Electronic Structure of the Water-Oxidation Catalyst [(bpy)$_2$(OH$_x$)RuORu(OH$_y$)(bpy)$_2$]$^{z+}$: Weak Coupling between the Metal Centers Is Preferred over Strong Coupling

Xiaofan Yang and Mu-Hyun Baik*

Department of Chemistry and School of Informatics, Indiana University, Bloomington, Indiana 47405

Received June 24, 2004; E-mail: mbaik@indiana.edu

Among the rare examples of structurally well-defined molecules capable of oxidizing water,[1−5] the blue Ru dimer [(bpy)$_2$(OH$_2$)Ru^{III}-ORu^{III}(OH$_2$)(bpy)$_2$]$^{4+}$ (bpy = 2,2′-bipyridine) is the most extensively studied.[6] Unfortunately, its instability during catalytic turnover prevents technological utilization. Rational approaches to increasing the robustness of the catalyst while enhancing its activity are difficult to conceive, in part because the catalytic mechanism of water oxidation is not known. A few reasonable proposals have been made,[7−10] but a consensus mechanism has not emerged to date. Computational studies would be helpful and allow for quantification of the energetic requirements of possible reaction pathways. However, high-level calculations of the Ru dimer[11] are difficult: (i) The bipyridine ligands cannot be represented adequately by a smaller model ligand, thus making computer models expensive and hard to analyze. (ii) The overall four-electron redox process is coupled to loss of protons requiring the protonation state at the various redox steps to be explored (Scheme 1). (iii) Some of the intermediates are necessarily mixed-valence complexes, and the question whether the electron is delocalized or trapped adds complexity. (iv) The exact nature of how the two metal centers interact with each other electronically is not known.

As a part of a systematic effort investigating the reactivity of bimetallic complexes that play a role for discovering renewable energy sources, we examined the electronic structure of the Ru dimer. We found that the widely accepted paradigm[12−16] that the two Ru^{III} d^5 and Ru^V d^3 centers are strongly coupled is not consistent with high-level DFT calculations.

EPR silence and magnetic susceptibility data[12] strongly suggested a singlet ground state for **[3,3]$^{4+}$**, which is unexpected, because the d^5-configuration of the low-spin Ru^{III} centers would intuitively implicate a triplet state for the dimer. The singlet can be obtained by two means: (a) the unpaired electrons could occupy the same orbital spanning over both metal centers, thus spin-pairing with each other and giving rise to a strong coupling of the metal centers, or (b) the electrons could reside in different orbitals, but couple antiferromagnetically (AF) to each other. Whereas both configurations explain the EPR data, the former is electronically unusual for an oxo-bridged bimetallic system. Direct interactions of this character are usually seen for M−M multiple bonds without a bridging ligand separating the metal centers. The concept of one orbital delocalized over three nuclei (Ru−O−Ru) was inspired by a MO study of Cl$_5$Ru^{IV}−O−Ru^{IV}Cl$_5$.[17] This early work utilized symmetry-adapted linear combinations of metal-based atomic orbitals to derive fully delocalized, symmetric MOs. Although that work examined a Ru(IV) d^4 dimer and thus did not involve long-range spin-pairing, it formed the base of the currently accepted concept for the electronic structure of the Ru dimer.[12]

Scheme 1 enumerates the redox couples in their respective protonation states that we explored exhaustively and systematically using high-level DFT methods[18] in combination with a continuum

Scheme 1
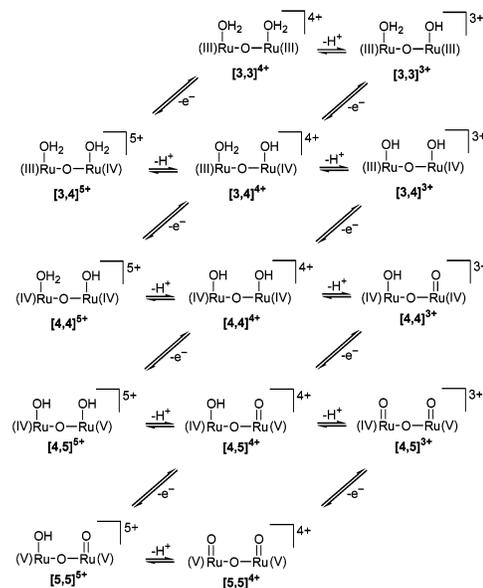
solvation model[19] and broken symmetry (BS)[20] orbitals to probe for the AF coupled states where necessary.

In all cases where a singlet state is possible (**[3,3]$^{4+}$**, **[3,3]$^{3+}$**, **[5,5]$^{5+}$**, **[5,5]$^{4+}$**), our calculations indicate a pronounced preference of the weakly AF coupled states over the strongly coupled singlet states with both electronic (ΔE(SCF)) and solution-phase free energy (ΔG(Sol)) differences between 10 and 35 kcal/mol (Table 1). Electronically, the pseudo-octahedral environment forces the five d-electrons of the low-spin Ru^{III} center to distribute among the three "t$_{2g}$-like" MOs, leaving one orbital singly occupied. Upon dimerization, these orbitals form six metal-dominated MOs that are in-phase and out-of-phase combinations of the t$_{2g}$-like orbitals. The symmetric singlet state will show five of these symmetric MOs that are completely delocalized across the Ru−O−Ru vector being doubly occupied. The broken symmetry calculation, on the other hand, will show at least one MO in the α-electron and one in the β-electron subspaces, respectively, that are essentially localized on only one of the metal centers.[21] A detailed and thorough MO analysis of the AF coupled state is complicated and will be presented elsewhere. Here, we simply show the broken symmetry MO that contains the unpaired α-electron for **[3,3]$^{4+}$** to illustrate the localized nature of the BS orbital (Figure 1). Of course, there exists a corresponding β-MO that promotes localization of opposite spin on the other metal center, leading to weak coupling in the broken symmetry framework. Among the three t$_{2g}$-like orbitals, d$_{yz}$ is best suited to accommodate the excess spin, since the d$_{xz}$ and d$_{xy}$ orbitals will be involved in π-type interactions across the Ru−O−Ru vector.

Table 1. Energy Differences between the Symmetric and AF Coupled Singlet States of **[3,3]**$^{4+}$, **[3,3]**$^{3+}$, **[5,5]**$^{5+}$, and **[5,5]**$^{4+}$ in kcal/mol

	ΔE(SCF)	ΔG(Sol)
[3,3]$^{4+}$	12.54	16.62
[3,3]$^{3+}$	9.29	10.20
[5,5]$^{5+}$	16.56	12.90
[5,5]$^{4+}$	34.36	36.12
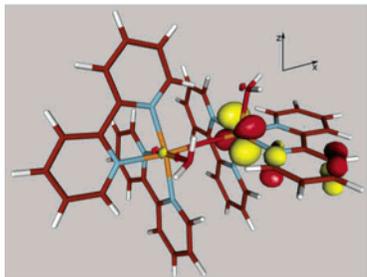
Figure 1. Metal-dominated broken symmetry MO (α-spin) that promotes antiferromagnetic coupling. Isosurface drawn at 0.05 au.

Table 2. Calculated and Experimental Redox Potentials in V^a

	$E_{1/2}$(calcd)	$E_{1/2}$(exp)	difference
[5,5]$^{4+}$ + 3e$^-$ + 3H$^+$ → [3,4]$^{4+}$	AF: 1.323	1.22[6]	0.103
	S: 1.845		0.625
[5,5]$^{4+}$ + 4e$^-$ + 4H$^+$ → [3,3]$^{4+}$	AF: 1.179	1.12[6]	0.059
	S: 1.424		0.304
[3,4]$^{4+}$ + e$^-$ + H$^+$ → [3,3]$^{4+}$	AF: 0.747	0.79[6]	−0.043
	S: 0.162		−0.628
[4,4]$^{4+}$ + e$^-$ + H$^+$ → [3,4]$^{4+}$	1.817	>1.45[9]	
[4,5]$^{3+}$ + e$^-$ + 2H$^+$ → [4,4]$^{4+}$	0.989	<1.45[9]	
[4,5]$^{3+}$ + 2e$^-$ + 3H$^+$ → [3,4]$^{4+}$	1.403	1.45[9]	−0.047
[5,5]$^{4+}$ + e$^-$ → [4,5]$^{3+}$	AF: 1.887	1.40[9]	0.487
	S: 3.453		2.053

^{a} Potentials from ref 6 are vs SSCE, whereas NHE potentials are reported from ref 9. Our computed potentials are referenced accordingly.

Whereas the consistent preference of the AF coupled over the symmetric singlet state is convincing from energetic perspectives, its consequence for the reactivity and chemical behavior of the Ru dimer is not immediately apparent. On the basis of the library of calculated structures and energies,[22] a series of proton-coupled redox reactions can be simulated[23] and compared to experiments.[6,9] Redox potentials are particularly important, because they form the very basis for the utilization of the Ru dimer as a water oxidation catalyst. They also report on the shapes of the redox reaction energy profile, providing valuable information about unusual properties that may play a key role for catalysis. Table 2 compares computed potentials with experimental values. Calculations were done both using strong coupling and weak antiferromagnetic coupling. If antiferromagnetic coupling is assumed, the agreement between simulation and experiment is excellent, with deviations being below 100 mV, except for the redox pair **[5,5]**$^{4+}$/**[4,5]**$^{3+}$, where an unusually large disagreement between theory and experiment of nearly 500 mV has been found. We have currently no explanation for this anomalous data point. If strong coupling (S) is assumed, we find essentially no correlation between computed and experimentally measured redox potentials. The redox pair **[5,5]**$^{4+}$/**[4,5]**$^{3+}$ is again the most problematic data point with a predicted redox potential of 3.45 V, which is not only well beyond any realistic potential range but also 2.05 V higher than what is measured experimentally. The disagreement is not as dramatic if the other redox pairs are examined but remains substantial, with deviations ranging from 300 to 630 mV.

Gratifyingly, our simulation also reproduces the observation of a single two-electron behavior[24] for the reaction [Ru^{IV}−O−Ru^{III}]$^{4+}$ → [Ru^V−O−Ru^{IV}]$^{3+}$ + 3H$^+$ + 2e$^-$, which indicates an intrinsic instability of the [Ru^{IV}−O−Ru^{IV}]$^{x+}$ ($x = 3$ or 4) intermediate with respect to disproportionation. Such a redox event is recognized as "potential inversion", where the second of the two redox-active electrons becomes easier to remove than the first.[25] In these cases, the observed potential is an average of the two one-electron potentials[26] and was reported to be 1.45 V vs NHE.[9] Thus, the two oxidation potentials were estimated to be >1.45 and <1.45 V, respectively. Our calculations place the first potential at 1.817 V and the second at 0.989 V, averaging to an observable potential of 1.403 V, which is in excellent agreement with the experiment.

In summary, we propose that the paramagnetic Ru^{III} and Ru^V centers in the water-oxidizing Ru dimer are weakly AF coupled singlet ground states. The assumption of a strong coupling leads to large errors when redox potentials are computed. We anticipate similarly dramatic effects when large-scale computer models are used to quantitatively examine the mechanism of the water oxidation reaction. These studies are currently in progress.

Supporting Information Available: Complete description of the computational details and Cartesian coordinates of all structures and all energy components (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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