symmetry, and hence calculating D_{π} poses a technical challenge for DFT.
- (17) In contrast to D_{pO} and D_{xy-pO} , for which the LS triradicaloid (hence spin-contaminated) configurations are shown in Scheme 1, it is not obvious that D_{π} is also spin-contaminated. It is an interesting observation in DFT calculations for the D_{π} state of **1** and **3** (but not **2**) that symmetry breakage happens to a certain extent (see $\langle S^2 \rangle$ in Table S1 in Supporting Information). For D_{π} , this occurs in a way that, in one of the two perpendicular $\text{Fe}=\text{O } \pi/\pi^*$ orbital sets, with a total occupation number of 2.0, the π bonding-orbital becomes less bonding due to partial α and β orbital localization on Fe and O, respectively, which can be visualized in the following way: $\text{Fe}(\text{V})=\text{O} \rightarrow \text{Fe}(\text{V})\bullet-\text{O}\bullet$, as a transition to more covalency, see, Isobe, H.; Yamanaka, S.; Okumura, M.; Yamaguchi, K.; Shimada, J. *J. Phys. Chem. B* **2011**, *115*, 10730–10738. Using natural orbitals, this symmetry breakage shows itself by having partial occupancy in π^* , which corresponds to some

multireference character of this $\pi(\text{FeO})$ bond, as previously analyzed for $\text{Fe}-\text{O}_2$ bonding in iron-oxy complexes in: Chen, H.; Ikeda-Saito, M.; Shaik, S. *J. Am. Chem. Soc.* **2008**, *130*, 14778–14790. Nevertheless, spin contamination caused by this symmetry breakage does not affect the important geometric parameters of the D_{π} state, such as the $\text{Fe}-\text{O}$ bond distance (see Figure S1 in the Supporting Information).

(18) Note that the SORCI adiabatic gap for **2** (not reported in ref 11) will be larger than the vertical gap based on the HS geometry reported therein.

(19) Note that a smaller basis set is used in Table 2 than in Table 1 for DFT calculations, which can serve as an indication of near convergence for the basis set in our DFT calculations.

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(22) We have tried to calculate by means of UB3LYP complexes **6** and **7**, which have higher positive charges ($3+$) than **4**. However, we found that in the case of the LS state, unpaired electrons undergo delocalization into the TPA ligand (pyridine ring), possibly due to the known self-interaction error (SIE) of the approximate functional, as found before in the hydrogen abstraction of weak C–H bonds for positively charged Fe^{IV} -oxo species.²³ Even in implicit solvent model calculations, the delocalization persists. This result cannot be considered reliable unless the SIE suspicion can be removed, which is not a simple matter. Thus, accurate DFT calculation of **6** and **7** may remain very challenging.

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