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Electron Localization in the Ground State of the Ruthenium Blue Dimer

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The ruthenium blue dimer $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)\ (bpy)_2]^{4+}$ has been widely studied since its discovery some 30 years ago.[1] The interest stems from its ability to catalyze the oxidation of water into dioxygen, a complex cycle involving four protons and four electrons.[2] This molecule remains one of the few capable of catalyzing this process. Recently, the existing molecular orbital “strong coupling” model[1] for the blue dimer has been challenged by Yang and Baik,[3] who argued for an antiferromagnetic, “weak coupling”, ground state, involving unpaired electrons in the δ orbitals. This suggestion was based on hybrid DFT computations (B3LYP). Using the identical functional and essentially the same basis set, we have been unable to reproduce their results. In this communication, we compare our B3LYP results with those of complete active space self-consistent field (CASSCF) calculations in an attempt to clarify the nature of the ground state.

The frontier orbitals of the blue dimer are built by coupling the 10 electrons contributed by two $Ru^{III}(d^5)$ centers, each of which finds itself in a pseudo-octahedral environment. With the Ru−Ru axis denoted by z, this geometry leads to a natural splitting between the $\sigma(d_{x^2-y^2}, d_{z^2})$, $\pi(d_{xz},d_{yz})$, and $\delta(d_{xy})$ orbitals. The σ orbitals lie high in energy; we need to consider interactions only among the lower-lying π and δ manifolds. Based upon a series of experiments, Weaver et al.[1] proposed the MO diagram shown in Figure 1. The lowest two orbitals are bonding and principally O(2p) in character. A pair of nonbonding (or weakly bonding) δ (d_{xy}) orbitals arise from the d manifold, followed by the in-phase combinations of the (d_{xz},d_{yz}) orbitals (π_1, π_2) and finally the antibonding combination $(\pi_1{}^*, \pi_2{}^*)$. Three candidates for the ground state were discussed by Weaver et al.: the closed shell $[...\delta^4\pi_1{}^2\pi_2{}^2\pi_1{}^{*2}]$ strong coupling configuration, the triplet state $[...\delta^4\pi_1{}^2\pi_2{}^2\ \pi_1{}^*\pi_2{}^*]$, and a weak coupling valence bond-like singlet arising from coupling localized $S = {}^1/_2$ Ru centers. Magnetic susceptibility measurements confirmed the existence of a singlet ground state, with the triplet lying 0.5 kcal/mol higher. While acknowledging that a weak coupling antiferromagnetic ground state was consistent with the magnetic results, they argued that the strong coupling limit was most consistent with additional spectroscopic and electrochemistry data.

Recently, however, Yang and Baik proposed a different interpretation.[3] In their original communication, they reported that the B3LYP functional yielded a weak coupling singlet ground state. The orbitals containing the antiferromagnetically coupled spins were not in the d_π manifold, but rather d_δ in character. Antiferromagnetic communication between the two metal centers implies overlap with the bridging oxygen, and the d_δ orbitals would seem to be the least appropriate for this.

At the time, our simultaneous B3LYP investigations with a nearly identical basis set were yielding a triplet ground state, in contradiction with both experiment and the previous theory work. In addition, while we found that a broken symmetry antiferromagnetic singlet lay slightly (8.8 kcal/mol) above the triplet, it was a *different* weak coupling singlet from that found by Yang and Baik, as it involved the d_π orbitals. In a subsequent publication, Yang and Baik reported that indeed the triplet was the B3LYP ground state.[4] However, our attempts to find their d_δ solution repeatedly collapsed to the d_π solution reported here.

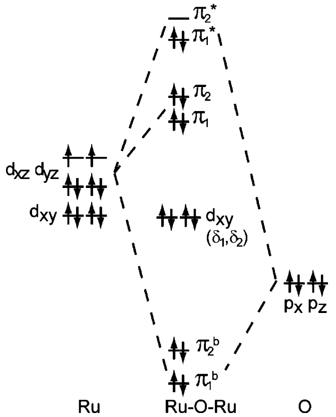

Figure 1. Molecular orbitals involving the Ru d electrons in the blue dimer at the closed shell electronic state.

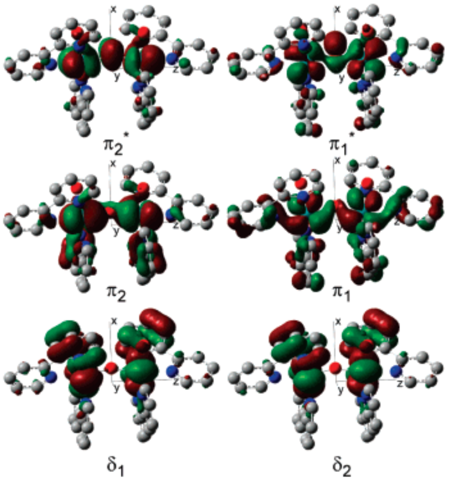

Figure 2. Molecular orbitals involving the Ru d electrons in the blue dimer at the closed shell electronic state.

Our work employs the LANL2 relativistic effective core potential and associated uncontracted basis set for Ru and Os, the 6-311+g* basis for Fe, the 6-31 g* basis for the ligands (C, N, O, Cl, and H), and the B3LYP approximation as implemented in Gaussian03 package.[5] Three variants of the Ru blue dimer were studied: $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$, $[(bpy)_2(O_2N)Ru^{III}ORu^{III}(NO_2)(bpy)_2]^{2+}$, $[(bpy)_2(Cl)Ru^{III}ORu^{III}(Cl)(bpy)_2]^{2+}$. All three ligands give qualitatively identical results, and we therefore concentrate on the first and leave the other two for the Supporting Information.

The B3LYP orbital energy diagram for the closed shell configuration agrees precisely with that of Figure 1. The associated orbitals are reproduced in Figure 2. As anticipated, in the closed shell configuration, the δ orbitals are doubly occupied while the empty

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orbital is an antibonding $d_\pi(yz)$. The triplet state $|\pi_1{*}\uparrow, \pi_2{*}\uparrow\rangle$ is found to be the ground state at this level of theory. At their respective minima, the triplet state lies 11.4 kcal/mol *lower* than the closed shell singlet. The simple open shell singlet $|\pi_1{*}\uparrow, \pi_2{*}\downarrow\rangle$ must lie above the corresponding triplet according to Hund's rules.

Now we proceed to look for the broken symmetry state. In order to pair antiferromagnetically via superexchange, one must prepare a configuration with two electrons shared among the bonding and antibonding orbital counterparts. Given the orbital energy diagram, the most plausible candidate involves π_2 and $\pi_2{*}$. In order to pair electrons in either π_1 or δ, we must first empty the corresponding antibonding orbital by exciting two electrons into $\pi_2{*}$. This is perhaps plausible for π_1 and less so for δ. Initial guesses based upon all three possibilities were tried, but only the $d_\pi(yz)$ was variationally stable. The other two both collapsed to this state. Although we were not able to optimize the geometry of the molecule in the broken symmetry state, at the optimal geometry of the closed shell singlet, the broken symmetry singlet lies 2.6 kcal/mol below the closed shell singlet. To summarize, B3LYP predicts a ground state triplet, followed by a d_{yz} broken symmetry open shell singlet.

In order to investigate the discrepancies between the DFT calculations and the experimental results, a calculation was run at the CASSCF level of theory. Our calculation partitioned 10 d electrons among the six frontier d orbitals shown in Figure 2. Structure optimization at this level of theory is computationally demanding, therefore, the CASSCF was run at two separate geometries: at the optimal geometry of the DFT closed shell and at that of the lowest triplet state. In both cases, the lowest energy state was a singlet dominated by two configurations: $\Psi = a\pi_2\alpha\pi_2\beta - b\pi_2{*}\alpha\pi_2{*}\beta$. This multiconfiguration wavefunction can also be written as a broken symmetry determinant with the non-orthogonal orbitals $(\pi_2 + \lambda\pi_2{*})\alpha$ and $(\pi_2 - \lambda\pi_2{*})\beta$ (with overlap of $(1 - \lambda^2)/(1 + \lambda^2)$), and λ is related to "a" and "b" by $a = 1/\sqrt{1+\lambda^4}$ and $b = \lambda^2/\sqrt{1+\lambda^4}$. The limits of $\lambda = 0$ and $\lambda = 1$ correspond to the extreme behaviors of strong coupling and antiferromagnetic weak coupling, respectively. The non-orthogonal representation allows for a direct comparison between the CASSCF output and a natural orbital representation of the broken symmetry states obtained from DFT (albeit the CASSCF is based upon Hartree−Fock orbitals and the other on Kohn−Sham orbitals). In the DFT calculations, there were only two natural orbitals with populations significantly less than 2. These partial populations correspond to the eigenvalues of the density matrix for the mixing of the same π_2 and $\pi_2{*}$ orbitals as in the CASSCF, therefore, they are directly related to the coefficients a and b stated above (the partial populations correspond to $2a^2$ and $2b^2$).

For the ruthenium blue dimer, the CASSCF calculation revealed the lowest state to be a broken symmetry singlet with 80% localization (see Table 1) for both geometries that we explored. The lowest triplet state was found 5.8 kcal/mol higher than the singlet at the geometry of the DFT closed shell state and 2.4 kcal/mol higher than the singlet at the geometry of the DFT triplet state. This is somewhat higher than the 0.5 kcal/mol observed experimentally, presumably due to the neglect of higher order dynamical correlation effects not recovered by the CASSCF. The electrons were localized in the d_{yz} orbital of each metal center, as was expected from the MO diagram in Figure 1. In the CASSCF ground state, only two states contribute to the wavefunction, one with π_2 doubly occupied (with amplitude of 0.84) and one with $\pi_2{*}$ doubly occupied (with amplitude of −0.54) leading to $\lambda = 0.81$. The DFT broken symmetry state has partial localization in the same molecular orbitals with $\lambda = 0.70$. This gives very strong support that the broken symmetry state obtained from DFT is similar in makeup to the CASSCF state. By this measure, the localization is approximately three-quarters of the way from the strong coupling limit toward the weak, anti-ferromagnetic coupling limits.

Table 1. Electron Localization for Fe, Ru, and Os Dimers[a]

dimer	a	b	$\lambda^{\mathrm{CASSCF}}$	λ^{BS}
Fe	0.7570	−0.6533	0.93	0.84
Ru	0.8377	−0.5430	0.81	0.70
Os	0.8466	−0.5322	0.79	0.68

[a] The a and b columns correspond to the CASSF coefficients for the multiplet $\Psi = a\pi_2\alpha\pi_2\beta + b\pi_2{*}\alpha\pi_2{*}\beta$. This multiplet can be written as a broken symmetry determinant of two non-orthogonal orbitals: $(\pi_2 + \lambda\pi_2{*})\alpha$ and $(\pi_2 - \lambda\pi_2{*})\beta$. The two values of λ correspond to the output of CASSCF and to the DFT broken symmetry state (BS).

The electronic coupling of the Ru blue dimer was compared with the analogous Fe and Os dimers. As Weaver et al. had anticipated, it was found that the Fe dimer is shifted toward the weak coupling limit with respect to Ru, while Os is shifted slightly toward the strong coupling limit (see Table 1).

In conclusion, CASSCF predicts that the ground state of the ruthenium blue dimer is a singlet state, in agreement with magnetic susceptibility measurements. The spin coupling is roughly three-quarters of the way toward the weak coupling limit. The partial localization occurs in the d_π manifold. Singlet coupling involving the d_δ orbitals is a highly excited state. These results are echoed by the B3LYP DFT results, with the important caveat that B3LYP places the triplet too low in energy, thus yielding an incorrect prediction of the ground state.

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Supporting Information Available: Cartesian coordinates of all the molecules studied for this paper, each one with the total energy in atomic units. Complete results of the CASSCF calculation of the three lowest excited states of the blue dimer. Complete ref 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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