

Theoretical Evidence Favoring True Iron(V)-Oxo Corrole and Corrolazine Intermediates

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Although many formally Fe(V) intermediates are known in the form of peroxidase compound I intermediates and their synthetic models, “true” d^3 Fe^{VO} intermediates have remained elusive and hence a Holy Grail of sorts for many bioinorganic chemists. Very recently, Newcomb and co-workers provided transient absorption spectroscopic evidence suggestive of Fe^{VO} corrole intermediates. Here, we report DFT calculations predicting nearly isoenergetic Fe^{VO} and Fe^{IV}O corrolato²⁻ states for Fe(corrolato)(O) intermediates. In the course of a theoretical search for systems in which a true Fe^{VO} state might be favored by a clear and substantial margin of energy, we have identified corrolazine as a promising supporting ligand; thus, we find that with corrolazine, the Fe^{VO} states are favored by at least 0.5 eV over Fe^{IV}O corrolazinato²⁻ states.

Introduction

Iron-oxo intermediates formally at the Fe(V) oxidation level have long been known in the form of peroxidase compound I intermediates and their synthetic mimics,¹ but the existence of true Fe^{VO} intermediates has remained questionable,² although genuine Fe^VN species have been spectroscopically characterized.³ A recent report by Newcomb and co-workers now suggests that a true Fe^{VO} species may actually have been observed via transient absorption spectroscopy.⁴ The putative Fe^{VO} transient, which could be obtained via either the reaction of an Fe(III) corrole with mCPBA or photolysis of an Fe^{IV}-nitrito or -chlorato corrole complex, decayed relatively slowly to another transient, for which an Fe^{IV}O corrole²⁻ formulation was proposed.⁴ Using DFT calculations (PW91/STO-TZP, as implemented in the ADF 2004 program system⁵), we set out to determine

whether the calculated energetics (listed in Table 1) associated with these electronic structures support the proposed assignments.⁶ In brief, the DFT energetics results are indeed qualitatively consistent with experimental observations. We have also examined two additional electron-deficient corrole derivatives, β -octafluorocorrole,⁷ recently prepared in our laboratory, and corrolazine,⁸ recently prepared by Goldberg and co-workers, in terms of their ability to support true Fe^{VO} intermediates. Here, too, theory makes exciting predictions, especially in the corrolazine case, as described below.

Fe^{VO} Corroles. The ground state for Fe(Cor)(O) (Cor³⁻ = corrolato) was found to be ²A', with a $d_{xy}^2 d_{xz}^1$ Fe^{VO}

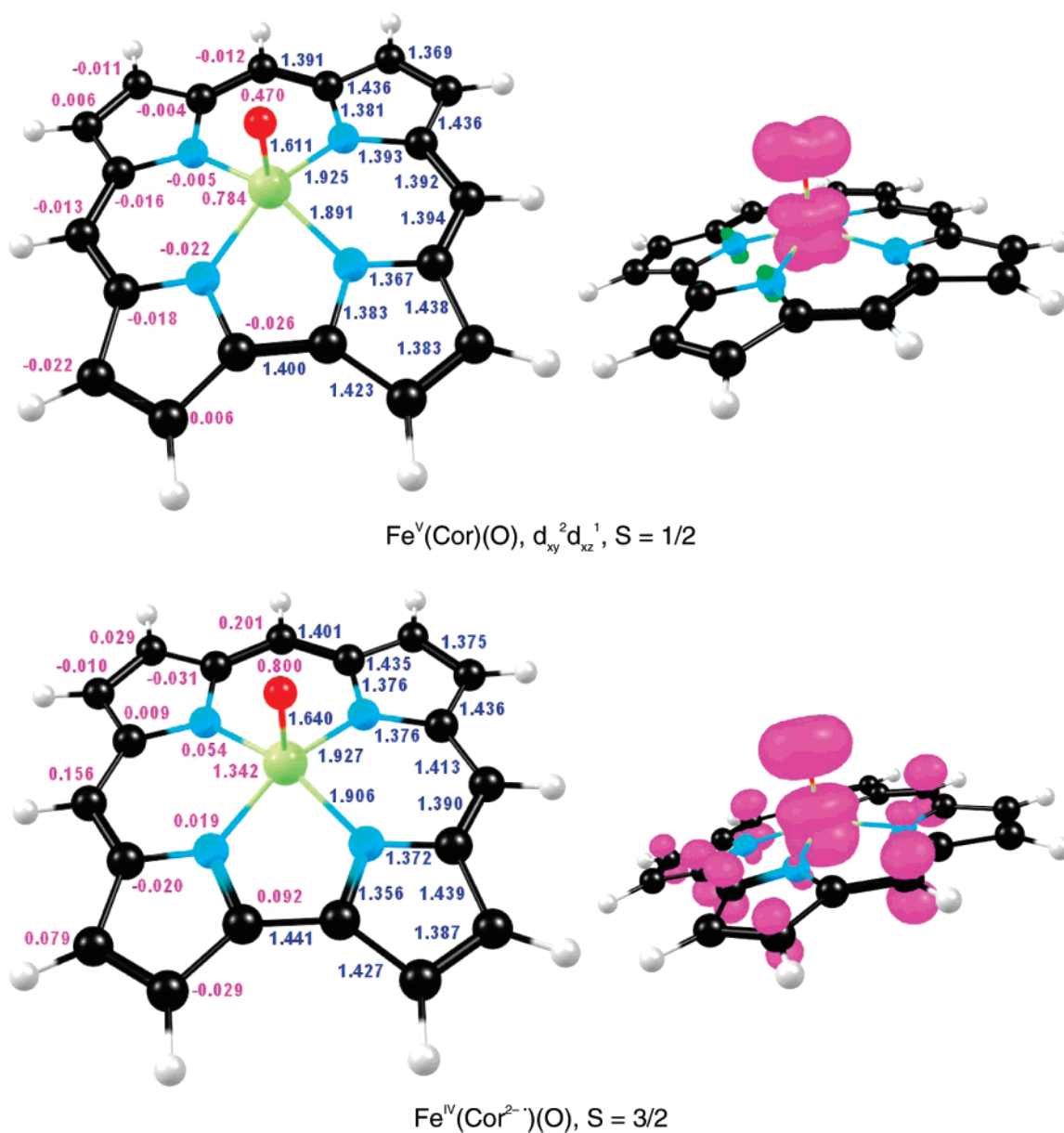
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Table 1. Energetics (eV) of Different Species and States Studied^a

| compd | S | configuration | PW91 | single-point energies at PW91 geometries | | | | | | | |
|---------------------------|-----|---|-------------|--|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | | | | BLYP | RPBE | revPBE | OLYP | mPBE | OPBE | B3LYP | O3LYP |
| Fe(Cor)(O) | 1/2 | $d_{xy}^2d_{xz}^1$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 1/2 | $d_{xy}^2d_{yz}^1$ | 0.08 | 0.09 | 0.09 | 0.09 | 0.11 | 0.09 | 0.11 | 0.06 | 0.10 |
| | 3/2 | $d_{xy}^2d_{xz}^1d_{yz}^1$ Cor ²⁻ | 0.24 | 0.21 | 0.19 | 0.20 | 0.12 | 0.23 | 0.15 | -0.20 | -0.12 |
| [Fe(Cor)(N)] ⁻ | 1/2 | $d_{xy}^2d_{xz}^1$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 1/2 | $d_{xy}^2d_{yz}^1$ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.10 | 0.07 |
| | 3/2 | $d_{xy}^2d_{xz}^1d_{yz}^1$ Cor ²⁻ | 1.53 | 1.51 | 1.49 | 1.50 | 1.50 | 1.52 | 1.51 | 1.65 | 1.62 |
| Fe(F ₈ Cor)(O) | 1/2 | $d_{xy}^2d_{xz}^1$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 1/2 | $d_{xy}^2d_{yz}^1$ | 0.10 | 0.11 | 0.11 | 0.11 | 0.13 | 0.10 | 0.12 | 0.12 | 0.13 |
| | 3/2 | $d_{xy}^2d_{xz}^1d_{yz}^1$ F ₈ Cor ²⁻ | 0.27 | 0.24 | 0.22 | 0.24 | 0.17 | 0.26 | 0.19 | -0.18 | -0.09 |
| Fe(Cz)(O) | 1/2 | $d_{xy}^2d_{xz}^1$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 1/2 | $d_{xy}^2d_{yz}^1$ | 0.08 | 0.09 | 0.08 | 0.08 | 0.10 | 0.08 | 0.09 | 0.06 | 0.08 |
| | 3/2 | $d_{xy}^2d_{xz}^1d_{yz}^1$ Cz ²⁻ | 0.65 | 0.65 | 0.58 | 0.59 | 0.51 | 0.62 | 0.50 | 0.59 | 0.52 |

^a Energy zero levels are shown in bold.**Figure 1.** (Left) Mulliken spin populations (magenta) and optimized distances (Å, blue); (right) spin density plots.

electronic configuration, whereas a $^2A''$ state with a $d_{xy}^2d_{yz}^1$ $\text{Fe}^{\text{V}}\text{O}$ configuration was only 0.08 eV higher in energy. Both these states exhibit very short FeO distances of around 1.6

Å, as shown in Figure 1, with nearly all the spin density concentrated on the FeO unit.⁹ A low-lying $S = 3/2$ state was also found, 0.24 eV above the ground state, that

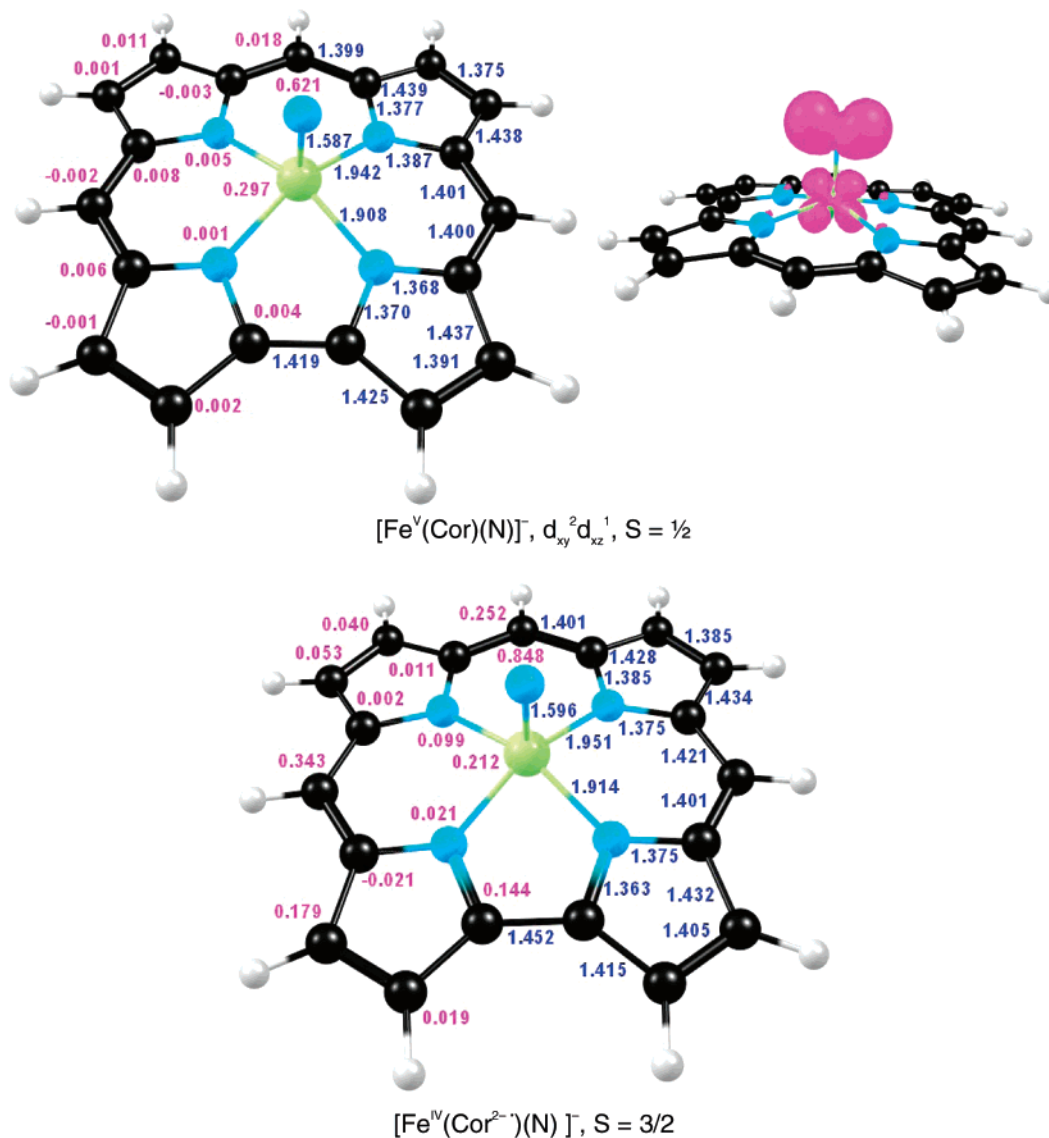


Figure 2. Mulliken spin populations (magenta) and optimized distances (Å, blue); a spin density plot is shown in magenta.

corresponds to a $d_{xy}^2 d_{xz}^1 d_{yz}^1$ Fe^{IV}O Cor²⁻ description. Note from Figure 1 the characteristic compound I-like spin density profile for this electronic state, namely a total of about 2 spins on the FeO unit and 1 spin on the macrocycle. The small calculated energy differences between these states do not permit a definitive assignment of the experimentally observed transients, but single-point calculations with a wide variety of pure and hybrid functionals unanimously indicate that they are approximately isoenergetic. In particular, note from Table 1 that the hybrid B3LYP functional exhibits a small preference for the Fe^{IV}O Cor²⁻ state relative to the Fe^VO states. Overall, it seems that the near-degeneracy of these states very nicely mirrors the experimentally observed scenario.

(9) Key calculations on electron distributions and spin density profiles of high-valence iron-oxo intermediates: (a) Ghosh, A.; Almlöf, J.; Que, L., Jr. *J. Phys. Chem.* **1994**, *98*, 5576–5579. (b) Ghosh, A.; Almlöf, J.; Que, L., Jr. *Angew. Chem., Int. Ed.* **1996**, *35*, 770–772. (c) Ghosh, A.; Tangen, E.; Gonzalez, E.; Que, L., Jr. *Angew. Chem., Int. Ed.* **2004**, *43*, 834–838. (d) Conradie, J.; Swarts, J. C.; Ghosh, A. *J. Phys. Chem. B* **2004**, *108*, 452–456. (e) Ghosh, A.; Tangen, E.; Ryeng, H.; Taylor, P. R. *Eur. J. Inorg. Chem.* **2004**, 4555–4560.

The existence of the ultrahigh Fe(V) oxidation state in the presence of the easily oxidizable corrole ligand may seem paradoxical. Indeed, a ubiquitous theme in corrole chemistry is the issue of ligand noninnocence.^{7,10} However, it appears that in the presence of the strongly electron-donating oxo or nitrido axial ligand, a noninnocent corrole ligand is not an absolute necessity; indeed, the axial oxo or nitride ligand may accommodate a good fraction of the oxidation equivalents. A parallel may be drawn here between Fe(corrolato)-

(10) Key references to noninnocent corrole and related ligands: (a) Ghosh, A.; Wondimagegn, T.; Parusel, A. B. *J. Am. Chem. Soc.* **2000**, *122*, 5100–5104. (b) Cai, S.; Walker, F. A.; Licoccia, S. *Inorg. Chem.* **2000**, *39*, 3466–3478. (c) Steene, E.; Wondimagegn, T.; Ghosh, A. *J. Phys. Chem. B* **2001**, *105*, 11406–11413. Addition/correction: *J. Phys. Chem. B* **2002**, *106*, 5312–5312. (d) Zakhariyeva, O.; Schunemann, V.; Gerdan, M.; Licoccia, S.; Cai, S.; Walker, F. A.; Trautwein, A. X. *J. Am. Chem. Soc.* **2002**, *124*, 6636–6648. (e) Isocorrole: van Oort, B.; Tangen, E.; Ghosh, A. *Eur. J. Inorg. Chem.* **2004**, 2442–2445. (f) Simkhovich, L.; Gross, Z. *Inorg. Chem.* **2004**, *43*, 6136–6138 and references therein. (g) Nardis, S.; Paolesse, R.; Licoccia, S.; Fronczek, F. R.; Vicente, M. G. H.; Shokhireva, T. K.; Cai, S.; Walker, F. A. *Inorg. Chem.* **2005**, *44*, 7030–7046. (h) Norcorrole: Ghosh, A.; Wasbotten, I. H.; Davis, W.; Swarts, J. C. *Eur. J. Inorg. Chem.* **2005**, 4479–4485.

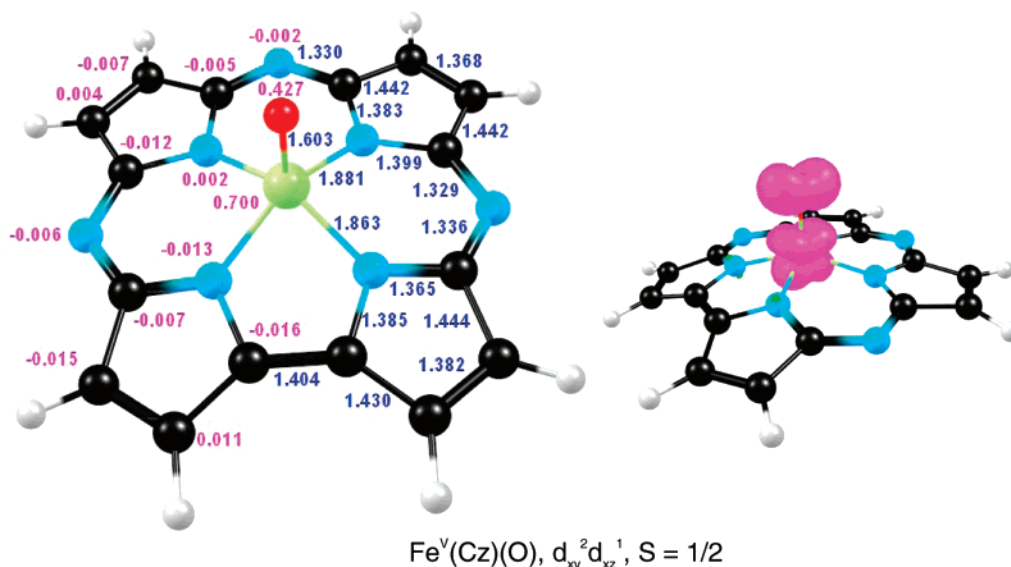


Figure 3. (Left) Mulliken spin populations (magenta) and optimized distances (Å, blue); (right) spin density plot.

Cl and $[\text{Fe}(\text{corrolato})]_2\text{O}$ complexes: whereas ^1H NMR spectroscopy, DFT calculations, and electrochemical studies suggest an Fe^{III} -corrole $^{2-}$ formulation for the former, a true Fe^{IV} description is indicated for the μ -oxo dimers.^{7,10c}

$[\text{Fe}(\text{Cor})(\text{N})]^-$. For the axial nitrido complex $[\text{Fe}(\text{Cor})(\text{N})]^-$, a pair of near-degenerate $S = 1/2$ $\text{Fe}^{\text{V}}\text{N}$ states (analogous to the Fe^{VO} states mentioned above) were identified as the lowest-energy states. As in the case of $\text{Fe}(\text{Cor})(\text{O})$, the lowest $S = 3/2$ state again corresponds to a $d_{xy}^2 d_{xz}^1 d_{yz}^1$ Fe^{IV} -corrole $^{2-}$ description, but with a twist: in the nitride case, the $S = 3/2$ state is more than 1.5 eV above the ground state. Another key difference between the $S = 1/2$ Fe^{VO} and Fe^{VN} involves the Fe spin population (Figure 2), which is much higher in the former species (ca. 0.75) than in the latter (0.3).

β -Octafluorocorrole-Based Intermediates. Although sometimes dismissed as mere speculation, a key goal of quantum chemical studies is to predict the existence of as-yet unknown molecules and materials with novel electronic structures and properties. In that spirit, we have conducted a theoretical search for electron-deficient ligand systems that might stabilize true Fe^{VO} states by a substantial margin of energy over $\text{Fe}^{\text{IV}}\text{O}$ ligand radical states. Interestingly, compared with unsubstituted Cor, the electron-deficient β -octafluorocorrole (F_8Cor)⁷ ligand does not exhibit a substantially stronger preference for the Fe^{VO} state relative to $\text{Fe}^{\text{IV}}\text{O}$ $\text{F}_8\text{Cor}^{2-}$ states (see Table 1). Although intriguing, this finding is not entirely surprising; thus, ^1H NMR, electrochemistry, and DFT studies all indicate that *meso*-triaryl $\text{Fe}(\text{F}_8\text{Cor})\text{Cl}$ derivatives exhibit roughly the same degree of macrocycle noninnocence as analogous $\text{Fe}(\text{Cor})\text{-Cl}$ derivatives.⁷

Fe^{VO} Corrolazines. As shown in Table 1 (also see Figure 3), the corrolazine (Cz)⁸ ligand exhibits a pronounced preference for Fe^{VO} ground states compared with $\text{Fe}^{\text{IV}}\text{O}$ Cz^{2-} states. Both pure and hybrid functionals unanimously

show that the Fe^{VO} states are favored by at least 0.5 eV over the $\text{Fe}^{\text{IV}}\text{O}$ Cz^{2-} states. This prediction is very reminiscent of the fact that a β -octaarylcorrolazine-based Mn^{VO} complex^{8b} is so stable as to be readily isolable and purifiable by column chromatography; however, in this case, it is not clear whether the stability of the Mn^{VO} species owes more to the electronic character of the corrolazine ligand or to the steric protection afforded by the peripheral aryl substituents.

Conclusion

In sum, DFT calculations strongly suggest that true Fe^{VO} intermediates, supported by corrole and corrolazine ligands, should be experimentally accessible. In the case of corrole and octafluorocorrole, our calculations predict nearly equienergetic Fe^{VO} and $\text{Fe}^{\text{IV}}\text{O}$ Cor^{2-} states, which is qualitatively consistent with the possible (but not yet certain) experimental observation of both these states in transient absorption experiments. Excitingly, for the corrolazine ligand, our calculations predict true Fe^{VO} intermediates favored by a substantial margin of energy over $\text{Fe}^{\text{IV}}\text{O}$ Cz^{2-} states. In our opinion, the fact that both pure and hybrid DFT functionals are essentially unanimous vis-à-vis these results lends particular credence to this study. Last but not least, both Newcomb and co-workers' experiments⁴ and our calculations raise the question of whether true Fe^{VO} intermediates might actually be involved in the reaction pathways of heme proteins such as P_{450} cytochromes,¹ which remains a key issue for future studies in this field.

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Supporting Information Available: Optimized Cartesian coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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