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[18] A spin crossover near the minima of ^{4}**2** and ^{2}**2** will simply lead to low-spin epoxidation through the low-energy path available to ^{2}**2** (see Scheme 1).

[19] It is likely that the fate of ^{4}**2**-III is more complex in view of the fact that propylene undergoes an unusual hydrogen/deuterium exchange during its epoxidation. See: J. T. Groves, G. E. Avaria-Neisser, K. M. Fish, M. Imachi, R. L. Kuczkowski, *J. Am. Chem. Soc.* **1986**, *108*, 3837.

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Chameleon States: High-Valent Metal–Oxo Species of Cytochrome P450 and Its Ruthenium Analogue**

François Ogliaro, Samüel P. de Visser, John T. Groves,* and Sason Shaik*

There is a continuing search for efficient and robust catalysts that can perform monooxygenation of organic compounds.[1] High-valent metal–oxo porphyrin species **1** (Figure 1) constitute such an important family.[2] The members of this family are analogous to the principal oxidant of enzymes such as cytochrome P450 (CP450) or chloroperoxidase (CPO), and this analogy endows the (L)PorM^{z}O species with an added allure. While iron and manganese are the most ubiquitous metal centers in biological systems, ruthenium is present in artificially designed systems which are attractive potent catalysts.[2c] A fundamental question concerns the nature of the ground state of these catalysts, and the relationship between their electronic structure and monooxygenation capability. This is the focus of the present paper which uses density functional (DFT) calculations to compare the electromeric states for $[(L)PorM^{z}O]$ (M = Fe, Ru; z = III–V; L = SH and SCH_3). As shall be seen, the Fe and Ru

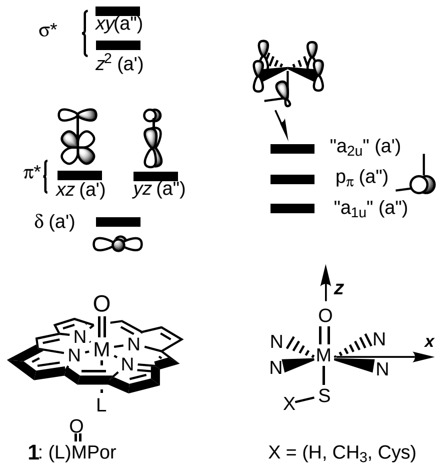

Figure 1. Key orbitals for **1** with thiolate ligands.

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[*] Prof. S. Shaik, Dr. F. Ogliaro, Dr. S. P. de Visser
Department of Organic Chemistry and
The Lise Meitner-Minerva Center for
Computational Quantum Chemistry
The Hebrew University of Jerusalem
91904 Jerusalem (Israel)
Fax: (+972) 2-658-4680
E-mail: sason@yfaat.ch.huji.ac.il

Prof. J. T. Groves
Department of Chemistry, Princeton University
Princeton, NJ 08544-1009 (USA)
Fax: (+1) 60-9-258-0348
E-mail: jtgroves@pop.princeton.edu

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states are very different in both spin and metal oxidation states. Furthermore, medium polarity exerts a strong influence on most of the low-lying states of both iron and ruthenium complexes which behave like chameleon states, changing nature in response to the environment.

We briefly review the rich chemical patterns that are associated with the ground states of these oxidants, by reference to the key orbitals of **1** (L = thiolate) in Figure 1. The orbital set on the left-hand side involves the five d-type orbitals of the metal, labeled as δ, π*, and σ* according to the bonding between the iron center and the oxygen atom.[3] The set on the right-hand side shows relevant porphyrin and ligand orbitals. The "a_{2u}" orbital is delocalized primarily over the porphyrin ring and the axial thiolate ligand, and hence this orbital depends on the nature of the axial ligand.[3] The second orbital is a p_π-type orbital of the ligand, while the third is "a_{1u}".[4] The latter two orbitals are antisymmetric to the xz plane and in principle can mix, albeit weakly due to a very small overlap. In the high-valent catalysts, there are nine electrons, which have to be distributed among the entire set of orbitals. The occupation mode in these orbitals determines the oxidation state of the metal and the porphyrin, as well as the spin situation of the complex.

The ground state of the principal oxidant of CP450 is considered to be the triradicaloid species $[(L)Por^{+\bullet}Fe^{IV}O]$ (called also compound I (Cpd I)).[5] It involves triplet electrons in the π* orbitals of the $Fe^{IV}O$ moiety weakly coupled to a third electron in the "a_{2u}" orbital.[3, 6] The one-electron reduced species ($[(L)PorFe^{IV}O]$, Compound II (Cpd II)) is a less reactive oxidant.[2b,c] Derivatives of $[PorRu^{IV}O]$ are also inactive as catalysts and behave by analogy to Cpd II.[2c, 7, 8] It was thought initially that the active monooxygenating species in ruthenium catalysts was the dioxo compound $[PorRu^{VI}O_2]$[9] (singlet δ^2 state). It has become evident that the more active form of the ruthenium catalyst is in fact the $[(L)PorRu^{V}O]$.[2c, 10] While few $[L_5Ru^{V}O]$ catalysts are known with a variety of macrocyclic ligands,[11] the putative active species of $[(L)PorRu^{V}O]$ has not been isolated nor has it ever been characterized by any physical means. In the iron chemistry, an Fe^{V} species used to be implicated in the Gif reagent,[12] but not anymore. The highly sought $[PorFe^{V}O]$ species was reported in a recent experimental study[2b, 13] of iron porphyrin chemistry, in a chemical equilibrium between Cpd I and the iron(v) species, $[(L)PorFe^{V}O]$. The equilibrium between the species was found to be sensitive to the environment and to substituents on porphyrin. However, unlike $[(L)PorRu^{V}O]$, which is expected to be a low-spin ($S = 1/2$) $\delta^2 \pi^{*1}$ state,[11a] the Fe^{V} electromer was reported to possess a high-spin ($S = 3/2$) $\delta^1 \pi^{*2}$ ground state and to be less reactive than its Cpd I electromer.[2b, 13] The paucity of data on the natures and structures of the Ru^{V} and Fe^{V} species, along with their puzzling reactivity patterns pose a fundamental research agenda which is addressed here by means of hybrid (B3LYP) DFT calculations.

Calculations were done with the JAGUAR 4.0 package,[14] using wherever possible both restricted (RODFT) and unrestricted (UDFT) hybrid functional, B3LYP[15] with full geometry optimization and frequency characterization. The effect of the medium was studied with JAGUAR's implementation of the polarized continuum model, using a dielectric constant of 5.7, which mimics a nonpolar environment. The LACVP/6-31G basis set was used in all calculations.[16] Two metal centers, M = Fe, Ru, and two ligands, L = HS^-, CH_3S^-, were compared.

Table 1 collects the relative data for the various electromeric states. The orbital occupation (see Figure 1) of all the states is given along with the commonly used state designation and its C_s symmetry. For example, the first two states are designated as $^{2,4}A_{2u}(M^{IV})$ to emphasize the single occupancy of the "a_{2u}" orbital, and the formal oxidation state IV of the metal determined by the d^4 occupation. The quartet and doublet spin situations characterize the ferromagnetic and antiferromagnetic coupling between the "a_{2u}" electron and those occupying the two π* orbitals. Designations of other states follow similar logic.[3] Among them are the $^{2,4}\Pi_S(M^{IV})$ and $^{2,4}A_{1u}(M^{IV})$ states where, in addition to the singly occupied π* orbitals, a third one is either the sulfur p_π or porphyrin "a_{1u}" orbitals, respectively. Among the possible M^{V} states, entry 10 in Table 1 lists the state discussed by Watanabe et al.[2b, 13] with the $\delta^1 \pi^{*1} \pi^{*1}$ open shell. Table 1, entries 8 and 9 show the corresponding low-spin doublet states $^2\Pi_{xz,yz}(M^{V})$ with $\delta^2 \pi^{*1}$ occupation. Also shown is either the $^2\Pi_{yz}(M^{III})$ state, which corresponds to $[(L)Por^{++}M^{III}O]$ with a single electron in π^*_{yz}.

It is apparent that for iron, the ground state is the antiferromagnetic state $^2A_{2u}(Fe^{IV})$ (Table 1, entry 2), for both

Table 1. States, orbital occupancies (refer to Figure 1), and relatives energies for the isolated molecule and for the molecule in a polarizing medium.

Entry	State	C_S symmetry	Orbital occupancy	E_{rel} [kcal mol^{-1}] Fe, L = SH (SCH_3) $\varepsilon = 1$	 $\varepsilon = 5.7$	 Ru $\varepsilon = 1$	 $\varepsilon = 5.7$
1	$^4A_{2u}(M^{IV})$	$^4A''$	$a_{1u}^2\ p_\pi^2\ \delta^2\ \pi_{xz}^{*1}\ \pi_{yz}^{*1}\ a_{2u}^1$	0.0 (0.00)	0.0	0.0	0.0
2	$^2A_{2u}(M^{IV})$	$^2A''$	$a_{1u}^2\ p_\pi^2\ \delta^2\ \pi_{xz}^{*1}\ \pi_{yz}^{*1}\ a_{2u}^1$	− 0.07 (+ 0.03)	− 0.12	− 0.56	− 0.35
3	$^4\Pi_S(M^{IV})$	$^4A'$	$a_{1u}^2\ p_\pi^1\ \delta^2\ \pi_{xz}^{*1}\ \pi_{yz}^{*1}\ a_{2u}^2$	+ 5.66 (+ 0.47)	+ 8.85	+ 3.89	+ 9.34
4	$^2\Pi_S(M^{IV})$	$^2A'$	$a_{1u}^2\ p_\pi^1\ \delta^2\ \pi_{xz}^{*1}\ \pi_{yz}^{*1}\ a_{2u}^2$	+ 5.63 (+ 0.31)	+ 8.69	[a]	[a]
5	$^6\Delta_{xy}(M^{IV})$	$^6A'$	$a_{1u}^2\ p_\pi^2\ \delta^1\ \pi_{xz}^{*1}\ \pi_{yz}^{*1}\ a_{2u}^1\ \sigma_{xy}^{*1}$	+ 14.27	+ 15.05	[a]	[a]
6	$^4A_{1u}(M^{IV})$	$^4A'$	$a_{1u}^1\ p_\pi^2\ \delta^2\ \pi_{xz}^{*1}\ \pi_{yz}^{*1}\ a_{2u}^2$	+ 21.27[b]	[a]	+ 17.31[b]	[a]
7	$^2\Pi_{xz}(M^{V})$	$^2A'$	$a_{1u}^2\ p_\pi^2\ \delta^2\ \pi_{xz}^{*1}\ \pi_{yz}^{*0}\ a_{2u}^2$	+ 21.66 (+ 21.25)	[a]	− 5.14	+ 0.25
8	$^2\Pi_{yz}(M^{V})$	$^2A''$	$a_{1u}^2\ p_\pi^2\ \delta^2\ \pi_{xz}^{*0}\ \pi_{yz}^{*1}\ a_{2u}^2$	+ 16.34 (+ 20.45)	[a]	− 3.57	+ 1.38
9	$^2\Pi_{yz}(M^{III})$	$^2A''$	$a_{1u}^2\ p_\pi^2\ \delta^2\ \pi_{xz}^{*2}\ \pi_{yz}^{*1}\ a_{2u}^0$	+ 26.43[c]	[a]	[a]	[a]
10	$^4\Delta(M^{V})$	$^4A''$	$a_{1u}^2\ p_\pi^2\ \delta^1\ \pi_{xz}^{*1}\ \pi_{yz}^{*1}\ a_{2u}^2$	+ 26.55[b]	[a]	+ 20.58[b]	[a]

[a] Converged on the lower energy state with the same symmetry. [b] Single point calculation using the $^4A_{2u}$ geometry. [c] Single point calculation using the $^2\Pi_{yz}(M^{V})$ geometry.

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the isolated molecule as well as when it is under the influence of medium polarization. The iron(v) states (Table 1, entries 7 and 8) are much higher lying. Changing the ligand to CH_3S^-, which is a better π- and σ-donor than $L = HS^-$, does not change this conclusion. Here, the axial ligand does not affect the $^2A_{2u}(Fe^{IV}) - {}^2\Pi_{xz,yz}(Fe^V)$ energy gap. Likewise, the $^4\Delta(Fe^V)$ state of Cpd I (Table 1, entry 10) is significantly higher lying than the $^2A_{2u}(Fe^{IV})$ ground state. The $^4A_{1u}(Fe^{IV})$ state (Table 1, entry 6), which was assigned as the ground state in a few Cpd I species of iron porphyrin complexes with substituted porphyrin,[4] is found here to lie 21.27 kcal mol^{-1} higher than $^2A_{2u}(Fe^{IV})$.

In contrast to the situation for iron, the ground state for ruthenium is the $^2\Pi_{xz}(M^V)$, followed by $^2\Pi_{yz}(M^V)$ (Table 1, entries 7 and 8). In both states an electron from the d-manifold (π*) is shifted to fill the "a_{2u}" hole, leaving behind a d^3 configuration with a single unpaired electron in either one of the π orbitals (Figure 1). By analogy with the iron system, the $^4A_{1u}(Ru^{IV})$ and $^4\Delta(Ru^V)$ states are calculated to lie considerably higher than the ground state. Medium polarization packs the states $^{4,2}A_{2u}(Ru^{IV})$ and $^2\Pi_{xz,yz}(M^V)$ within 1.73 kcal mol^{-1}, and endows the ruthenium complex with a ground state that is likely to be an equilibrating $Ru^{IV}-Ru^V$ mixture. Another difference with respect to iron, is that ruthenium complexes have a stronger preference for antiferromagnetic coupling.

Figure 2 shows the key geometric details of the low-energy states for the iron and ruthenium complexes in the isolated and "solvated" states. The C_1 and C_s geometries[3, 17] of the ground state for the iron complex are almost identical, and therefore all other species were investigated at the C_s point group. The Fe–O bond length is almost constant for all the states in the isolated molecule and when under the influence of medium polarity. The r_{Fe-O} value of 1.62 – 1.66 Å is in accord with experimentally determined values in a variety of Cpd I and Cpd II species.[2, 5] The Ru–O bond length varies between 1.78 – 1.82 Å, where generally $r_{Ru^{IV}-O} > r_{Ru^V-O}$. Experimental Ru–O distances for $Ru^{VI,\,VIII}$ or for pentacoordinated Ru^V complexes with macrocyclic ligands other than porphyrin cluster lie between 1.70 – 1.77 Å, and exhibit the same shortening with an increase in the oxidation state of the metal.[2, 8, 10, 11] X-ray data obtained for a closely related *trans*-dioxo-Ru^{VI}-porphyrin complex $[Ru^{VI}(tdcpp)O_2]$ (tdcpp = $C_9H_{15}Cl_6O_4P$) revealed two long Ru=O bonds of 1.729 Å.[2c]

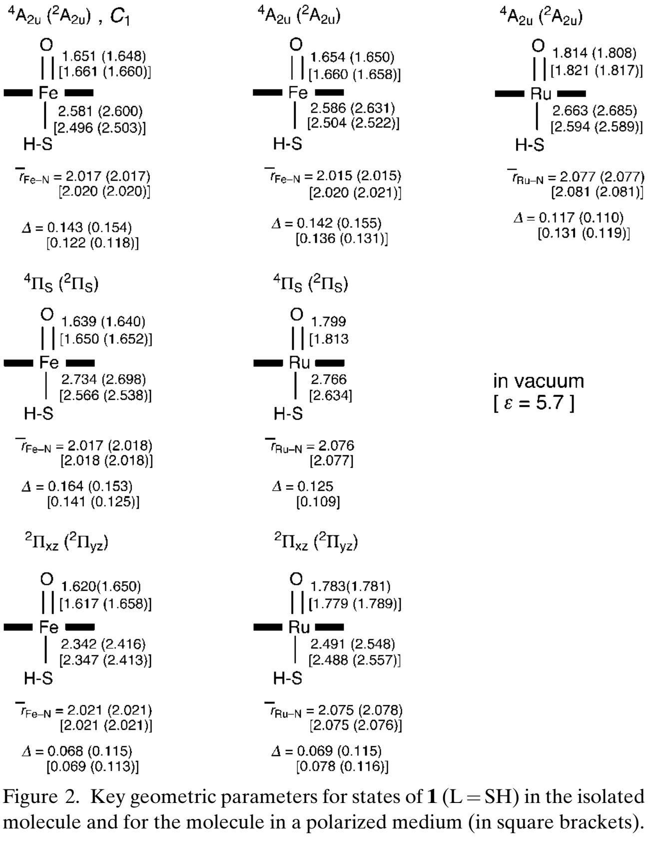

Figure 2. Key geometric parameters for states of **1** (L = SH) in the isolated molecule and for the molecule in a polarized medium (in square brackets).

The M–S bond length is more variable and exhibits a significant response to the state identity and the polarity of the medium. With the exception of $^2\Pi_{xz,yz}(M^V)$ states, which show hardly any response to medium polarity, in all other states increasing polarity causes a significant shortening of this bond. This is in accord with previous studies[3, 17] of the Fe–S bond, which revealed a very flexible bond (the stretch frequency is $\omega_{FeS} = 160\,cm^{-1}$ compared with 320 cm^{-1} calculated for the resting state), which undergoes shortening and strengthening due to hydrogen bonding and medium polarity. This effect in $^{4,2}A_{2u}(Fe^{IV})$ was shown to persist up to triple-ζ polarized basis sets.[17]

Figure 3 shows the spin density distribution for the various states. The $^{4,2}A_{2u}(M^{IV})$ and $^{2,4}\Pi_S(M^{IV})$ states are seen to undergo a dramatic change in their electronic structure with medium polarization effect. Both states contain two triplet electrons on the M=O moiety, and this feature is fixed whether the molecule is isolated or "solvated". But the third unpaired electron "shifts its location" upon "solvation". Thus, the $^{4,2}A_{2u}(Fe^{IV})$ states change from a thiolate-centered radical to a porphyrin-centered radical (see C_1 structure).[18] The $^{4,2}A_{2u}(Ru^{IV})$ states already have a dominant porphyrin-radical character in vacuum, and polarity further accentuates this character. The $^{2,4}\Pi_S(M^{IV})$ states undergo an even more dramatic change from almost a pure thiolate radical state to a mixed porphyrin – thiolate radical state. Thus, $^{4,2}A_{2u}(M^{IV})$ and $^{2,4}\Pi_S(M^{IV})$ are chameleon states with a hybrid nature that adjusts to the change in the environment.

In contrast, the $^2\Pi_{xz,yz}(M^V)$ states exhibit a less significant change since the electronic structure does not allow any sulfur→porphyrin electron shift. In UDFT there is some change which is larger in Ru than in Fe, but in RODFT the spin distribution is fixed. These less mutable electronic structures are in harmony with the unchanged geometries of these states. At present we are unable to tell whether the UDFT spin density is an artifact of spin contamination ($\langle S^2 \rangle$ = 1.12 – 1.14 in Ru) or is a real electronic effect. We therefore focus on the RODFT results, which are free of the spin contamination. According to these results, the $^2\Pi_{xz,yz}(M^V)$ states are localized $\pi^*_{xz,yz}(M = O)$ radicals.

Two questions arise at this point: 1) what are the roots of M–S bond shortening and its characteristic electronic reorganization in the chameleon states? 2) What causes the preference of ruthenium for Ru^V and iron for Fe^{IV}? These questions are addressed in Figures 4 and 5.

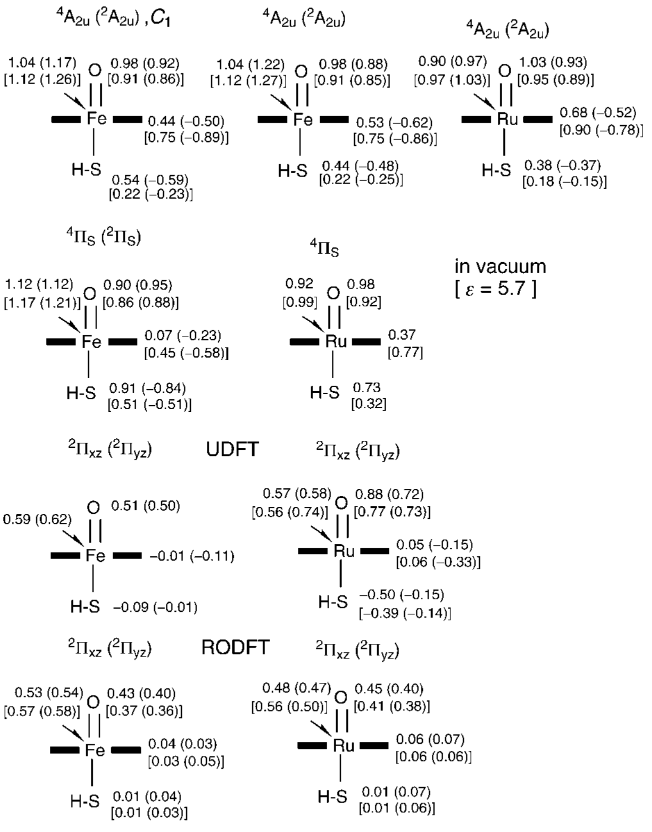

Figure 3. Group spin-densities in states of **1** (L = SH) for isolated states and for the molecule in a polarized medium (in square brackets).

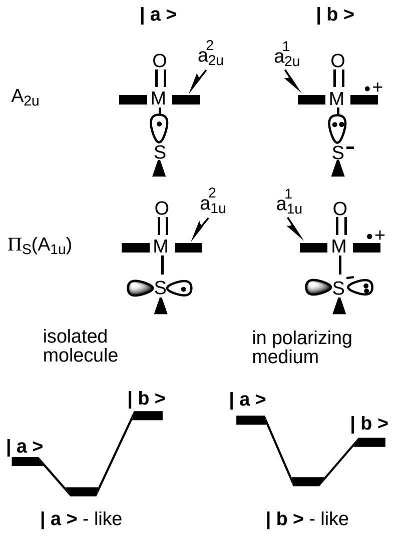

Figure 4. Resonance structures (|**a**⟩ and |**b**⟩), which contribute to the "redox mesomerism" in the A_{2u} and Π_s states of **1**; L = HS, and their mixing in the isolated molecule and in a polarizing medium.

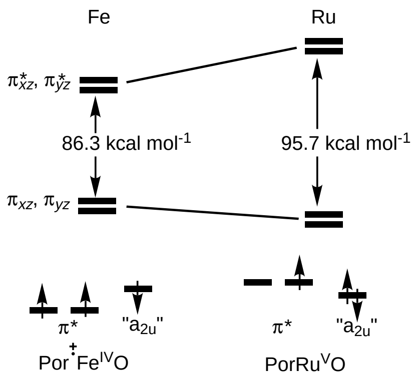

Figure 5. $\pi-\pi^*$ orbital energy gaps for **1**; L = HS with M = Fe and Ru, and corresponding π^* – "a_{2u}" relative orbital ordering.

Following our recent study[17] of hydrogen bonding and polarity effect on the $^{4,2}A_{2u}(Fe^{IV})$ states, Figure 4 shows the resonance structure hybrids, |**a**⟩ and |**b**⟩, which contribute to the $^{4,2}A_{2u}(M^{IV})$ and $^{2,4}\Pi_S(M^{IV})$ states. In the A_{2u} states, these hybrids involve shifting one electron from the p_σ hybrid of the thiolate to the pure porphyrin a_{2u} orbital, while for the Π_S states the shift is between the p_π and a_{1u} orbitals.[19] The resonance mixing diagrams show that the mixing of the structures to form hybrid states, as recognized before[2, 20] and termed "redox mesomerism".[2a, 20c] In the isolated molecular state, the thiolate radical structures, |**a**⟩, are lower in energy and the resulting state has a predominant thiolate radical nature of the σ- or π-types, in accord with the state identity. On the other hand, in a polarizing medium (or by mere hydrogen bonding to the thiolate[17]) structures |**b**⟩, which are polarizable due to the internal charge separation, are stabilized and become the lower ones. The resulting state now has a predominant porphyrin radical character. In the solvated $^{4,2}A_{2u}(M^{IV})$ states, the radical is located in the a_{2u} orbital and predominantly on porphyrin, while in the solvated $^{2,4}\Pi_S(M^{IV})$ states the radical is localized in the a_{1u} orbital and a more appropriate designation of these latter states is $^{4,2}A_{1u}(M^{IV})$-like. What determines the chameleon character of the states is the closeness of the resonance structures. The donor property of the axial ligand is crucial; ligands which are both good σ- and π-donors will give rise to chameleon states. In contrast, poor donor ligands do not lead to such chameleon behavior, and will generate states with fixed porphyrin-radical natures.

The different oxidation state preference of iron and ruthenium can be understood by consideration of the mixing of the metal and oxygen orbitals to form the π and π* orbitals (Figure 5). Thus, the 3d orbitals of iron are spatially smaller than the ruthenium 4d orbitals, and therefore the corresponding 3d(Fe) – 2p(O) overlap is significantly smaller than the 4d(Ru) – 2p(O) overlap.[21] This causes a stronger interaction for the ruthenium, which can be seen from the calculated π and π* orbital energy gaps. The weak interaction in iron leaves the π* orbitals below "a_{2u}" and leads to a $[Por^{+\bullet}Fe^{IV}O]$ ground state. In contrast, due to the strong interactions in ruthenium, the π* orbitals rise above "a_{2u}" and the ground state becomes $[PorRu^VO]$. It is apparent that a corresponding $[PorFe^VO]$ state can be stabilized, as concluded by Watanabe et al.,[2b, 13] when the "a_{2u}" orbital of the porphyrin is sufficiently lowered by electron-withdrawing substituents on the porphyrin. However, the $[PorFe^VO]$ and $[PorRu^VO]$ states will still be different in their spin state preferences due to the fact that the 3d – 3d exchange is significantly larger than the 4d – 4d exchange.[21] Thus, to enjoy the stabilizing 3d – 3d exchange, $[PorFe^VO]$ will have a propensity for a $\delta^1\pi^{*1}_{xz}\,\pi^{*1}_{yz}$ orbital occupancy in a $^4\Delta(Fe^V)$ state. In contrast, the smaller

4d–4d exchange in ruthenium will prefer the low-spin $^2\Pi_{xz,yz}(\mathrm{Ru^V})$ states, as observed in this study.

In conclusion, the $\mathrm{Ru^VO}$ complex is shown to be distinctly different in its electronic structure than the iron. The vacant π^* orbital in the $\mathrm{Ru^VO}$ catalyst will endow this reagent with a heightened electrophilic nature, which will be more pronounced with substrates which are better electron donors. Preliminary experimental results by one of us[22] reveal indeed such a heightened electrophilic nature in the oxidation reactions of substituted toluene by a ruthenium porphyrin catalyst. The electrophilicity of the ruthenium catalyst is found to be larger than the corresponding Cpd I of iron, and even larger than that of an electronegative hydrogen abstractor, a bromine atom. Another interesting aspect of the ruthenium catalyst is the equilibrium of the closely lying $^2\Pi_{xz,yz}(\mathrm{Ru^V})$ and Cpd I states $^{4,2}\mathrm{A_{2u}}(\mathrm{Ru^{IV}})$. Moreover, for an axial ligand which is a good π-donor the $^{4,2}\Pi_\mathrm{S}(\mathrm{Ru^{IV}})$/$^{4,2}\mathrm{A_{1u}}(\mathrm{Ru^{IV}})$ states equilibrium will also be important. Within this dense manifold of ground states, a multistate reactivity may develop with mixed electrophilic and Cpd I–radical characters. Finally, sensitivity to the polarity of the environment is expected in view of the chameleon nature of the $^{4,2}\mathrm{A_{2u}}(\mathrm{Ru^{IV}})$ states.

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