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“True” Iron(V) and Iron(VI) Porphyrins: A First Theoretical Exploration

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High-valent iron porphyrins at the formal Fe(V) oxidation level are well-established as Compound I intermediates for heme proteins such as peroxidases and catalases as well as for their synthetic model compounds.[1−8] However, these intermediates are generally not describable as “true” iron(V) intermediates but are better described as iron(IV)-oxo ligand radical species. The ligand radical may reside on the porphyrin or the axial ligand, or it may be delocalized on both the porphyrin and the axial ligand. The spin coupling between the $S = 1$ ferryl unit and the $S = {}^{1}/_{2}$ ligand radical is generally weakly ferromagnetic, as in most peroxidases[9] and catalases,[10] resulting in $S = {}^{3}/_{2}$ ground states. For chloroperoxidase (CPO-I), the radical may be significantly localized on the axial cysteinate ligand[11,12] and the metal-radical spin coupling is antiferromagnetic, resulting in an $S = {}^{1}/_{2}$ ground state[13,14] that is unique for Compound I intermediates. Morishima and co-workers described a synthetic, supposedly iron(V)-oxo (“perferryl”) intermediate, formulated as Fe^{V}(porphyrinato)(O)(OCH$_3$);[15,16] however, theoretical calculations suggest that this species is not truly Fe(V) but is better described as involving a ferryl unit coordinated to a methoxy radical.[17]

“True” iron(V) complexes are rare. By “true” iron(V) species, we mean $S = {}^{3}/_{2}$ complexes with an unpaired electron distribution that may be approximately described as originating from a $d_{xy^1}d_{xz^1}d_{yz^1}$ metal d electron configuration. The best known examples of such complexes are nitridoiron(V) porphyrin species, reported by Wagner and Nakamoto[18,19] more than a decade ago and obtained via laser irradiation of five-coordinate iron(III) octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) azide complexes at ca. 30 K. The resonance Raman spectra of the resulting intermediates exhibited a band at 876 cm^{-1} that was assigned to an Fe^{V}N stretch on the basis of isotope substitution experiments. The lower frequency of the Fe^{V}N stretch relative to the metal-nitrido stretching frequencies in Cr^{V}(TTP)(N) (1017 cm^{-1}) and Mn^{V}(TPP)(N) (1052 cm^{-1}) stretching frequencies has been attributed to the antibonding Fe(d$_\pi$)−N(p$_\pi$) interactions present in the Fe(V) case.[20] More recently, Wieghardt and co-workers have reported mononuclear nonheme nitridoiron(V) complexes, obtained by photolysis of *trans*-[(cyclam)Fe^{III}(N$_3$)$_2$](ClO$_4$)[21] and [(cyclam-acetato)Fe^{III}(N$_3$)](ClO$_4$)[22] and characterized as $S = {}^{3}/_{2}$ species by EPR and Mössbauer spectroscopies.

Not surprisingly, given the instability of the nitridoiron(V) species, they have not been thoroughly characterized experimentally. Thus, no information is available on such fundamental properties of these species as the Fe^{V}−N bond distance and the unpaired electron distribution. Intriguingly, no theoretical studies have been reported on these compounds either and, in our opinion, this may not reflect a lack of interest or effort on the part of researchers working in this area. Over the nine years or so since the first[23] density functional theory (DFT) calculations were published on peroxidase compound I and II model compounds,[9−11,24−26] we have attempted to carry out DFT calculations on nitridoiron(V) porphyrin complexes, but the calculations proved exceptionally resistant to convergence. We have now succeeded in accomplishing these calculations and report our results here. For all calculations, we have used the ADF[27] program system, the gradient-corrected Perdew−Wang 1991 (PW91) exchange-correlation functional, Slater-type triple-ζ plus polarization (TZP) basis sets, a fine mesh for numerical integrations, tight criteria for geometry optimizations, a spin-unrestricted formalism, and C_{4v} symmetry constraints. In addition, we also present the first results on the energetics of an Fe(V) state relative to Fe(IV)-oxo porphyrin π-cation radical states for a peroxidase Compound I model. Figure 1 presents highlights of some of the optimized geometries and Table 1 presents the gross atomic spin populations for selected molecules. The main results and conclusions may be summarized as follows.

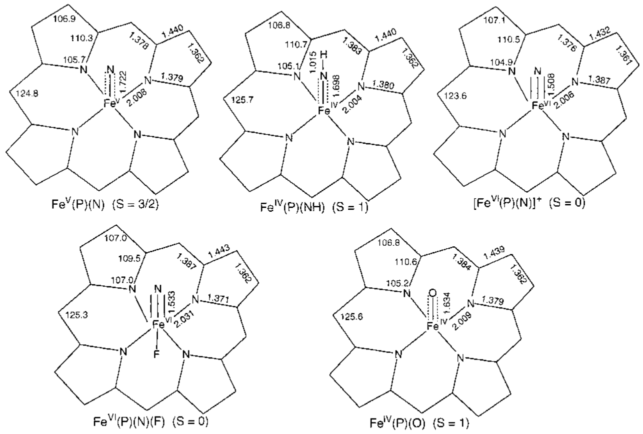

Figure 1. Selected optimized geometry parameters (Å, deg) of some high-valent iron porphyrins.

The optimized Fe^{V}−N bond distance in Fe^{V}(P)(N) ($S = {}^{3}/_{2}$) is 1.722 Å, comparable to and slightly longer than the Fe^{IV}−O bond distance of 1.684 Å in Fe^{IV}(P)(O) and the Fe^{IV}−N$_{\mathrm{imido}}$ bond distance of 1.698 Å in Fe^{IV}(P)(NH). In contrast, the Fe^{VI}−N$_{\mathrm{nitrido}}$ bond distances in [Fe^{VI}(P)(N)]$^+$ ($S = 0$) and Fe^{VI}(P)(N)(F) ($S = 0$) are dramatically shorter, 1.508 and 1.533 Å, respectively. These short distances reflect metal-nitrido triple bond character for the Fe(VI) complexes, which have a formal d_{xy}^2 d-electron configuration. Analogous triple bonding is well-known for Mn^{V}N complexes and an optimized Mn−N$_{\mathrm{nitrido}}$ bond distance of 1.514 Å has been found for Mn^{V}(P)(N) ($S = 0$).[28−30]

To discuss the spin density profiles of the different molecules, we begin by comparing Fe^{IV}(P)(O) and Fe^{IV}(P)(NH). In both cases, the entire unpaired spin density is localized on the axis defined by the iron atom and the oxide or imide axial ligand. The N$_{\mathrm{imido}}$ spin population of 1.289 in Fe^{IV}(P)(NH) is significantly higher than the

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Table 1. Gross Atomic Spin Populations

molecule	Fe	L_{axial}	N_{por}	C_{α}	C_{β}	C_{meso}
$Fe^{V}(P)(N)^{a}$	1.579	1.550	−0.018	−0.004	−0.003	−0.002
$Fe^{IV}(P)(NH)^{b}$	0.775	1.289	−0.003	0.000	0.000	−0.006
$Fe^{IV}(P)(O)^{b}$	1.199	0.826	−0.009	0.003	0.001	−0.006
$Fe^{V}(P)(O)(F)^{a}$	2.134	0.961	−0.036	0.000	−0.003	0.000
Fe^{IV}(“a_{2u}”-P•)(O)(F)^{a}	1.110	0.904	0.114	−0.045	−0.006	0.221
Fe^{IV}(“a_{1u}”-P•)(O)(F)^{a}	1.111	0.888	−0.048	0.141	0.029	−0.051

[a] $S = {}^{3}/_{2}$. [b] $S = 1$.

O spin population of 0.826 in $Fe^{IV}(P)(O)$. Consequently, The Fe spin population of 0.775 in $Fe^{IV}(P)(NH)$ is significantly lower than the Fe spin population of 1.199 in $Fe^{IV}(P)(O)$. These results suggest that the more electron-rich (basic) imido ligand can support a greater degree of radical character than the oxo ligand. Placing the spin density profile of $Fe^{V}(P)(N)$ against this context, we can see why the even more basic nitrido axial ligand carries a higher spin population (1.550) than either the imido ligand in $Fe^{IV}(P)(NH)$ or the oxo ligand in $Fe^{IV}(P)(O)$. The Fe spin population in $Fe^{V}(P)(N)$ is 1.579. If we assume that the Fe($3d_{xy}$) electron is completely localized on the iron (which is consistent with Table 1), then the Fe spin population that is directly attributable to the antibonding $Fe(d_{\pi})-N_{nitrido}(p_{\pi})$ orbital interactions is only about 0.58 that is considerably smaller than the Fe spin populations in $Fe^{IV}(P)(NH)$ and $Fe^{IV}(P)(O)$. This is clearly a consequence of the greater electron-richness of the nitrido ligand relative to the imido and oxo ligands.

Both spin-restricted and unrestricted calculations on $[Fe^{VI}(P)(N)]^{+}$ ($S = 0$) and $Fe^{VI}(P)(N)(F)$ ($S = 0$) yielded Kohn−Sham orbital energy spectra that exhibited a clean and significant HOMO-LUMO gap, suggesting that, at least theoretically, these species are stable entities. We speculate that with a trianionic corrolato equatorial ligand, Fe(VI) intermediates such as Fe^{VI}(corrolato)(N) or Fe^{VI}(corrolato)(O)(X) (X = F or other suitable monoanionic ligand) may be experimentally detectable. In fact, such intermediates may well be involved in ligand transfer reactions catalyzed by Fe^{IV}(corrolato)(X) complexes, reported by Gross and co-workers.[31,32]

Finally, we have investigated whether a true Fe^{V}-oxo porphyrin intermediate, i.e., one with a $d_{xy}{}^{1}d_{xz}{}^{1}d_{yz}{}^{1}$ metal d electron configuration, is a realistic proposition. As shown in Table 1, calculations on different electronic configurations of the neutral species $[Fe(P)(O)(F)]^{0}$ led to an $S = {}^{3}/_{2}$ ground-state involving an Fe^{IV}-oxo center coupled to an “A_{2u}-type” porphyrin π-cation radical as the ground state with the Fe(V) state 0.16 eV (3.7 kcal/mol) higher and the Fe^{IV}-oxo “A_{1u}-type” porphyrin π-cation radical 0.25 eV (5.8 kcal/mol) higher in energy (both numbers referring to the “a_{2u}-type” radical as the energy zero level). We have neglected here the possibility of pseudo-Jahn−Teller distortion of the porphyrin cation radical that can occur because of the near-degeneracy of the “A_{1u}” and “A_{2u}”-type radical states.[33] Should this distortion actually occur, it would mean that the energy of 0.16 eV of the Fe(V) state, relative to the lowest Fe^{IV}-oxo porphyrin π-cation radical state, may be regarded as the lower limit of the real energy difference. Nevertheless, the result that we do not succeed in finding an Fe(V) ground state for $[Fe(P)(O)(F)]^{0}$ is consistent with the finding that no true Fe^{V}-oxo porphyrin intermediate is known.

In summary, we have used DFT calculations to characterize a nitridoiron(V) porphyrin in terms of its geometry and spin density profile. The Fe(V) calculations exhibit exceptionally narrow convergence radii and we believe that for this reason they have long eluded researchers working on high-valent iron intermediates. The nitrido ligand appears to be uniquely capable of stabilizing a “true” Fe(V) center, in the sense defined in this paper. In contrast, an axial ligand set consisting of an oxide and a fluoride favor an Fe^{IV}-oxo porphyrin π-cation radical as the ground state.

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Supporting Information Available: Complete sets of optimized Cartesian coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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