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# A Self Improved Water Oxidation Catalyst; Is One Site Really Enough?

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*((Dedication----optional))*

The replacement of fossil fuels by green and renewable solar energy carriers is one of the most important challenges our society is facing today. Intense research is currently being devoted to this topic, with emphasis on the development and characterization of new catalysts for water splitting such as the dinuclear Ru complexes introduced in this paper.[1]

Nature has been using sunlight to oxidize water and generate carbohydrates (solar fuels) in photosynthesis for over 2.5 billion years.[2] Artificial systems inspired by Nature have been designed to capture solar light and extract reducing equivalents (protons and electrons) from water to generate useful chemical fuels. Therefore, mastering and understanding water oxidation catalysis is one of the key elements needed for this strategy to succeed. While the research field is becoming extremely active,[3] significant advances are still needed to develop a sufficiently rugged and efficient water oxidation catalyst that could be useful in large scale practical applications.

Since the discovery by Thummel et al.[4] that even mononuclear Ru complexes were active as water oxidation catalysts (WOCs), there has been a vivid development of several studies on this type of complexes.[5] Several catalysts have been developed and considerable knowledge on this type of catalysts has been advanced.[6] From a mechanistic perspective, Meyer *et al.*[7] offered a description of water oxidation at a molecular level. It was proposed that the O-O bond formation would take place through a water nucleophilic attack (WNA) pathway, as shown in a simplified manner on the left side of Scheme 1. Catalysts such as $[Ru(trpy)(bpym)(H_2O)]^{2+}$ (trpy: 2,2':6',2"-terpyridine; bpym: 2,2'-bipyrimidine),[8] have been reported to have impressive turn over numbers (TNs) larger than 28.000. However, practical applications require catalysts with TNs that are at least a few orders of magnitude higher. In order to design such highly efficient water oxidation catalysts, it is of paramount importance to understand the pathways that lead oxygen evolution from water and also the different reactions coupled to the catalytic cycle that might drive the intervening species towards unproductive pathways and decomposition. In addition, understanding pathways that derail from the initial catalytic cycle and generate new catalytic species with superior performance would be particularly valuable.

Here we report the synthesis and characterization of new dinuclear Ru complexes of general formula $[(trpy)(5,5'\text{-}X_2\text{-}bpy)Ru^{IV}(\mu\text{-}O)Ru^{IV}(trpy)(O)(H_2O)]^{4+}$ (bpy is 2,2'-bipyridine; X = H for $\mathbf{1}^{4+}$ and X = F for $\mathbf{2}^{4+}$) that are highly efficient and very robust WOCs. We find that these complexes are generated in the catalytic cycle of their related mononuclear counterparts $[Ru(trpy)(5,5'\text{-}X_2\text{-}bpy)(H_2O)]^{2+}$.[9] Addition of $[Ru^{VI}(trpy)(O)_2(H_2O)]^{2+}$, $\mathbf{3}^{2+}$, to $[Ru^{II}(trpy)(bpy)(H_2O)]^{2+}$, $\mathbf{4}^{2+}$, in the presence of Ce(IV) in acidic conditions generates complex $\mathbf{1}^{4+}$ (polypyridyl ligands not shown),

$$[Ru^{II}(H_2O)]^{2+} + [Ru^{VI}(O)_2(H_2O)]^{2+} \rightarrow [Ru^{IV}\text{-}O\text{-}Ru^{IV}(O)(H_2O)]^{4+} + H_2O \quad (1)$$

Similarly, addition of $\mathbf{3}^{2+}$ to $[(trpy)(5,5'\text{-}F_2\text{-}bpy)Ru^{II}(H_2O)]^{2+}$, $\mathbf{5}^{2+}$, forms the related dinuclear fluoro complex $\mathbf{2}^{4+}$. Complexes $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ were thoroughly characterized by analytic, spectroscopic and electrochemical techniques. The X-ray crystal structures of $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ were solved by means of single crystal XRD and their Ortep views are shown in Figure 1 and in the Supporting Information, respectively. It is interesting to point out here the short Ru-O distance (1.747 Å) in $\mathbf{1}^{4+}$ that falls in the lower range of values reported for $Ru^{IV}$=O groups.[10]

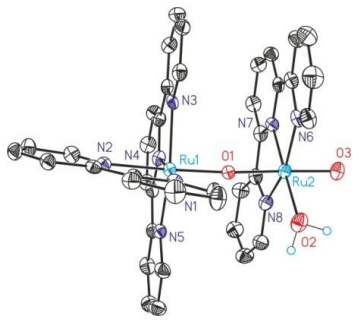


***Figure 1.*** Ortep plot (ellipsoids drawn at 50 % probability) of the X-ray structure of $\mathbf{1}^{4+}$. Color codes: Ru, cyan; O, Red; N, Blue, C, black. H atoms are not shown except for the aqua ligands that are represented as small light blue circle.

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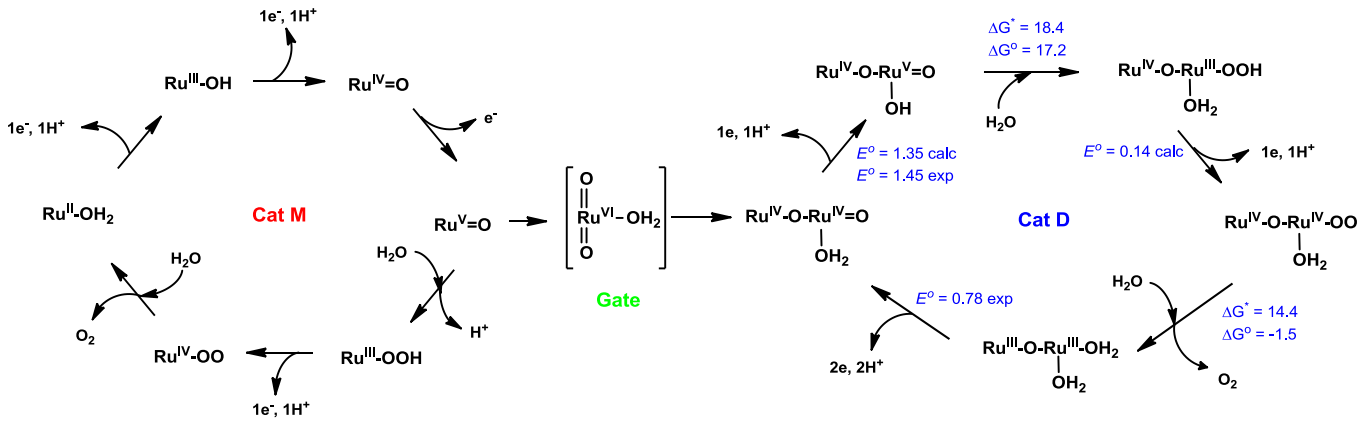


***Scheme 1.*** Proposed interconnection of catalytic schemes (polypyridyl ligands are not shown). Energies are reported in kcal/mol and redox potentials are reported in V *vs*. the SSCE reference electrode. DFT calculations at M06-L level of theory (*calc*) are compared to experiments (*exp*).

In sharp contrast to the short Ru-O distance in $\mathbf{1}^{4+}$, the Ru-O distance for the $Ru^{IV}$-$OH_2$ group of the same metal center is 2.120 Å. Additionally, the nearly linear Ru-O-Ru angle (176.1°) is worth noting. Complexes $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ are diamagnetic, as expected for high field $\mu$-oxo dinuclear $d^4$ Ru complexes,[11] and their NMR spectra are presented in the SI.

Complex $\mathbf{2}^{4+}$ has a very strong vibrational band at 801 $cm^{-1}$, as shown in the resonance Raman (rR) spectrum (Figure 2), that we assign to the Ru=O stretching mode. Labeling experiments with $H_2{}^{18}O$ lead to a downshift of this mode to 760 $cm^{-1}$ corresponding to an isotopic shift of 41 $cm^{-1}$. Mixed labeling achieved with a 1:1 $H_2{}^{16}O$:$H_2{}^{18}O$ mixture do not generate any new modes in the rR spectrum, consistently with a terminal Ru=O bond. The frequency of this mode is in agreement with related Ru=O complexes reported in the literature.[10e],[12] A very interesting feature of the rR spectrum is the small bands at 727, 714, 700 and 675 $cm^{-1}$ that can be used as a fingerprint for the identification of this complex.

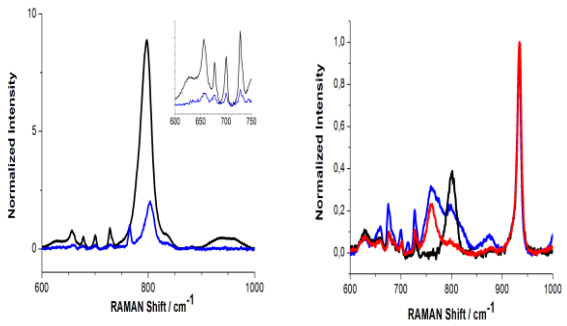


***Figure 2.*** Left, overlay of rR spectra of $\mathbf{2}^{4+}$ (black) and the reaction product obtained after addition of 3 eq. of Ce(IV) to complex $\mathbf{5}^{2+}$ (blue), both measured in 0.1 M HOTf in $H_2{}^{16}O$. The inset shows an enlargement of the fingerprint region mentioned in the main text. Right, overlay of rR spectra obtained after reaction of 3 eq. of Ce(IV) with complex $\mathbf{5}^{2+}$ in 0.1 M $HClO_4$ in $H_2{}^{16}O$ (black), $H_2{}^{18}O$ (red) and $H_2{}^{16}O$:$H_2{}^{18}O$ (1:1) (blue). Further experimental details are given in SI.

The electrochemistry of complexes $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ was carried out in 0.1 M triflic acid, was explored by means of CV, DPV and Coulometry, and is reported in Figure 3 and the SI. Complex $\mathbf{1}^{4+}$ undergoes a 2-electron reduction, as confirmed by Coulometry, from the formal oxidation state IV,IV to III,III, associated with two proton transfer steps according to (polypyridyl ligands not shown),

$$[Ru^{IV}\text{-}O\text{-}Ru^{IV}(O)(H_2O)]^{4+} + 2e^- + 2H^+ \rightarrow [Ru^{III}\text{-}O\text{-}Ru^{III}(H_2O)_2]^{4+} \quad E^o = 0.78 \text{ V } vs. \text{ SSCE} \quad (2)$$

On the anodic part, a further electron transfer process is observed together with a large current intensity, assigned to the electrocatalytic oxidation of water to dioxygen. A one-electron process that generates a very reactive species responsible for the O-O bond formation (eqs 3-4) is proposed, followed by a sequence of reactions leading to dioxygen formation (Scheme 1, right side),

$$[Ru^{IV}\text{-}O\text{-}Ru^{V}(O)(OH)]^{4+} + 1e^- + 1H^+ \rightarrow [Ru^{IV}\text{-}O\text{-}Ru^{IV}(O)(H_2O)]^{4+} \quad E_{onset} = 1.45 \text{ V } vs. \text{ SSCE} \quad (3)$$

$$[Ru^{IV}\text{-}O\text{-}Ru^{V}(O)(OH)]^{4+} + H_2O \rightarrow [Ru^{IV}\text{-}O\text{-}Ru^{III}(OOH)(OH_2)]^{4+} \quad (4)$$

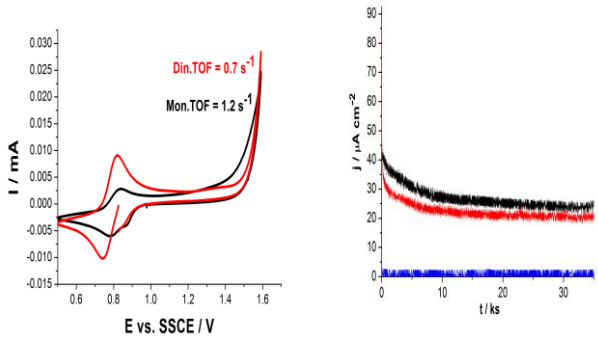


***Figure 3.*** Left, CV of 0.5 mM solutions of $\mathbf{1}^{4+}$(red) and $\mathbf{4}^{2+}$(black) in 0.1 M HOTf (pH = 1.0) using a polished glassy carbon working electrode, a Pt wire counter electrode and a $Hg/Hg_2SO_4$, $K_2SO_4$ (sat.) as reference electrode (potentials reported *vs*. SSCE). Right, controlled potential electrolysis at 1.6 V *vs*. SSCE of a 0.4 mM solution of $\mathbf{4}^{2+}$ (black) and $\mathbf{1}^{4+}$ (red) complexes in 0.1 M triflic acid and a blank experiment without catalyst (blue). An activated boron doped diamond disk (3 mm diameter) was used as a working electrode, Pt wire as a counter electrode and a $Hg/Hg_2SO_4$, $K_2SO_4$ (sat) reference electrode (potentials are converted to SSCE).

Formal oxidation states are indicated to facilitate electron counting even though it is well known that the oxo-bridge promotes charge transfer interactions between the Ru metal centers.[13] DFT

calculations at the M06-L[14] level of theory (see SI for details) were carried out to characterize the reaction intermediates as well as the transition states, providing a complete catalytic cycle (Scheme 1, right). The O-O bond formation step through water nucleophilic attack to $[Ru^{IV}\text{-}O\text{-}Ru^{V}(O)(OH)]^{4+}$ (equation 4) was found to be the rds of the catalytic cycle with a $\Delta G^{\ddagger}$ of 18.4 kcal/mol. The optimized transition state structure features a water molecule which forms the O-O bond with concomitant transfer of a proton to the neighboring Ru-OH group (Figure 4, left), to generate the corresponding hydroperoxo complex, $[Ru^{IV}\text{-}O\text{-}Ru^{III}(OOH)(OH_2)]^{4+}$.

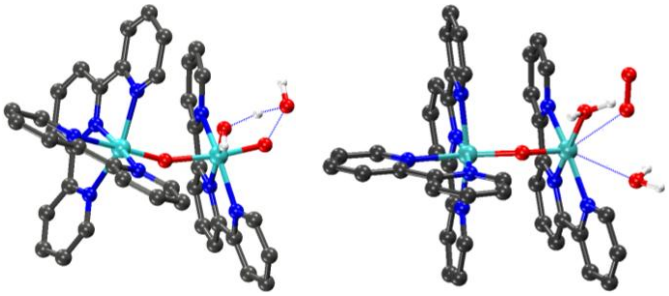

***Figure 4***. Ball and stick representation of the optimized transition state structures for the O-O bond formation (right) and $O_2$ evolution steps (left). H atoms are only shown for the aqua and hydroxy ligands.

The next step corresponds to a proton coupled electron transfer with a very low redox potential leading to the formation of a superoxo intermediate,

$$[Ru^{IV}\text{-}O\text{-}Ru^{III}(OOH)(OH_2)]^{4+} - 1e^- - 1H^+ \rightarrow [Ru^{IV}\text{-}O\text{-}Ru^{IV}(OO)(OH_2)]^{4+} \quad E^o = 0.14\ \text{V} \quad (5)$$

which subsequently evolves $O_2$ (Figure 4, right) and generates the initial complex,

$$[Ru^{IV}\text{-}O\text{-}Ru^{IV}(OO)(OH_2)]^{4+} + H_2O \rightarrow [Ru^{III}\text{-}O\text{-}Ru^{III}(OH_2)_2]^{4+} + O_2 \quad (6)$$

closing the catalytic cycle.

From the electrochemical experiments shown in Figure 3, TOF of 0.7 cycles per second for $\mathbf{1}^{4+}$ and 1.2 $s^{-1}$ for $\mathbf{4}^{2+}$ were calculated[15] which are comparable to mononuclear complexes reported in the literature.[8],[9],[16] The capacity of $\mathbf{1}^{4+}$ to act as a WOC was also tested electrochemically under a constant applied potential. A potentiometric experiment was performed for both $\mathbf{1}^{4+}$ and $\mathbf{4}^{2+}$ in order to evaluate their relative performance at longer time scales as shown in Figure 3. At an applied potential of 1.6 V *vs*. SSCE, initial current densities of approximately 40 μA/cm$^2$ are reached for $\mathbf{1}^{4+}$ and $\mathbf{4}^{2+}$. For $\mathbf{1}^{4+}$ the current density decreases to 20 μA at about 10 ks and is maintained constant thereafter. On the other hand, for $\mathbf{4}^{2+}$ the current slowly drops over time until it merges with that of $\mathbf{1}^{4+}$ at approximately 30 ks. This phenomenon is attributed to the slow but progressive and irreversible conversion of the mononuclear complex $\mathbf{4}^{2+}$ to the corresponding dinuclear $\mathbf{1}^{4+}$ complex, as proposed in Scheme 1, and demonstrated by UV-vis and rR spectroscopy (vide infra). At 35 ks TONs of 14930 and 6683 were obtained for $\mathbf{4}^{2+}$ and $\mathbf{1}^{4+}$ respectively.

The bulk electrolysis experiment at $E_{app}$ = 1.4 V was also followed spectrophotometrically by UV-vis absorption spectroscopy as indicated in Figure 5. Very interestingly, it was found that the absorption bands of $\mathbf{1}^{4+}$ at 457 and 690 nm start to emerge as the catalysis proceeds. After two days of applied constant potential, 23 % conversion of $\mathbf{4}^{2+} \rightarrow \mathbf{1}^{4+}$ was observed. This mononuclear to dinuclear conversion can also be observed in the rR spectra at the very early stages of the water oxidation reaction when adding 3 equivalents of Ce(IV) to $\mathbf{5}^{2+}$ (Figure 2). Indeed, shortly after Ce(IV) addition, the rR spectrum displays a highly intense band at 801 cm$^{-1}$ and four weaker bands at 727, 714, 700 and 675 cm$^{-1}$ characteristic of $\mathbf{2}^{4+}$. In sharp contrast, exposure of $\mathbf{1}^{4+}$ or $\mathbf{2}^{4+}$ for long periods of time under the same conditions (35 ks at 1.6 V *vs*. SSCE), does not show any change in the UV-vis spectrum. This manifests the ruggedness of $\mathbf{1}^{4+}$ as a water oxidation catalyst that does not show any sign of fatigue even after 35 ks controlled potential electrolysis at 1.6 V *vs*. SSCE.

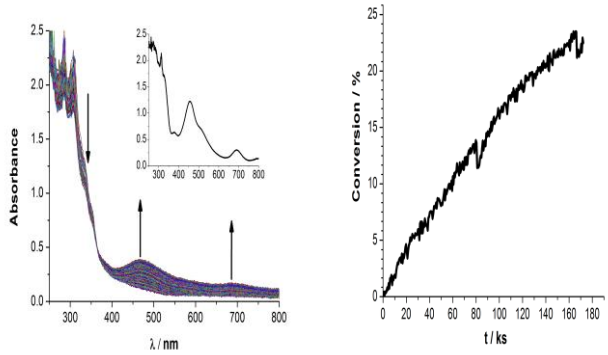


***Figure 5.*** Left, UV-vis absorption spectra monitoring the controlled potential electrolysis of a 0.5 mM solution of $\mathbf{4}^{2+}$ in 0.1 M HOTf, for two days at 1.4 V *vs*. SSCE using a Pt mesh working electrode, a Pt wire counter electrode and a Ag/AgCl, NaCl (3M) reference electrode. Spectra were recorded every ten minutes. Inset, UV-vis spectra of $\mathbf{1}^{4+}$ in 0.1 M HOTf. Right, conversion of mononuclear $\mathbf{4}^{2+}$ to dinuclear $\mathbf{1}^{4+}$ over time, based on absorbance change at 460 nm.

These experiments manifest the interconnection of the two catalytic cycles for the mononuclear $\mathbf{4}^{2+}$ and dinuclear $\mathbf{1}^{4+}$ species. The link between the two catalytic cycles is essentially $[Ru^{VI}(trpy)(O)_2(H_2O)]^{2+}$, $\mathbf{3}^{2+}$, that can be generated by bpy loss from the mononuclear complex, potentially at oxidation state V,

$$[(trpy)(bpy)Ru^{V}{=}O]^{3+} + Ce^{IV} + 2\ H_2O \rightarrow \textit{trans}\text{-}[(trpy)Ru^{VI}(O)_2(H_2O)]^{2+} + bpyH^+ + H^+ + Ce^{III} \quad (7)$$

The strong *trans* effect generated by the $Ru^{V}$=O group produces a weakening of one of the Ru-N bpy bonds that eventually leads to the loss of the bpy ligand. Furthermore, the *trans*-$Ru(O)_2$ entity is known to generate very stable complexes[17] and thus is an additional driving force for the bpy loss. Once the bpy ligand is released, the reaction of $\mathbf{3}^{2+}$ with $\mathbf{1}^{2+}$ (equation 1) constitutes the entry to the dinuclear catalytic cycle. The free energy values obtained at DFT level of theory indicate that the proposed interconversion pathway is feasible (Scheme S2 in the supporting information) and further supports this hypothesis. This interconversion process also occurs between $\mathbf{5}^{2+}$ and $\mathbf{2}^{4+}$, suggesting a general interconversion process of single site catalysts. These findings shed light on the *in-situ* generation of long lasting water oxidation catalysts based on dinuclear complexes.

The larger stability of the dinuclear complexes is due to a number of factors. First, the presence of two electronically coupled Ru centers through an oxo-bridge allows for fast intramolecular ET

within the species generated in the catalytic cycle. Thus, due to the involvement of two metal-centers, the burden of multiple electron transfer at a single site is overcome. Second, the presence of spatially separated non-symmetrical Ru centers allows fine-tuning of each site, i.e. to optimize one site for electron relay and the other site for proton-coupled ET, responsible for the primary interaction with the water molecules. Third, the *trans*-dioxo geometry at higher oxidation states stabilizes the dinuclear complex as opposed to the mononuclear $\mathbf{3}^{2+}$ that is not an active water oxidation catalyst. In addition the higher oxidation states of mononuclear mono-aqua Ru complexes suffer from ligand loss and subsequent decomposition. Fourth, the presence of the oxo-bridge and the terminal Ru=O group can act as anchors for hydrogen bonding if required, as nicely illustrated in the transition state structure depicted in Figure 4. This hydrogen bonding has been previously shown to be crucial for reducing the energy of activation of transition states.[18]

In summary, we have shown that WOCs based on mononuclear mono-aqua Ru complexes are slowly converted into active dinuclear catalysts through a self-assembly type of process. These dinuclear complexes are much more robust than the mononuclear precursors and exhibit similar activity as WOCs. Thus, we have shown for the first time that two interconnected catalytic cycles coexist where the mononuclear catalytic system is slowly and irreversibly converted to the more stable dinuclear catalytic system. We have further characterized the catalytic cycle based on DFT calculations, providing very good agreement with the available experimental observations.

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## *Water Oxidation*

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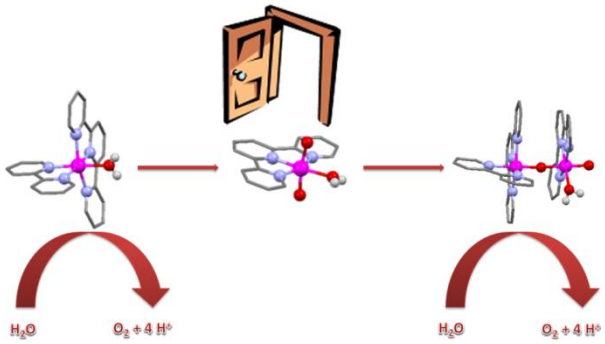
**A Self Improved Water Oxidation Catalyst: Is One Site Really Enough?**




We show for the first time that highly active mononuclear Ru-aqua water oxidation catalysts are transformed into dinuclear complexes during oxygen evolution catalysis, even from the very beginning of the catalytic process. The new dinuclear species are much more robust than their mononuclear counterparts and remain active catalyst for the water oxidation, establishing the coexistence of two different catalytic cycles in solution.

# Supporting Information for:

# A Self Improved Water Oxidation Catalyst: Is One Site Really Enough?

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**Experimental Section.**

**Materials:**

All reagents used in the present work were obtained from Aldrich Chemical Co. and Alfa Aesar and were used without further purification. Triflic Acid ($CF_3SO_3H$) was pursued from CYMIT. Reagent-grade organic solvents were obtained from SDS and high purity deionized water was obtained by passing distilled water through a nanopore Milli-Q water purification system.

**Preparations.**

$Ru(trpy)Cl_3$[1], $[Ru(trpy)(bpy)(H_2O)](PF_6)_2$ (**4**$^{2+}$)[2] and $[Ru(trpy)(5,5'\text{-}F_2bpy)(H_2O)](PF_6)_2$ (**5**$^{2+}$)[3] and $[Ru(trpy)(C_2O_4)(H_2O)]\cdot 2H_2O$[4] were prepared according to literature procedures. $[Ru(trpy)(O)_2(H_2O)](ClO_4)_2\cdot H_2O$ was prepared following a procedure slightly modified to the reported one[4].


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*$[Ru(trpy)(O)(H_2O)](ClO_4)_2\cdot H_2O$* (**3**$^{2+}$). $[Ru(trpy)(C_2O_4)(H_2O)]\cdot 2H_2O$ (50 mg, 0.079 mmols) was disolved with deoxygenated 2 M $HClO_4$ (8 mL) under Ar. The purple mixture was filtered with a Schlenck frit under Ar. If oxidation is thought to have occurred because the color of the solution changes from purple to blue, the filtered can be collected on a Zinc amalgam and stirred until the purple colour is recovered. The solution is added dropwise to a stirred solution of $(NH_4)_2Ce(NO_3)_6$ (1.5 g, 2.68 mmols) dissolved in the minimum amount of 2 M $HClO_4$. A yellow solid starts to precipitate a few minutes after the addition of the complex is finished. The mixture is left stirred for 2 hours and then it's kept in the fridge overnight. The yellow solid is filtered, washed with some drops of a cold 0.1 M $HClO_4$ solution and air-dried. Yield: 58 mg (93 %). rRAMAN (0.1 M HOTf, $cm^{-1}$): 835 s ($\nu_{sym}$(O=Ru=O)). $^1$H-NMR (400 MHz, 0.1 M DOTf): δ(ppm)= 9.31 (dd, *J* = 5.7, 1.2 Hz, 2H, H6-H6''), 8.91-8.82 (m, 5H, H3-H3''-H4'-H5'-H3'), 8.66 (ddd, *J* = 7.9, 7.9, 1.4 Hz, 2H, H4-H4'') and 8.17 (ddd, *J* = 7.9, 5.7, 1.3 Hz, 2H, H5'-H5'').

*$\{[Ru(trpy)(bpy)][Ru(O)(trpy)(H_2O)](\mu\text{-}O)\}(ClO_4)_4\cdot 4H_2O$* (**1**$^{4+}$) A 0.75 mM solution of $[Ru(trpy)(bpy)(H_2O)](PF_6)_2$ (67.5 mg, 0.085 mmols) in 0.1 M $HClO_4$ was prepared. An amount of 3 equivalents of $(NH_4)Ce(NO_3)_6$ (139.0 mg, 0.254 mmols) dissolved in the minimum amount of 0.1 M $HClO_4$ was added to the previous stirred solution. Then, $[Ru(trpy)(O)(H_2O)](ClO_4)_2$ (48.8 mg, 0.084 mmols) was added and the mixture was left stirred at room temperature for 3 days. A dark brown solid precipitated which was filtered and washed with drops of cold water. The solid was dried under vacuum for 5 hours. Yield: 54.6 mg (48%). Anal. Calcd for $C_{40}H_{40}Cl_4N_8O_{23}Ru_2$: C, 35.73; H, 3.00; N, 8.33. Found: C, 35.75; H, 2.50; N, 8.30.

*{[Ru(trpy)(5,5'-$F_2$bpy)][Ru(O)(trpy)($H_2O$)](μ-O)}($ClO_4$)$_4$·7$H_2O$* (**2**$^{4+}$) A procedure similar to **1**$^{4+}$ was followed. A 1.25 mM solution of [Ru(trpy)(5,5'-$F_2$bpy)($H_2O$)]($PF_6$)$_2$ (57,7 mg, 0.069 mmols) in 0.1 M $HClO_4$ was prepared and 3 equivalents of ($NH_4$)$_2$ e($NO_3$)$_6$ (114.4 mg, 0.209 mmols) dissolved in the minimum amount of 0.1 M $HClO_4$ were added to the stirred solution. Then, [Ru(trpy)(O)($H_2O$)]($ClO_4$)$_2$ (40 mg, 0.069 mmols) was added and the mixture was left stirred at room temperature for 2 days. After that, it was kept in the fridge at 8 ºC for another 2 days. A dark brown solid precipitated which was filtered and washed with drops of cold water. The solid was dried at air. Yield: 55.5 mg (56 %).Anal. Calcd for. $C_{40}H_{44}Cl_4F_2N_8O_{26}Ru_2$: C, 33.48, H, 3.09, N, 7.81. Found: C, 33.33, H, 2.33, N, 7.64.

**Equipment and measurements.**

UV/Vis spectroscopy was performed on a Cary 50 (Varian) UV/Vis spectrophotometer in 1 cm or 0.2 cm when indicated quartz cuvettes. Spectroelectrochemical experiments for {[Ru(trpy)(bpy)][Ru(O)(trpy)($H_2O$)](μ-O)}($ClO_4$)$_4$·4$H_2O$ were carried out with an Agilent UV-vis Torlon probe with an optical path length of 2 mm in a two compartment electrochemical cell. A Pt mesh was used as working electrode, a Pt wire as counter electrode and an Ag/AgCl, NaCl(sat) as reference electrode.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were performed on an IJ-Cambria CHI-660 potentiostat or a Bio-Logic SP-150 potentiostat using a three-electrode cell. Typical CV experiments were carried out at a scan rate of 100 mVs$^{-1}$. DPV experiments were carried out with the parameters: Pulses Height = 50 mV, Pulses Width = 50 ms, Step Height = 4 mV and Step Time = 200 ms. A glassy carbon electrode (2 mm diameter) was used as working electrode, platinum wire as auxiliary electrode, and a SSCE as a reference electrode. Working electrodes were polished with 0.05 micron alumina paste, and rinsed with distilled water and acetone followed by blow-drying before each measurement. When glassy carbon electrodes were activated, a procedure described by Meyer *et al.* was used[5]. All cyclic voltammograms presented in this work were recorded in the absence of light and inside a Faradaic cage. The electrochemical experiments were carried out in 0.1 M $CF_3SO_3H$ (pH 1.0). $E_{1/2}$ values reported in this work were estimated from CV experiments as the average of the oxidative and reductive peak potentials ($E_{pa}$ + $E_{pc}$)/2 or taken as E($I_{max}$) from DPV measurements. Controlled Potential Electrolysis (CPE) were carried out in a two compartment cell. The experiments at 1.6 V vs SSCE were made with a 3 mm activated[6] boron doped diamond working electrode, a Pt wire counter electrode and a Hg/$Hg_2SO_4$, $K_2SO_4$ (sat) reference electrode. For mononuclear complexes, the oxo compounds [Ru(trpy)(bpy)(O)]$^{2+}$ and [Ru(trpy)(5,5'-$F_2$bpy)(O)]$^{2+}$ were prepared electrochemically before oxidation at 1.6 V vs SSCE by applying the suitable potentials (0.78 V and 0.70 V vs. SSCE) and using a Pt mesh as working electrode. The measured potentials referring to the Hg/$Hg_2SO_4$, $K_2SO_4$ (sat) reference electrode were converted to SSCE according to literature values[7,8].

A 400 MHz Bruker Avance II spectrometer and a Bruker Avance 500 MHz were used to carry out NMR spectroscopy at room temperature. Samples were run in 0.1 M DOTf or 0.1 M $DNO_3$ with internal references

(residual protons). Elemental analysis was performed using an EA-1108, CHNS-O elemental analyzer from Fisons Instruments.

Samples for resonance Raman spectroscopy were prepared typically by mixing a 0.5 or 1 mM solution of the starting complex with the desired amount of $(NH_4)Ce(NO_3)_6$ and transferring 100 µL of the reaction solution to a aluminium crucible and subsequently frozen at appropriate times in liquid $N_2$. Then, the crucible was placed into a Linkam THMS 600 temperature controlled cryo stage to keep the temperature at -12 $^{o}$C. The rR spectrum was acquired using a Renishaw inVia Reflex RAMAN confocal microscope (Gloucestershire, UK), equipped with an Ar-ion laser at 514 nm and a Peltier-cooled CCD detector (-70 $^{o}$C) coupled to a Leica DM-2500 microscope. Calibration was carried out daily by recording the Raman spectrum of an internal Si standard. Rayleigh scattered light was appropriately rejected by using edge-type filters. For wide spectral ranges (200-1500 $cm^{-1}$), the spectra were recorded in segments with the accumulation of 5 scans of 20 s each. For a short spectral range (600-1000 $cm^{-1}$), the spectra were recorded with the accumulation of 10 scans of 10 s scan each. A 10x working distance microscope objective was used to focus 50% of the laser power (25 mW) onto the sample.


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**Single-Crystal X-Ray Structure Determination.**

Single crystals of $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ were obtained after the addition of some drops of an aqueous saturated $NaClO_4$ solution or an aqueous saturated $NH_4PF_6$ solution to 0.1 M HOTf solutions of the complexes. Crystals were also obtained after the addition of some drops of an aqueous saturated $NaClO_4$ solution to catalytic solutions of the complexes, i. e., after the addition of 100 equivalents of CAN to 1 mM solutions of the complexes in 0.1 M HOTf. All measured crystals were prepared under inert conditions immersed in perfluoropolyether as the protecting oil for manipulation.

*Data collection.* Crystal structure determination for $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ was carried out using a Apex DUO Kappa 4-axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 IuS using $MoK_\alpha$ radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus ($T$ = -173 $^\circ$C). Full-sphere data collection was used with $\omega$ and $\varphi$ scans. *Programs used:* Data collection APEX-2[7], data reduction Bruker Saint[5] V/.60A.

*Structure solution and refinement.* Crystal structure solution was achieved using direct methods as implemented in SHELXTL[8] and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on $F^2$ using all measured intensities was carried out using the program SHELXTL[9]. All non hydrogen atoms were refined including anisotropic displacement parameters.

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**Computational Methods**

*Density functional theory*. All geometries were fully optimized at the M06-L level[12-14] of density functional theory using the Stuttgart [8s7p6d2f | 6s5p3d2f] ECP28MWB contracted pseudopotential basis set[15] on Ru and the 6-31G(d) basis set[16] on all other atoms. Non-analytical integral evaluations made use of a pruned grid having 99 radial shells and 590 angular points per shell and an automatically generated density-fitting basis set was used within the resolution-of-the-identity approximation to speed the evaluation of Coulomb integrals as implemented in Gaussian 09 software package.[17] The nature of all stationary points was verified by analytic computation of vibrational frequencies, which were also used for the computation of zero-point vibrational energies, molecular partition functions (with all frequencies below 50 $cm^{-1}$ replaced by 50 $cm^{-1}$ when computing free energies), and for determining the reactants and products associated with each transition-state structure (by following the normal modes associated with imaginary frequencies). Partition functions were used in the computation of 298 K thermal contributions to free energy employing the usual ideal-gas, rigid-rotator, harmonic oscillator approximation.[18] Free energy contributions were added to single-point M06-L electronic energies computed with the SDD basis set on ruthenium and the 6-311+G(2df,p) basis set on all other atoms to arrive at final, composite free energies.

*Solvation and standard reduction potentials***.** Solvation effects associated with water as solvent were accounted for using the SMD continuum solvation model.[19] A 1 M standard state was used for all species in aqueous solution except for water itself, for which a 55.6 M standard state was employed. Thus, for all molecules but water, the free energy in aqueous solution is computed as the 1 atm gas-phase free energy, plus an adjustment for the 1 atm to 1 M standard-state concentration change of *RT* ln (24.5), or 1.9 kcal/mol, plus the 1 M to 1 M transfer (solvation) free energy computed from the SMD model. In the case of water, the 1 atm gas-phase free energy is adjusted by the sum of a 1 atm to 55.6 M standard-state concentration change, or 4.3 kcal/mol, and the experimental 1 M to 1 M solvation free energy, –6.3 kcal/mol. The 1 M to 1 M solvation free energy of the proton was taken from experiment as –265.9 kcal/mol.[20-23]

Standard reduction potentials were calculated for various possible redox couples to assess the energetic accessibility of different intermediates at various oxidation states. For a redox reaction of the form

$$O_{(\mathrm{aq})} + n\,e^{-}_{(\mathrm{g})} \rightarrow R_{(\mathrm{aq})} \qquad (1)$$

where *O* and *R* denote the oxidized and reduced states of the redox couple, respectively, and *n* is the number of electrons involved in redox reaction, the reduction potential $E^{\mathrm{o}}_{O|R}$ relative to NHE was computed as

$$E^{\mathrm{o}}_{O|R} = -\frac{\Delta G^{\mathrm{o}}_{O|R} - \Delta G^{\mathrm{o}}_{\mathrm{NHE}}}{nF} \qquad (2)$$

where $\Delta G^{\mathrm{o}}_{O|R}$ is the free energy change associated with eq. 1 (using Boltzmann statistics for the electron), $\Delta G^{\mathrm{o}}_{\mathrm{NHE}}$ is the free energy change associated with

$$\mathrm{H}^{+}_{(\mathrm{aq})} + e^{-}_{(\mathrm{g})} \rightarrow \frac{1}{2}\mathrm{H}_{2(\mathrm{g})} \qquad (3)$$

which is –4.28 eV with Boltzmann statistics for the electron,[22,24,25] and *F* is the Faraday constant. The calculated redox potentials were reported as E vs. SSCE by subtracting 0.244 V from E vs. NHE values.

*Non-single-determinantal state energies***.** Several possible intermediates in the water oxidation mechanism have electronic structures that are not well described by a single determinant. In such instances, standard Kohn-Sham DFT is not directly applicable,[18,26-28] and we adopt the Yamaguchi broken-spin-symmetry (BS) procedure[29,30] to compute the energy of the spin-purified low-spin (LS) state as

$$^{\mathrm{LS}}E = \frac{^{\mathrm{BS}}E\left(\frac{^{\mathrm{HS}}\langle S^2\rangle - {}^{\mathrm{LS}}\langle S^2\rangle}{^{\mathrm{HS}}\langle S^2\rangle - {}^{\mathrm{BS}}\langle S^2\rangle}\right) - {}^{\mathrm{HS}}E\left(\frac{^{\mathrm{BS}}\langle S^2\rangle - {}^{\mathrm{LS}}\langle S^2\rangle}{^{\mathrm{HS}}\langle S^2\rangle - {}^{\mathrm{BS}}\langle S^2\rangle}\right)}{} \qquad (4)$$

where HS refers to the single-determinantal high-spin coupled state that is related to the low-spin state by spin flip(s) and $\langle S^2 \rangle$ is the expectation value of the total spin operator applied to the appropriate determinant. This broken-symmetry DFT approach has routinely proven effective for the prediction of state-energy splittings in metal coordination compounds.[27,31-34]


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**Figure S1.** Ortep plot (50 % probability) of the crystal structure of the complex **5**$^{2+}$. Color codes: Ru, cyan; N, navy blue; F, green; O, red; H, blue empty circles.

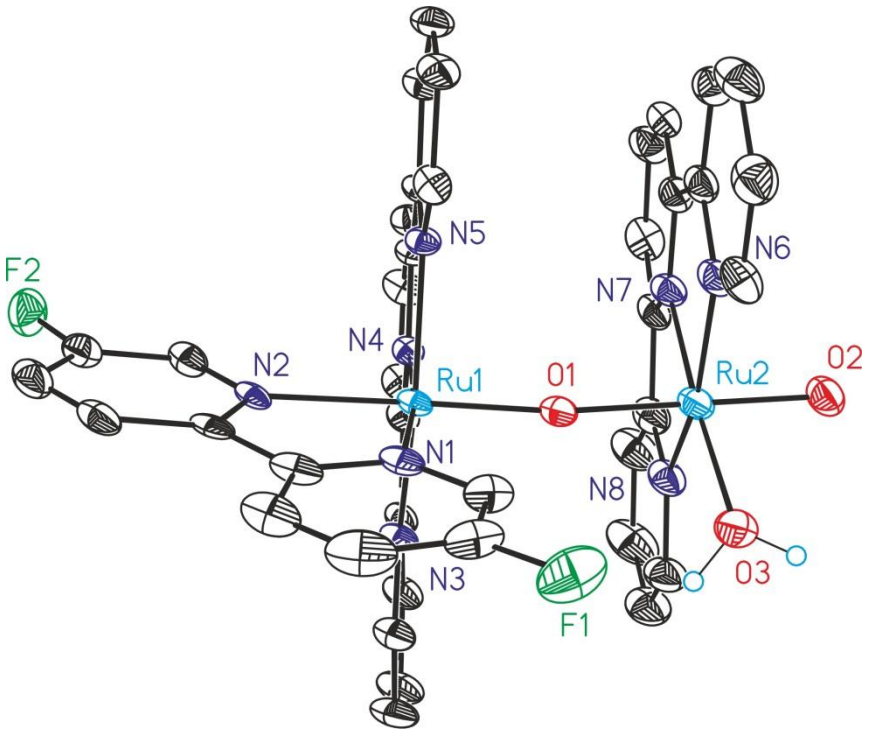
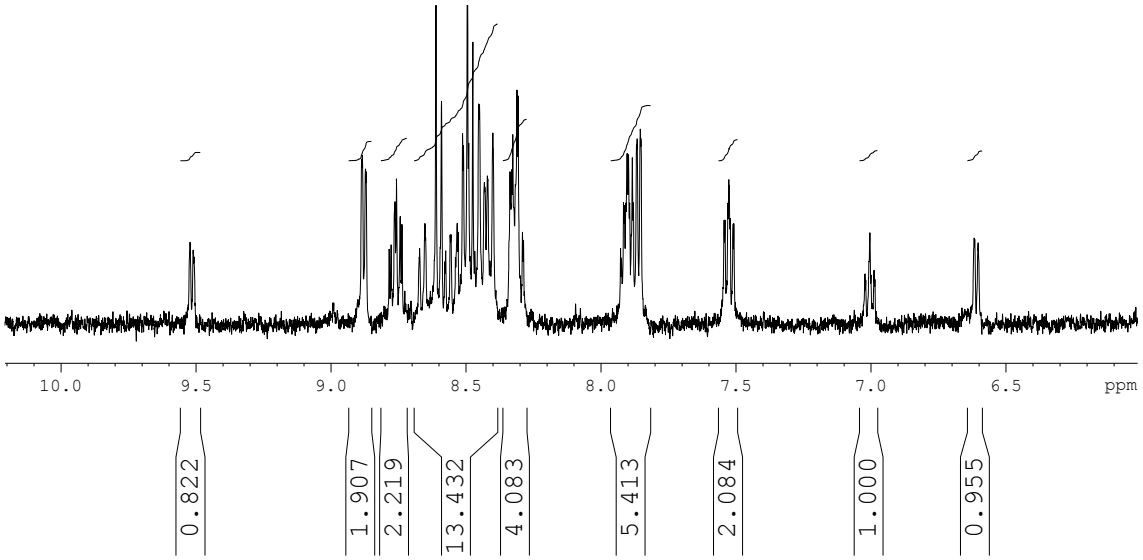
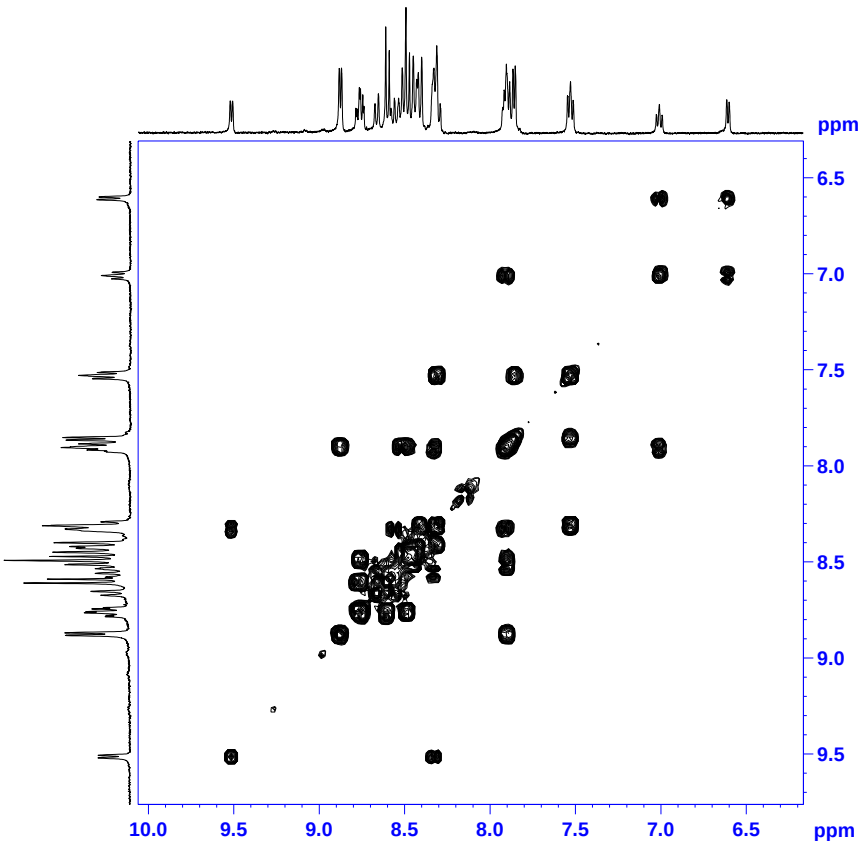


**Figure S2**. 1D and 2D NMR spectra (0.1 M $DNO_3$) for complex **1**$^{4+}$: (a) $^1$H-NMR, (b) COSYD, (c) NOESY, (d) DOSY.

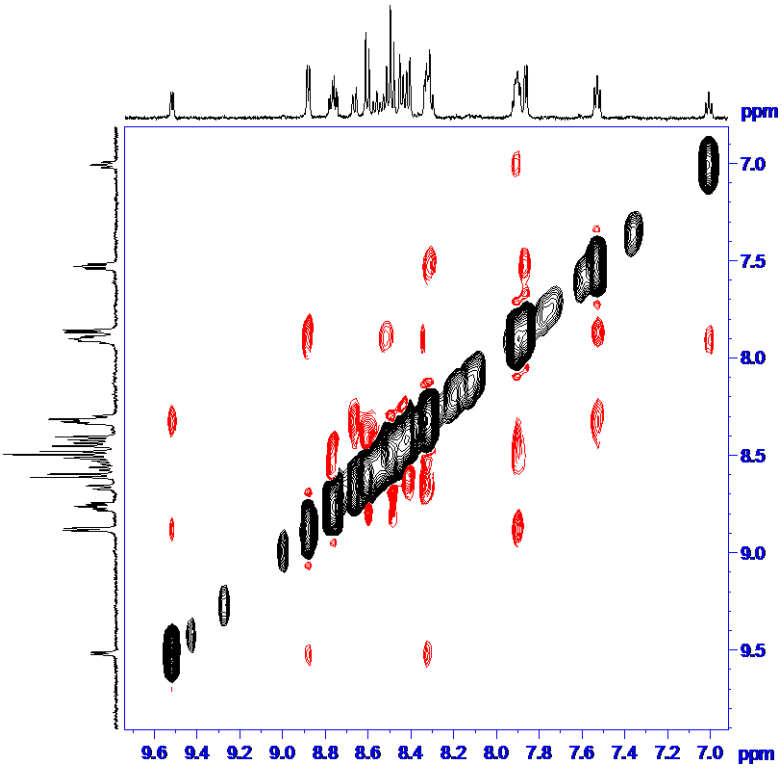
(a) $^1$H-NMR.




(b) COSYD



(c) NOESY.




d) DOSY. Experiments for 1 mM solutions of $\mathbf{1}^{4+}$(blue) and $\mathbf{3}^{2+}$(red) in $CF_3SO_3D$ 0,1 M. The $^1$H-NMR experiment of F2 axis corresponds to $\mathbf{1}^{4+}$. According to the relation between the diffusion coefficient (D) and the hydrodynamic radius ($r_s$) given by the Stokes-Einstein equation the ratio $r_s$(dinuclear)/$r_s$(mononuclear) can be calculated. The ratio is 2.29:1, means that the dinuclear complex is 2.29 times larger than the monononuclear one. Additionally the DOSY experiment shows that the observed group of peaks for $\mathbf{1}^{4+}$ belongs only to one compound.

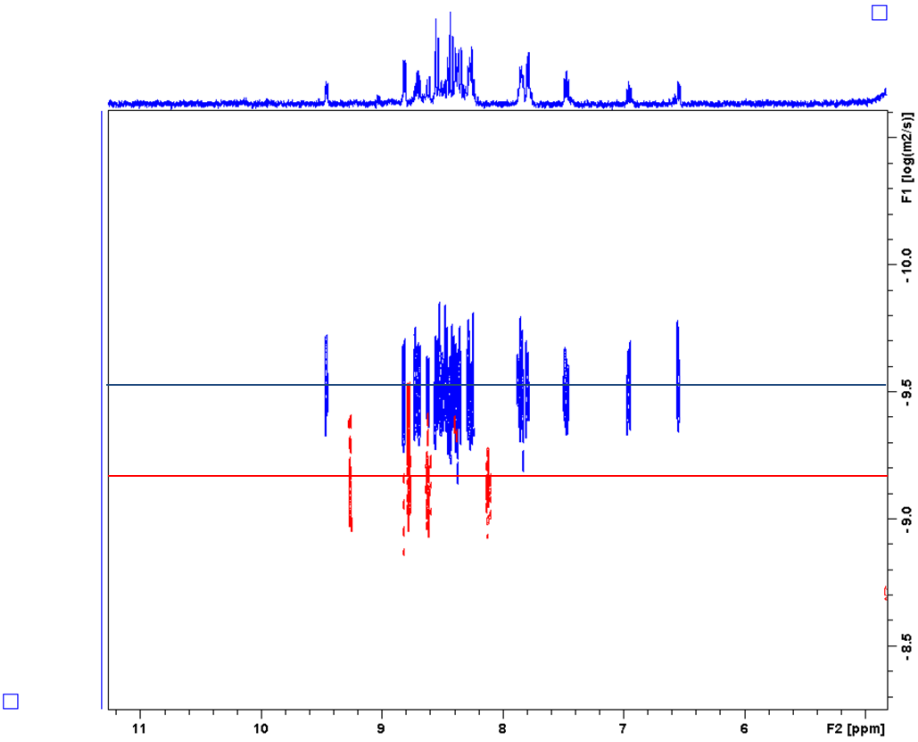
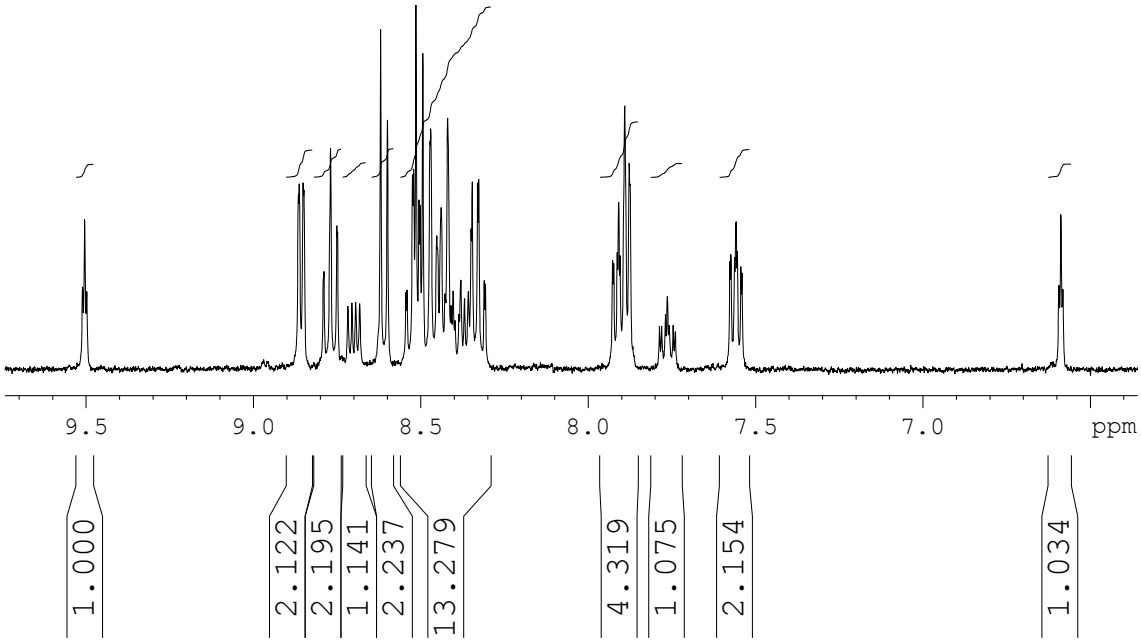
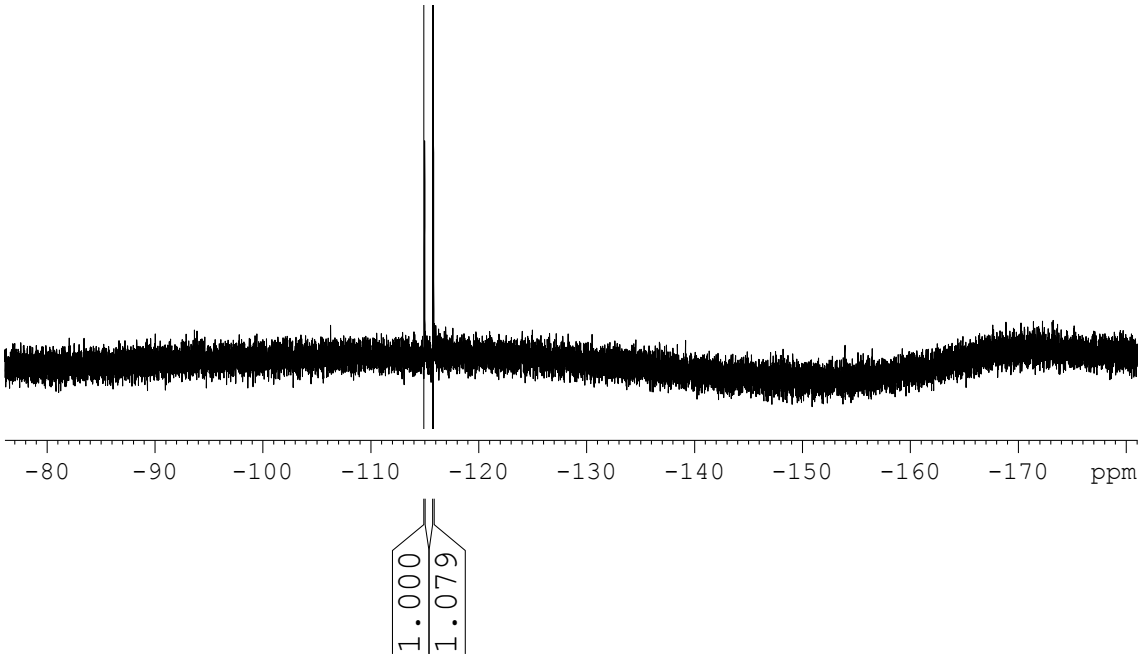


**Figure S3**. 1D and 2D NMR spectra (0.1 M $DNO_3$) for complex $\mathbf{1}^{4+}$: (a) $^{1}$H-NMR, (b) $^{19}$F-NMR, (c) COSYD{$^{19}$F}, (d) NOESY.

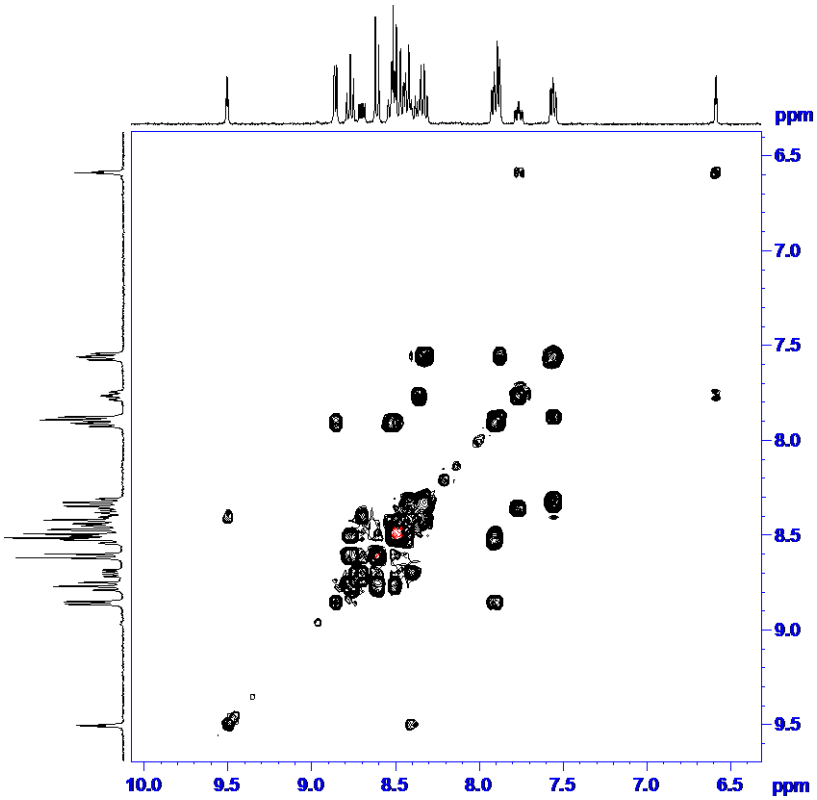
(a) $^{1}$H-NMR.




(b) $^{19}$F-NMR.



(c) COSYD{$^{19}$F}.




(d) NOESY.

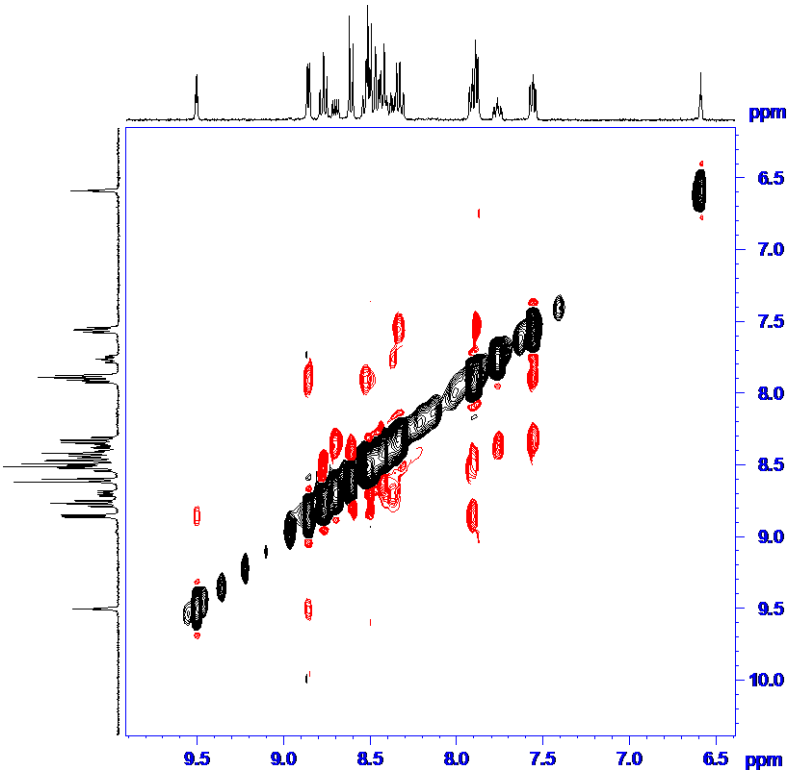


**Figure S4.** Spectroelectrochemistry experiments of a 0.4 mM solution of $\mathbf{1}^{4+}$ in 0.1 M HOTf. (Left upper) $2e^-$ reduction at 0.6 V, (right upper) $2e^-$ reoxidation at 1.0 V, (left bottom). CV experiment previous to electrolysis where the applied potentials are marked, (right bottom) UV-vis spectrums of the oxidation states of the dinuclear complex. Pt mesh working electrode, Pt wire counter electrode and SSCE reference electrode.

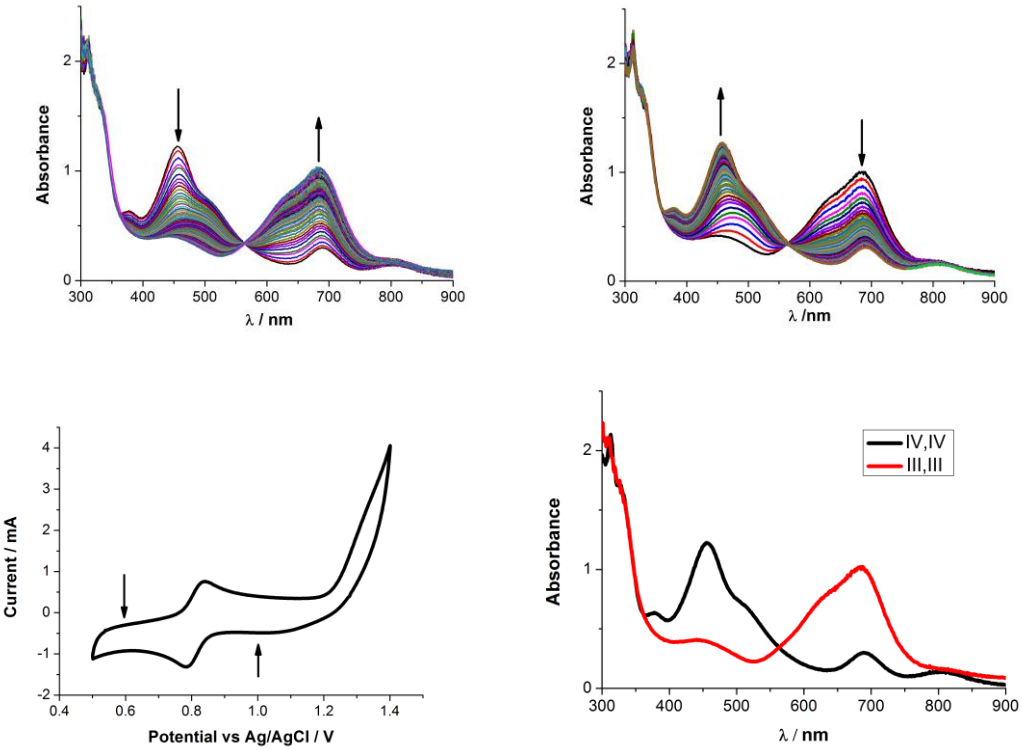



**Figure S5**. Differential Pulse Voltammetry (DPV) of 0.5 mM solutions of complexes $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ in 0.1 M HOTf. Activated boron-doped diamond working electrode, Pt wire counter electrode and $Hg/Hg_2SO_4$, $K_2SO_4$ (sat) reference electrode.

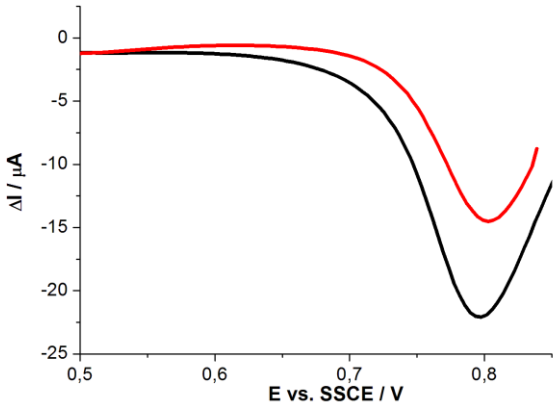


**Figure S6**. Cyclic Voltammetry of 0.5 mM solutions of **1**$^{4+}$ (black) and **4**$^{2+}$ (red) in 0.1 M HOTf. Scan rate 100 mV $s^{-1}$ using a polished glassy carbon working electrode, a Pt wire counter electrode and a $Hg/Hg_2SO_4$, $K_2SO_4$ (sat) reference electrode.

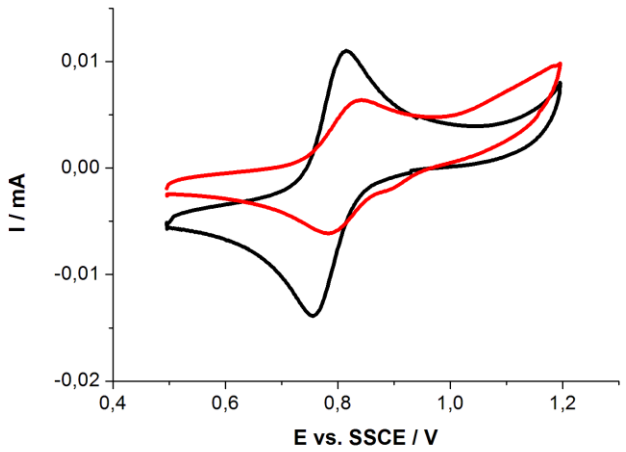



**Figure S7**. Cyclic Voltammetry of 0.5 mM solutions of **2**$^{4+}$ (black) and **5**$^{2+}$ (red) in 0.1 M HOTf. Scan rate 100 mV $s^{-1}$ using a polished glassy carbon working electrode, a Pt wire counter electrode and a $Hg/Hg_2SO_4$, $K_2SO_4$ (sat) reference electrode.

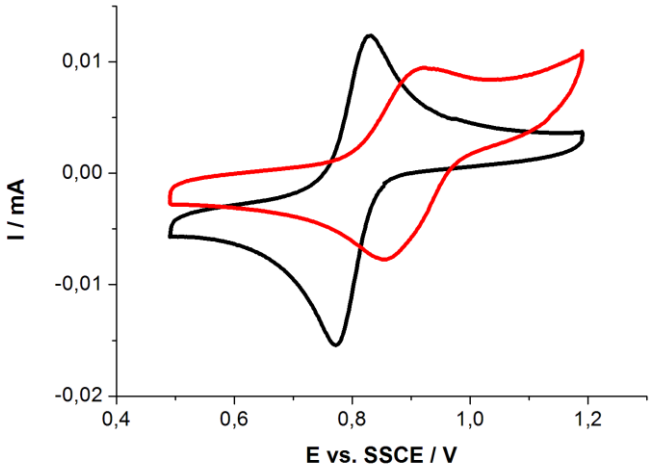


**Figure S8**. Controlled potential electrolysis at 1.6 V vs. SSCE of a 0.4 mM solution of **1**$^{4+}$ (black) and **2**$^{4+}$ (red) complexes in 0.1 M HOTf and a blank experiment without catalyst (blue). Activated boron doped diamond as working electrode, Pt wire as counter electrode and $Hg/Hg_2SO_4$, $K_2SO_4$ (sat) as reference electrode.

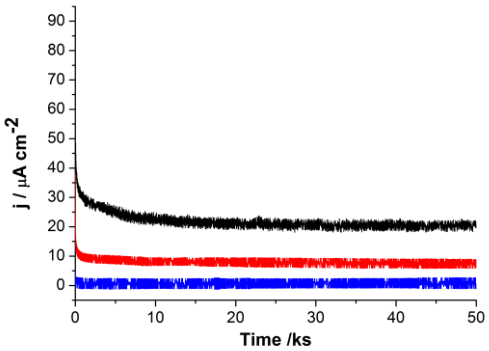



**Figure S9**. Controlled potential electrolysis at 1.6 V *vs*. SSCE of a 0.4 mM solution of **5**$^{2+}$ (black) and **2**$^{4+}$ (red) complexes in 0.1 M HOTf and a blank experiment without catalyst (blue). Activated boron doped diamond as working electrode, Pt wire as counter electrode and $Hg/Hg_2SO_4$, $K_2SO_4$ (sat) as reference electrode.

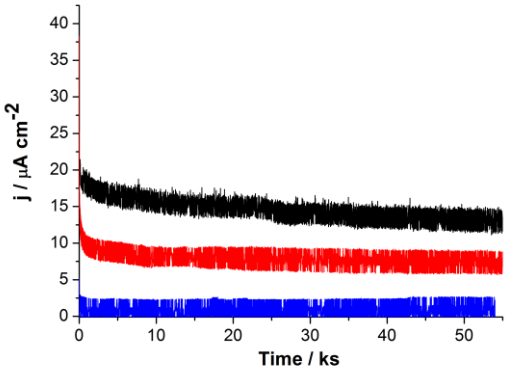


**Figure S10**. UV-vis spectrums before (black) and after 10 hours (red) controlled potential electrolysis at 1.6 V vs. SSCE of a 0.4 mM solution of **1**$^{4+}$ (upper) or **2**$^{4+}$ (bottom) in 0.1 M HOTf with 2 mm optical path length. The slight decrease in intensity after the long CPE is due to partial migration of the complexes toward the cathode.

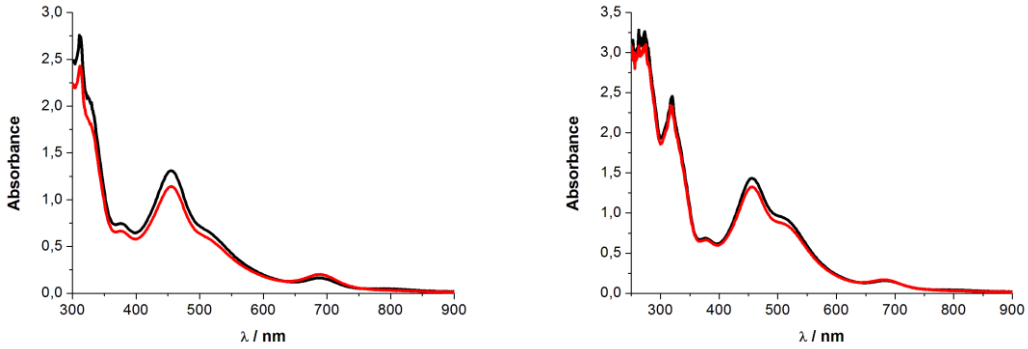



**Figure S11** (a) Left, rR spectrum of the reaction product obtained by the reaction of 3 equivalents of CAN with complex **4**$^{2+}$ in 0.1 M HOTf after 1255 min (b) Right, overlay of the rR spectra of **1**$^{4+}$ (black) in 0.1 M HOTf and (a) (red). The inset shows an enlargement of the fingerprint region.

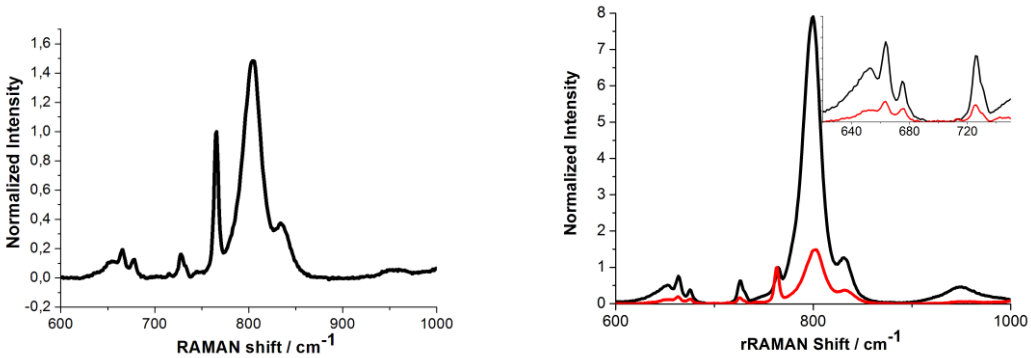
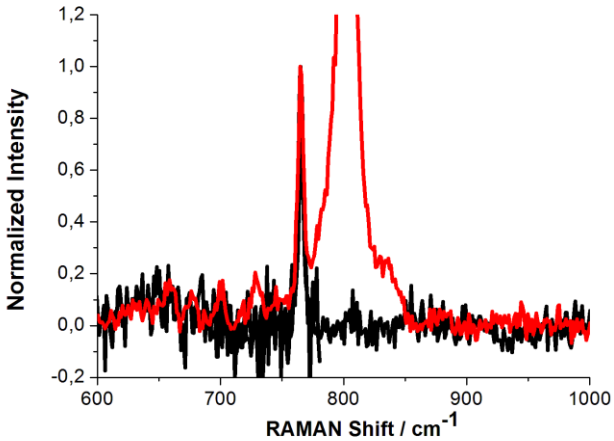
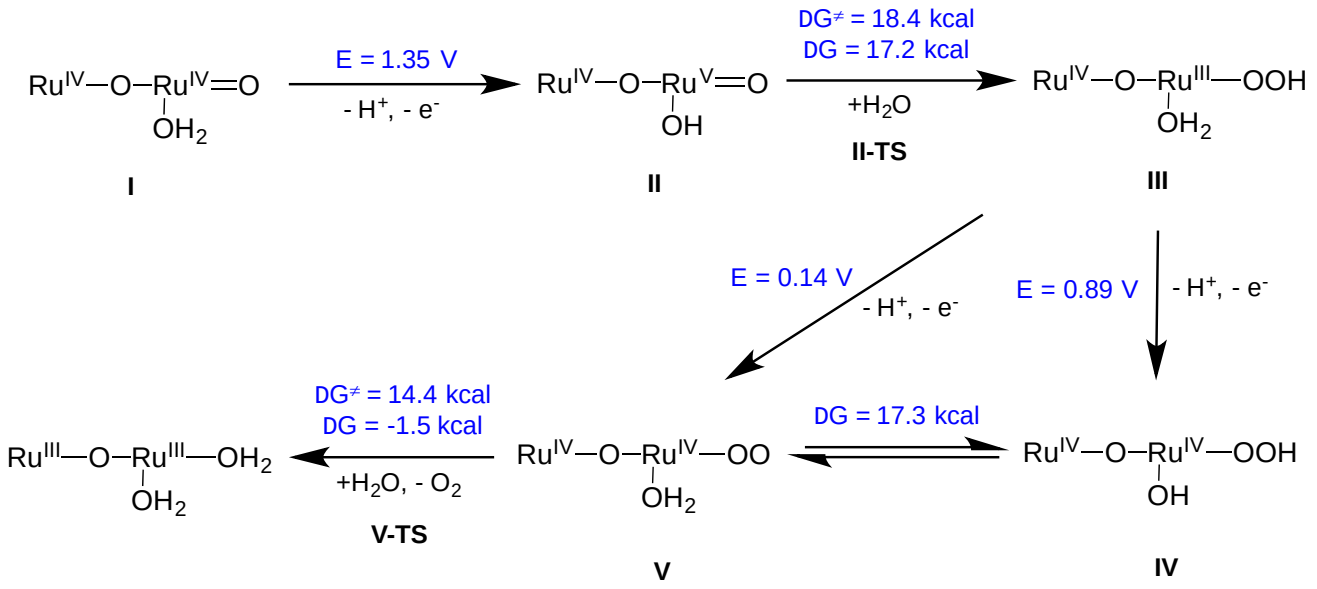


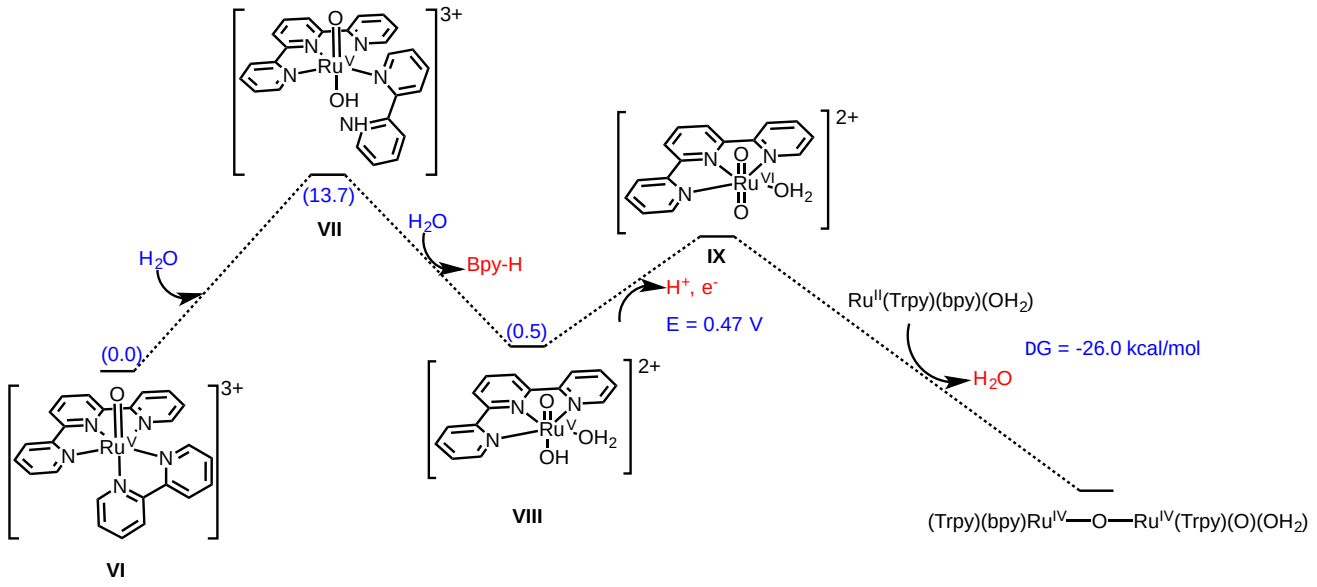

**Figure S12**. rR spectra before (black) and 1200 min after the addition of 3 equivalents of CAN (red) to complex **5**$^{2+}$ in 0.1 M HOTf.



**Scheme S1**. Proposed mechanism for catalytic water oxidation by **1**$^{4+}$ (denoted as I in the scheme) species. Supporting Trpy and Bpy ligands are not shown for clarity




**Scheme S2**. Proposed mechanism for the generation **3**$^{2+}$ (denoted as IX) and its subsequent interconversion to **1**$^{4+}$



**Electronic Energies and Cartesian Coordinates of Optimized Geometries (*see Scheme S1 and S2*)**

**I (Broken Symmetry Singlet)**

**E =** -2395.85521580 a.u.

| | | | |
|---|---|---|---|
| Ru | 1.38611100 | -0.03200100 | 0.07305500 |
| N | 0.73380200 | -0.99169300 | 1.84321300 |
| C | 0.25691100 | -0.10498000 | 2.77535900 |
| C | -0.20947700 | -0.55555500 | 4.00829400 |
| C | -0.17915600 | -1.91649000 | 4.30466600 |
| C | 0.31089900 | -2.80488600 | 3.35206600 |
| C | 0.75623800 | -2.30141700 | 2.13398500 |
| N | 2.23109900 | -1.65708900 | -0.98130900 |
| C | 1.58314600 | -2.39017300 | -1.90736600 |
| C | 2.18453600 | -3.43662200 | -2.58933300 |
| C | 3.51402900 | -3.74537100 | -2.30625200 |
| C | 4.18947700 | -2.99208700 | -1.35435200 |
| C | 3.53404300 | -1.94669900 | -0.70025200 |
| N | 3.36651200 | -0.09987900 | 0.81648200 |
| C | 3.87987500 | 0.73440700 | 1.74297400 |
| C | 5.18498000 | 0.63863400 | 2.20128800 |
| C | 6.00333600 | -0.36300300 | 1.68473600 |
| C | 5.48303400 | -1.22863900 | 0.72971300 |
| C | 4.16249200 | -1.08589300 | 0.30425100 |
| N | 1.95984800 | 1.55084300 | -1.19869500 |
| C | 2.58492500 | 1.47896600 | -2.38644900 |
| C | 2.96029900 | 2.60817500 | -3.10636200 |
| C | 2.68074300 | 3.86457500 | -2.57586700 |
| C | 2.03689700 | 3.94884300 | -1.34354200 |
| C | 1.68704300 | 2.78523500 | -0.66220200 |
| N | 0.83799200 | 1.54074200 | 1.16881600 |
| C | 0.32332600 | 1.31760200 | 2.40179600 |
| C | -0.03034800 | 2.40781000 | 3.19783500 |
| C | 0.16954400 | 3.69685100 | 2.70341000 |
| C | 0.71552900 | 3.89414000 | 1.43531800 |
| C | 1.05301900 | 2.78015200 | 0.66532400 |
| H | -0.57399300 | 0.15332700 | 4.74819900 |
| H | -0.51859600 | -2.27358600 | 5.27449500 |
| H | 0.36844400 | -3.87215500 | 3.54975700 |
| H | 0.55073200 | -2.09914400 | -2.09058300 |
| H | 1.62362000 | -3.99574300 | -3.33387300 |
| H | 4.01997100 | -4.55798400 | -2.82231700 |
| H | 5.22754500 | -3.21782700 | -1.12721400 |
| H | 3.21081200 | 1.50341000 | 2.12305200 |
| H | 5.54841500 | 1.33878200 | 2.94863400 |
| H | 7.03253000 | -0.46954600 | 2.01957300 |
| H | 6.11008600 | -2.01440900 | 0.31790500 |
| H | 2.79628800 | 0.47571300 | -2.75276400 |
| H | 3.47427400 | 2.49714000 | -4.05772300 |
| H | 2.97148200 | 4.76858600 | -3.10632300 |
| H | 1.82681800 | 4.92266300 | -0.90735700 |

| | | | |
|---|---|---|---|
| H | -0.42812400 | 2.26542700 | 4.19959200 |
| H | -0.07943900 | 4.55605200 | 3.32235500 |
| H | 0.89271000 | 4.90273200 | 1.07028600 |
| H | 1.15413300 | -2.95346500 | 1.35838400 |
| Ru | -2.05397400 | -0.25621800 | -1.33385400 |
| O | -0.33773800 | -0.19413500 | -0.64026900 |
| N | -2.32795400 | -2.30668600 | -0.87063400 |
| N | -2.93919200 | -0.08415300 | 0.42211200 |
| N | -2.21292600 | 1.88705400 | -1.18610500 |
| C | -2.08251100 | -3.37275600 | -1.64389200 |
| H | -1.59275100 | -3.17038600 | -2.59448800 |
| C | -2.45823600 | -4.66019700 | -1.27264800 |
| H | -2.26011500 | -5.49505500 | -1.93964200 |
| C | -3.10950700 | -4.84232500 | -0.05694200 |
| H | -3.42988700 | -5.83323200 | 0.25722600 |
| C | -3.37458000 | -3.73368900 | 0.74536500 |
| H | -3.91074100 | -3.86020200 | 1.68262700 |
| C | -2.99009800 | -2.46568900 | 0.31851100 |
| C | -3.32257500 | -1.22959900 | 1.04008900 |
| C | -4.03871300 | -1.13447400 | 2.23302100 |
| H | -4.37445400 | -2.02754000 | 2.75341100 |
| C | -4.36554600 | 0.12649800 | 2.72861000 |
| H | -4.94515300 | 0.21068300 | 3.64537400 |
| C | -3.99688800 | 1.27964900 | 2.03704400 |
| H | -4.29982500 | 2.25561900 | 2.40700800 |
| C | -3.28219800 | 1.15683700 | 0.84612000 |
| C | -2.90382800 | 2.25018600 | -0.06161800 |
| C | -3.27446800 | 3.57735100 | 0.14319600 |
| H | -3.84388600 | 3.86023200 | 1.02519400 |
| C | -2.95801500 | 4.53805800 | -0.81542200 |
| H | -3.27553500 | 5.56978800 | -0.68079400 |
| C | -2.25850300 | 4.15356500 | -1.95492500 |
| H | -2.01466500 | 4.86646400 | -2.73837300 |
| C | -1.90477200 | 2.81534400 | -2.09965400 |
| H | -1.37556300 | 2.46316500 | -2.98323000 |
| O | -3.54847300 | -0.24957600 | -2.17776500 |
| O | -1.19627500 | -0.64073600 | -3.39751900 |
| H | -1.94349100 | -0.66978700 | -4.02662100 |
| H | -0.52942900 | -0.07047500 | -3.81470700 |

**I (Triplet)**

**E =** -2395.83428496 a.u.

| | | | |
|---|---|---|---|
| Ru | 1.38182400 | 0.09802300 | 0.03854900 |
| N | 1.04504000 | -1.55561600 | 1.30711600 |
| C | 0.41031300 | -1.20884400 | 2.47391300 |
| C | 0.14049700 | -2.17104800 | 3.44408000 |
| C | 0.53181500 | -3.49226300 | 3.23694300 |
| C | 1.17589700 | -3.83046900 | 2.04959700 |
| C | 1.41274900 | -2.83337700 | 1.11063800 |
| N | 2.52110800 | -0.88264000 | -1.45391300 |
| C | 2.00425900 | -1.44469600 | -2.56404600 |

| | | | |
|---|---|---|---|
| C | 2.78717800 | -2.09693300 | -3.50481200 |
| C | 4.16297300 | -2.17666500 | -3.29543200 |
| C | 4.70172500 | -1.60491800 | -2.14959100 |
| C | 3.86590100 | -0.96144800 | -1.23466800 |
| N | 3.36581800 | 0.22507700 | 0.78422000 |
| C | 3.72082500 | 0.82665500 | 1.93757300 |
| C | 5.03408200 | 0.89320100 | 2.37587400 |
| C | 6.03061300 | 0.31877600 | 1.58892300 |
| C | 5.67428600 | -0.29964500 | 0.39607500 |
| C | 4.33575800 | -0.33890500 | 0.00457700 |
| N | 1.57574400 | 2.12866800 | -0.49179900 |
| C | 2.20822100 | 2.63723300 | -1.56164400 |
| C | 2.25440600 | 4.00271500 | -1.82045800 |
| C | 1.62193600 | 4.87461600 | -0.93809800 |
| C | 0.96962300 | 4.35431400 | 0.17694900 |
| C | 0.95970400 | 2.97792800 | 0.39273300 |
| N | 0.49153200 | 0.98941400 | 1.58594500 |
| C | 0.09838100 | 0.22086700 | 2.63191800 |
| C | -0.48631500 | 0.82754300 | 3.74237900 |
| C | -0.64653900 | 2.21454100 | 3.74936400 |
| C | -0.21783200 | 2.98083900 | 2.66797900 |
| C | 0.36856400 | 2.33890100 | 1.57437300 |
| H | -0.34829400 | -1.88876400 | 4.37378000 |
| H | 0.34994000 | -4.24328400 | 4.00286200 |
| H | 1.51055600 | -4.84639300 | 1.85590500 |
| H | 0.92588100 | -1.34691500 | -2.67424300 |
| H | 2.32689400 | -2.53163300 | -4.38819100 |
| H | 4.80799300 | -2.67784600 | -4.01347000 |
| H | 5.77178300 | -1.66248500 | -1.97079500 |
| H | 2.91301300 | 1.26492500 | 2.52040500 |
| H | 5.26769900 | 1.38753700 | 3.31498200 |
| H | 7.07273100 | 0.35366700 | 1.89833700 |
| H | 6.44252000 | -0.74780900 | -0.22788400 |
| H | 2.68948200 | 1.91608000 | -2.21921700 |
| H | 2.78647800 | 4.36902300 | -2.69467400 |
| H | 1.64914800 | 5.94905100 | -1.10591800 |
| H | 0.48917200 | 5.02346200 | 0.88703200 |
| H | -0.79085800 | 0.24095500 | 4.60574800 |
| H | -1.08140000 | 2.70289200 | 4.61872200 |
| H | -0.31141000 | 4.06371200 | 2.69603300 |
| H | 1.91956100 | -3.04372700 | 0.17077800 |
| Ru | -2.06588400 | -0.32970200 | -1.42585000 |
| O | -0.22339100 | -0.02692800 | -0.94071400 |
| N | -2.01208500 | -2.36991700 | -0.91001000 |
| N | -2.83195300 | -0.23518600 | 0.38236900 |
| N | -2.43352700 | 1.78818200 | -1.27327500 |
| C | -1.63448900 | -3.40207800 | -1.67828200 |
| H | -1.19759000 | -3.14470700 | -2.64097500 |
| C | -1.82027000 | -4.72313400 | -1.28450200 |
| H | -1.52503600 | -5.53166500 | -1.94815600 |
| C | -2.41609600 | -4.97684900 | -0.05220700 |
| H | -2.59798600 | -5.99839100 | 0.27458600 |
| C | -2.80331000 | -3.90569800 | 0.75087100 |

| | | | |
|---|---|---|---|
| H | -3.29207100 | -4.09104000 | 1.70446600 |
| C | -2.60384400 | -2.60206100 | 0.30393700 |
| C | -3.05885700 | -1.40860000 | 1.02760100 |
| C | -3.74073100 | -1.38632600 | 2.24375700 |
| H | -3.95194000 | -2.30831900 | 2.77951800 |
| C | -4.20501500 | -0.16878500 | 2.73787700 |
| H | -4.76807100 | -0.14374900 | 3.66835400 |
| C | -3.99692200 | 1.01066500 | 2.02417400 |
| H | -4.40788800 | 1.94739700 | 2.39170900 |
| C | -3.30528900 | 0.96140500 | 0.81445100 |
| C | -3.08113700 | 2.08664700 | -0.10563100 |
| C | -3.53329400 | 3.38097700 | 0.14189600 |
| H | -4.06334200 | 3.61243100 | 1.06262700 |
| C | -3.34474900 | 4.37312600 | -0.81786600 |
| H | -3.72577000 | 5.37779500 | -0.64805300 |
| C | -2.68801900 | 4.05393700 | -2.00223900 |
| H | -2.54096500 | 4.79174700 | -2.78666800 |
| C | -2.24785200 | 2.74715300 | -2.18844700 |
| H | -1.75043800 | 2.44567400 | -3.10752900 |
| O | -3.62017400 | -0.49638600 | -2.15663100 |
| O | -1.33263100 | -0.62956800 | -3.54738800 |
| H | -2.11923600 | -0.79178800 | -4.10393300 |
| H | -0.82898200 | 0.05745400 | -4.01480300 |

**I (Quintet)**

**E =** -2395.82711977 a.u.

| | | | |
|---|---|---|---|
| Ru | 1.43433700 | 0.07959200 | -0.00325100 |
| N | 0.84146400 | -1.38127100 | 1.41288800 |
| C | 0.26710400 | -0.82802200 | 2.52886100 |
| C | -0.14739900 | -1.63661900 | 3.58458800 |
| C | 0.03352900 | -3.01644400 | 3.51101600 |
| C | 0.61781800 | -3.56379000 | 2.37244200 |
| C | 1.00739100 | -2.71116900 | 1.34464800 |
| N | 2.51357800 | -1.14396600 | -1.36835800 |
| C | 1.96885300 | -1.68430100 | -2.47704300 |
| C | 2.69881900 | -2.46994900 | -3.35634300 |
| C | 4.04393400 | -2.71199200 | -3.08430600 |
| C | 4.60815300 | -2.15892000 | -1.94130100 |
| C | 3.82857100 | -1.37390400 | -1.08965700 |
| N | 3.42612400 | -0.00970900 | 0.83755500 |
| C | 3.82084100 | 0.60157200 | 1.97219100 |
| C | 5.11469200 | 0.51497700 | 2.46284700 |
| C | 6.04845600 | -0.23544100 | 1.75179100 |
| C | 5.65108900 | -0.86869500 | 0.57966300 |
| C | 4.33460700 | -0.74607300 | 0.13437200 |
| N | 1.93229700 | 1.99731200 | -0.74330000 |
| C | 2.62466100 | 2.29972500 | -1.85211600 |
| C | 2.91215400 | 3.61158100 | -2.21683100 |
| C | 2.46606800 | 4.64687900 | -1.40155200 |
| C | 1.74664300 | 4.33912500 | -0.24788000 |
| C | 1.48886200 | 3.00881000 | 0.07161700 |

| | | | |
|---|---|---|---|
| N | 0.69530900 | 1.24115500 | 1.44357400 |
| C | 0.17685100 | 0.64191400 | 2.54381100 |
| C | -0.32306600 | 1.43751000 | 3.57343000 |
| C | -0.26120700 | 2.82610800 | 3.44206300 |
| C | 0.30194100 | 3.41121400 | 2.30860100 |
| C | 0.79389200 | 2.58513400 | 1.29661300 |
| H | -0.58707600 | -1.19332900 | 4.47514600 |
| H | -0.26315800 | -3.65207600 | 4.34274400 |
| H | 0.79017700 | -4.63332600 | 2.28186400 |
| H | 0.91673400 | -1.45574600 | -2.63707500 |
| H | 2.22044500 | -2.88018600 | -4.24179100 |
| H | 4.64721900 | -3.32114700 | -3.75353600 |
| H | 5.65586500 | -2.33827800 | -1.71723000 |
| H | 3.06379000 | 1.17997800 | 2.49865400 |
| H | 5.38140400 | 1.02775000 | 3.38304500 |
| H | 7.07359600 | -0.32637600 | 2.10365800 |
| H | 6.37067000 | -1.45547800 | 0.01572100 |
| H | 2.95506900 | 1.45623600 | -2.45486800 |
| H | 3.48296200 | 3.80788900 | -3.12078600 |
| H | 2.68254300 | 5.68309100 | -1.65186500 |
| H | 1.40460200 | 5.13741600 | 0.40641000 |
| H | -0.73492500 | 0.99418700 | 4.47661000 |
| H | -0.63084600 | 3.45927500 | 4.24590000 |
| H | 0.37479300 | 4.49321000 | 2.23439100 |
| H | 1.47486700 | -3.08763600 | 0.43657700 |
| Ru | -2.23231500 | -0.27992200 | -1.40278900 |
| O | -0.08997700 | -0.03699800 | -0.96626700 |
| N | -2.16440800 | -2.31430700 | -0.84703800 |
| N | -2.97213100 | -0.16557800 | 0.41695700 |
| N | -2.53643200 | 1.82056300 | -1.23649300 |
| C | -1.78144100 | -3.35913200 | -1.59484200 |
| H | -1.34088500 | -3.11604900 | -2.55960700 |
| C | -1.96800400 | -4.67564400 | -1.18459800 |
| H | -1.66933800 | -5.49283900 | -1.83595500 |
| C | -2.57355700 | -4.91377000 | 0.04541300 |
| H | -2.75945100 | -5.93066600 | 0.38400900 |
| C | -2.96632000 | -3.83080400 | 0.82973200 |
| H | -3.46257700 | -4.00184400 | 1.78221200 |
| C | -2.76231800 | -2.53426200 | 0.36487700 |
| C | -3.20597300 | -1.32953800 | 1.07820800 |
| C | -3.86717100 | -1.28969400 | 2.30459100 |
| H | -4.08349100 | -2.20520300 | 2.84939600 |
| C | -4.30024200 | -0.06188300 | 2.80254800 |
| H | -4.84569200 | -0.02278800 | 3.74290100 |
| C | -4.08064500 | 1.11041700 | 2.08104500 |
| H | -4.46269600 | 2.05763300 | 2.45268800 |
| C | -3.41367700 | 1.03996600 | 0.85893700 |
| C | -3.17683800 | 2.15091600 | -0.07165100 |
| C | -3.61663200 | 3.45232600 | 0.15613100 |
| H | -4.14226300 | 3.70196700 | 1.07457400 |
| C | -3.42426700 | 4.42670400 | -0.82070500 |
| H | -3.79470100 | 5.43769400 | -0.66655400 |
| C | -2.77821400 | 4.07924700 | -2.00275600 |

| | | | |
|---|---|---|---|
| H | -2.62989500 | 4.80119500 | -2.80144900 |
| C | -2.34967500 | 2.76628400 | -2.16808900 |
| H | -1.86215100 | 2.44557100 | -3.08580500 |
| O | -3.77559800 | -0.49038100 | -2.18165100 |
| O | -1.43773700 | -0.60469100 | -3.49319000 |
| H | -2.21578700 | -0.81181700 | -4.04651500 |
| H | -0.97261100 | 0.10117300 | -3.97153600 |

**II (Doublet)**

**E =** -2395.21049798 a.u.

| | | | |
|---|---|---|---|
| Ru | 1.37396300 | -0.18203200 | 0.15296300 |
| N | 1.28778400 | -0.62029900 | 2.21726800 |
| C | 1.23328100 | 0.50921800 | 2.99598000 |
| C | 1.20661100 | 0.41114700 | 4.38429300 |
| C | 1.24605500 | -0.84314600 | 4.99045100 |
| C | 1.30882600 | -1.97924800 | 4.18988300 |
| C | 1.32768400 | -1.82509600 | 2.80751100 |
| N | 1.78656600 | -2.11522200 | -0.61691900 |
| C | 0.84387500 | -2.97674800 | -1.04116000 |
| C | 1.15133900 | -4.22800100 | -1.55237100 |
| C | 2.48823200 | -4.61064000 | -1.63404400 |
| C | 3.46576800 | -3.72809500 | -1.19151700 |
| C | 3.09866000 | -2.48190100 | -0.68093200 |
| N | 3.50646200 | -0.33419900 | 0.29655900 |
| C | 4.32615900 | 0.61617200 | 0.79058600 |
| C | 5.70375900 | 0.47035500 | 0.84098400 |
| C | 6.26944900 | -0.70743400 | 0.35856800 |
| C | 5.43302700 | -1.69359700 | -0.15097200 |
| C | 4.05269100 | -1.49373300 | -0.17475700 |
| N | 1.69314700 | 0.97802500 | -1.58927500 |
| C | 1.90700500 | 0.54340000 | -2.84087300 |
| C | 2.18065800 | 1.41194700 | -3.89317000 |
| C | 2.23736800 | 2.77892900 | -3.63773300 |
| C | 2.00884500 | 3.23620900 | -2.34093700 |
| C | 1.73897100 | 2.32350700 | -1.32390600 |
| N | 1.35444300 | 1.66030500 | 0.92352500 |
| C | 1.27331800 | 1.78832100 | 2.27089800 |
| C | 1.30974600 | 3.06553100 | 2.83127600 |
| C | 1.44944700 | 4.16778000 | 1.98815800 |
| C | 1.57530400 | 3.99848400 | 0.60881600 |
| C | 1.53588300 | 2.70781700 | 0.08189200 |
| H | 1.17116400 | 1.30857900 | 4.99709500 |
| H | 1.23835800 | -0.92725200 | 6.07488300 |
| H | 1.35177800 | -2.97531800 | 4.62250600 |
| H | -0.17829300 | -2.61865700 | -0.95504300 |
| H | 0.35640700 | -4.89213100 | -1.88162500 |
| H | 2.76766800 | -5.58307300 | -2.03280100 |
| H | 4.51230500 | -4.01436600 | -1.24306600 |
| H | 3.85124000 | 1.52272400 | 1.15881000 |
| H | 6.31716900 | 1.26767100 | 1.25190100 |
| H | 7.34640400 | -0.85797100 | 0.37976900 |

| | | | |
|---|---|---|---|
| H | 5.86010000 | -2.61864200 | -0.52772000 |
| H | 1.84497600 | -0.53182000 | -2.98880100 |
| H | 2.35630900 | 1.01440500 | -4.88941100 |
| H | 2.46560600 | 3.48312400 | -4.43500300 |
| H | 2.06169500 | 4.30046700 | -2.12249800 |
| H | 1.25494700 | 3.20761600 | 3.90746800 |
| H | 1.49242100 | 5.16791000 | 2.41402000 |
| H | 1.72960800 | 4.86220400 | -0.03311000 |
| H | 1.37926300 | -2.68273000 | 2.14004700 |
| Ru | -2.14831400 | -0.20930900 | -1.10903500 |
| O | -0.43552300 | -0.28994000 | -0.12587700 |
| N | -2.88367300 | -2.11415200 | -0.52486300 |
| N | -3.26116100 | 0.22360100 | 0.57206400 |
| N | -2.08511400 | 1.92225200 | -1.02367200 |
| C | -2.76915200 | -3.23245700 | -1.26270200 |
| H | -2.15957300 | -3.15440700 | -2.16041300 |
| C | -3.41278400 | -4.41261800 | -0.91209200 |
| H | -3.30874700 | -5.29022300 | -1.54498600 |
| C | -4.20248200 | -4.43277600 | 0.23392500 |
| H | -4.72724600 | -5.33822700 | 0.53047000 |
| C | -4.34191700 | -3.26629400 | 0.98207300 |
| H | -4.98567700 | -3.25623400 | 1.85791600 |
| C | -3.69100600 | -2.10349200 | 0.57968400 |
| C | -3.88620200 | -0.79248300 | 1.20798100 |
| C | -4.69933500 | -0.51828700 | 2.30779700 |
| H | -5.21756800 | -1.31646600 | 2.83255300 |
| C | -4.86805700 | 0.80500800 | 2.70787900 |
| H | -5.51047800 | 1.03633700 | 3.55446600 |
| C | -4.24886400 | 1.83693400 | 2.00459600 |
| H | -4.41993800 | 2.87087200 | 2.29238800 |
| C | -3.44283300 | 1.51968200 | 0.91253900 |
| C | -2.80581700 | 2.47456200 | -0.00271700 |
| C | -2.97584300 | 3.85536000 | 0.06474300 |
| H | -3.56066100 | 4.29548200 | 0.86858000 |
| C | -2.44443500 | 4.66605600 | -0.93534500 |
| H | -2.60843100 | 5.74121900 | -0.90989400 |
| C | -1.73799500 | 4.08014500 | -1.98206900 |
| H | -1.34177800 | 4.67426900 | -2.80193100 |
| C | -1.57864300 | 2.69937700 | -1.99304100 |
| H | -1.05696400 | 2.18274300 | -2.79612700 |
| O | -3.52627900 | -0.04004900 | -2.16592500 |
| O | -1.04030100 | -0.67107200 | -2.62979000 |
| H | -1.58253600 | -0.69213600 | -3.44441200 |

**II-TS (Doublet)**

**E =** -2471.60297748 a.u.

| | | | |
|---|---|---|---|
| Ru | -1.43572300 | 0.21349700 | 0.12193200 |
| N | -1.33120500 | 0.56710500 | 2.20529700 |
| C | -1.33353200 | -0.59538800 | 2.93493300 |
| C | -1.32123300 | -0.55915000 | 4.32645200 |
| C | -1.31618600 | 0.66785000 | 4.98745100 |

| | | | |
|---|---|---|---|
| C | -1.31862100 | 1.83899300 | 4.23685600 |
| C | -1.32609000 | 1.74513300 | 2.84896000 |
| N | -1.73206300 | 2.20828300 | -0.52509800 |
| C | -0.73944400 | 3.06445700 | -0.83744700 |
| C | -0.97601000 | 4.36222700 | -1.26232400 |
| C | -2.29438500 | 4.80344900 | -1.36855200 |
| C | -3.32171000 | 3.93247400 | -1.02940200 |
| C | -3.02431200 | 2.63607400 | -0.60287800 |
| N | -3.54456700 | 0.45236300 | 0.23027900 |
| C | -4.41426200 | -0.49093000 | 0.64501700 |
| C | -5.78649700 | -0.29221300 | 0.66600000 |
| C | -6.29239800 | 0.93139500 | 0.23465200 |
| C | -5.40368700 | 1.91030400 | -0.19460200 |
| C | -4.03199000 | 1.65802400 | -0.18904000 |
| N | -1.76772400 | -0.86856000 | -1.66564200 |
| C | -1.98081700 | -0.38505400 | -2.89932800 |
| C | -2.24760200 | -1.20362300 | -3.99134000 |
| C | -2.30459500 | -2.58065700 | -3.79732300 |
| C | -2.09311100 | -3.09125500 | -2.51880000 |
| C | -1.82837900 | -2.22415200 | -1.46068100 |
| N | -1.47358200 | -1.65683700 | 0.81372600 |
| C | -1.40818300 | -1.84199100 | 2.15575200 |
| C | -1.48042900 | -3.13854400 | 2.66423300 |
| C | -1.63113300 | -4.20449200 | 1.77652000 |
| C | -1.72783500 | -3.97859200 | 0.40395000 |
| C | -1.65628000 | -2.66835800 | -0.07042700 |
| H | -1.33327100 | -1.48291200 | 4.89974700 |
| H | -1.32144400 | 0.70419400 | 6.07452700 |
| H | -1.32592200 | 2.81638700 | 4.71205800 |
| H | 0.26780200 | 2.66881200 | -0.71440400 |
| H | -0.14305400 | 5.01883500 | -1.50076500 |
| H | -2.51964000 | 5.81408200 | -1.70110900 |
| H | -4.35338400 | 4.26686700 | -1.09222400 |
| H | -3.98462300 | -1.43459000 | 0.97338000 |
| H | -6.44179500 | -1.08588800 | 1.01469500 |
| H | -7.36299500 | 1.12287000 | 0.23350100 |
| H | -5.78375600 | 2.87065700 | -0.53143000 |
| H | -1.94131400 | 0.69793200 | -2.99964200 |
| H | -2.41800500 | -0.76200300 | -4.96966200 |
| H | -2.52454200 | -3.24944900 | -4.62651200 |
| H | -2.15478200 | -4.16321200 | -2.34505900 |
| H | -1.44340500 | -3.32429600 | 3.73449800 |
| H | -1.70274900 | -5.21916100 | 2.16218300 |
| H | -1.88459700 | -4.81297900 | -0.27510000 |
| H | -1.33318400 | 2.63275900 | 2.21976400 |
| Ru | 2.13007200 | 0.10840200 | -0.88947000 |
| O | 0.41098000 | 0.24830100 | -0.14986400 |
| N | 2.86112600 | 2.01992300 | -0.28929100 |
| N | 2.98925900 | -0.36672600 | 0.84960600 |
| N | 1.91684000 | -2.01400800 | -0.92038400 |
| C | 2.92528400 | 3.14668700 | -1.01530400 |
| H | 2.43169800 | 3.12133600 | -1.98454400 |
| C | 3.61413600 | 4.27478200 | -0.58403100 |

| | | | |
|---|---|---|---|
| H | 3.65654600 | 5.15726100 | -1.21698300 |
| C | 4.26261300 | 4.23165900 | 0.64575900 |
| H | 4.81750800 | 5.09271700 | 1.01156100 |
| C | 4.22519900 | 3.05464700 | 1.39133600 |
| H | 4.76449800 | 2.99456700 | 2.33326100 |
| C | 3.53808400 | 1.94709100 | 0.90356100 |
| C | 3.58433700 | 0.62477100 | 1.55013300 |
| C | 4.24780100 | 0.30037500 | 2.73420300 |
| H | 4.74319700 | 1.06431200 | 3.32737900 |
| C | 4.30017800 | -1.03424400 | 3.13284100 |
| H | 4.82998500 | -1.30150500 | 4.04444000 |
| C | 3.71670200 | -2.03548700 | 2.35596100 |
| H | 3.80614100 | -3.07643400 | 2.65509400 |
| C | 3.05794000 | -1.67773600 | 1.18055500 |
| C | 2.48336900 | -2.59680800 | 0.18121300 |
| C | 2.57593900 | -3.98418500 | 0.26596100 |
| H | 3.03975700 | -4.45321500 | 1.13026100 |
| C | 2.12259300 | -4.77054200 | -0.79207200 |
| H | 2.22699400 | -5.85260300 | -0.74875200 |
| C | 1.57438700 | -4.15564900 | -1.91399900 |
| H | 1.24893800 | -4.73543400 | -2.77432200 |
| C | 1.48868300 | -2.76649900 | -1.94013200 |
| H | 1.09622800 | -2.21773200 | -2.79580200 |
| O | 3.61020900 | -0.13508000 | -1.74477000 |
| O | 1.32214400 | 0.44085600 | -2.82830200 |
| H | 0.76288000 | 1.22606800 | -2.93704300 |
| O | 3.54568700 | 1.07801000 | -3.47918200 |
| H | 2.33876500 | 0.70526300 | -3.35074500 |
| H | 4.10028200 | 0.45637800 | -3.99081100 |

**III (Doublet)**

**E =** -2471.62148502 a.u.

| | | | |
|---|---|---|---|
| Ru | 1.46490000 | -0.20215500 | 0.07938400 |
| N | 1.18745400 | -0.67710600 | 2.11560300 |
| C | 1.06068800 | 0.43762600 | 2.90642400 |
| C | 0.92181000 | 0.31594300 | 4.28688400 |
| C | 0.92039800 | -0.94710500 | 4.87414400 |
| C | 1.05226800 | -2.06928900 | 4.06206200 |
| C | 1.18256600 | -1.89102200 | 2.68906600 |
| N | 1.89543100 | -2.13106600 | -0.67400900 |
| C | 0.97376500 | -2.99237000 | -1.14628600 |
| C | 1.30082900 | -4.24788600 | -1.63335000 |
| C | 2.63969000 | -4.63770800 | -1.63534800 |
| C | 3.59402700 | -3.76068200 | -1.13638300 |
| C | 3.20501900 | -2.50907500 | -0.65275300 |
| N | 3.55525500 | -0.37147200 | 0.37131300 |
| C | 4.34202100 | 0.56869300 | 0.93183100 |
| C | 5.71305200 | 0.41633300 | 1.07306700 |
| C | 6.30651500 | -0.75663900 | 0.61363900 |
| C | 5.50330600 | -1.73293700 | 0.03557800 |
| C | 4.12833900 | -1.52834900 | -0.07757700 |

| | | | |
|---|---|---|---|
| N | 1.88523800 | 0.99815200 | -1.61427900 |
| C | 2.21532800 | 0.59942200 | -2.85327000 |
| C | 2.52218500 | 1.49303500 | -3.87330800 |
| C | 2.49246200 | 2.85748100 | -3.59830500 |
| C | 2.15652200 | 3.28014300 | -2.31469100 |
| C | 1.85816600 | 2.33991900 | -1.33022200 |
| N | 1.34008300 | 1.62255600 | 0.87012300 |
| C | 1.14243600 | 1.72931900 | 2.20743000 |
| C | 1.10538300 | 2.99677100 | 2.79001600 |
| C | 1.28784700 | 4.11756600 | 1.98058200 |
| C | 1.51903300 | 3.97421500 | 0.61266000 |
| C | 1.54992600 | 2.69212900 | 0.06401400 |
| H | 0.83480500 | 1.20330400 | 4.90917600 |
| H | 0.82974000 | -1.04938600 | 5.95316600 |
| H | 1.06779900 | -3.07219900 | 4.48042400 |
| H | -0.05429400 | -2.63497400 | -1.09838300 |
| H | 0.52184200 | -4.91200400 | -1.99945500 |
| H | 2.93589100 | -5.61395600 | -2.01188000 |
| H | 4.63937500 | -4.05588200 | -1.11972600 |
| H | 3.84347600 | 1.47151400 | 1.27774300 |
| H | 6.29980700 | 1.20569400 | 1.53510100 |
| H | 7.37905200 | -0.91148700 | 0.70518000 |
| H | 5.95236700 | -2.65435400 | -0.32443500 |
| H | 2.24101000 | -0.47717800 | -3.01409900 |
| H | 2.79270800 | 1.11998100 | -4.85765500 |
| H | 2.74092800 | 3.58441200 | -4.36836400 |
| H | 2.14729100 | 4.34172200 | -2.07802800 |
| H | 0.96369600 | 3.11699600 | 3.86100000 |
| H | 1.27902400 | 5.11026100 | 2.42513200 |
| H | 1.69776600 | 4.85181600 | -0.00370500 |
| H | 1.29540000 | -2.73711300 | 2.01423200 |
| Ru | -2.10861000 | -0.11981500 | -0.95654500 |
| O | -0.36044800 | -0.29710400 | -0.33392500 |
| N | -2.80510300 | -2.06413900 | -0.45360200 |
| N | -2.92606900 | 0.25950500 | 0.78746700 |
| N | -1.94512200 | 1.97750300 | -0.91996400 |
| C | -2.83683400 | -3.17616800 | -1.20396300 |
| H | -2.37022700 | -3.10415300 | -2.18468600 |
| C | -3.44735800 | -4.35173300 | -0.78249000 |
| H | -3.46039200 | -5.22082100 | -1.43482700 |
| C | -4.05277000 | -4.37535600 | 0.46967700 |
| H | -4.54726200 | -5.27424400 | 0.83098400 |
| C | -4.04390200 | -3.21940300 | 1.24806400 |
| H | -4.54249900 | -3.21485600 | 2.21397100 |
| C | -3.42943900 | -2.06641400 | 0.76795900 |
| C | -3.48645900 | -0.77180200 | 1.46572200 |
| C | -4.12303200 | -0.51146500 | 2.67846000 |
| H | -4.58912300 | -1.31185900 | 3.24680700 |
| C | -4.19060400 | 0.80195600 | 3.14175400 |
| H | -4.70051300 | 1.01701700 | 4.07798200 |
| C | -3.64874000 | 1.84485300 | 2.39332400 |
| H | -3.74966100 | 2.87143100 | 2.73573900 |
| C | -3.01614200 | 1.55306200 | 1.18528900 |

| | | | |
|---|---|---|---|
| C | -2.48632000 | 2.51956000 | 0.21526500 |
| C | -2.58719400 | 3.90180400 | 0.35946000 |
| H | -3.03691800 | 4.32958500 | 1.25225900 |
| C | -2.15463500 | 4.73394000 | -0.67023900 |
| H | -2.26186000 | 5.81285200 | -0.58136600 |
| C | -1.61661900 | 4.16633300 | -1.82238900 |
| H | -1.29701100 | 4.78190100 | -2.65971800 |
| C | -1.52809100 | 2.78097900 | -1.90861100 |
| H | -1.13507900 | 2.27845000 | -2.79133600 |
| O | -3.80681200 | 0.19777600 | -1.77870600 |
| O | -1.40435200 | -0.35807000 | -3.05989200 |
| H | -0.83835100 | -1.10115300 | -3.32424500 |
| O | -4.05380000 | -0.72863400 | -2.84693800 |
| H | -2.23634200 | -0.46843600 | -3.57260200 |
| H | -4.89869200 | -0.37952800 | -3.20129800 |

**IV (Broken Symmetry Singlet)**

**E =** -2470.98677137 a.u.

| | | | |
|---|---|---|---|
| Ru | 1.46704000 | -0.18894000 | 0.13938700 |
| N | 1.49943900 | -0.54179000 | 2.22274100 |
| C | 1.51491800 | 0.61956100 | 2.95449600 |
| C | 1.56775600 | 0.57974600 | 4.34494400 |
| C | 1.61637400 | -0.64869500 | 5.00085900 |
| C | 1.60810400 | -1.81808700 | 4.24719800 |
| C | 1.54862600 | -1.72166700 | 2.86089500 |
| N | 1.76238900 | -2.16162500 | -0.57686600 |
| C | 0.76739200 | -3.00234900 | -0.91380800 |
| C | 1.00214800 | -4.28264400 | -1.39096900 |
| C | 2.31798800 | -4.71757500 | -1.53098100 |
| C | 3.34957600 | -3.85519600 | -1.18085900 |
| C | 3.05513400 | -2.57785000 | -0.70154100 |
| N | 3.58956600 | -0.40562200 | 0.15295100 |
| C | 4.46626600 | 0.53769600 | 0.55367500 |
| C | 5.83904800 | 0.34690000 | 0.53047400 |
| C | 6.33727500 | -0.87032000 | 0.07198700 |
| C | 5.44142000 | -1.84897400 | -0.34172200 |
| C | 4.06908500 | -1.60333500 | -0.29541700 |
| N | 1.70362800 | 0.89188600 | -1.66361800 |
| C | 1.83904900 | 0.40135200 | -2.90529300 |
| C | 2.07096600 | 1.21918700 | -4.00667500 |
| C | 2.16612800 | 2.59408600 | -3.81349300 |
| C | 2.01776400 | 3.10960700 | -2.52719800 |
| C | 1.78887200 | 2.24590800 | -1.45870400 |
| N | 1.53759700 | 1.68227700 | 0.83289200 |
| C | 1.53678600 | 1.86694900 | 2.17539700 |
| C | 1.62619000 | 3.16494200 | 2.67931500 |
| C | 1.73027400 | 4.22955400 | 1.78444600 |
| C | 1.76772700 | 4.00207900 | 0.40843200 |
| C | 1.67918400 | 2.69154000 | -0.06066500 |
| H | 1.58688500 | 1.50248000 | 4.91967000 |
| H | 1.67039600 | -0.68773300 | 6.08649600 |

| | | | |
|---|---|---|---|
| H | 1.65523200 | -2.79617500 | 4.71859800 |
| H | -0.23498500 | -2.60232900 | -0.78730700 |
| H | 0.16710200 | -4.92869100 | -1.64917600 |
| H | 2.54026000 | -5.71427700 | -1.90483200 |
| H | 4.38105900 | -4.18084700 | -1.28044000 |
| H | 4.04173300 | 1.47497500 | 0.90593400 |
| H | 6.50076700 | 1.14042000 | 0.86703800 |
| H | 7.40825700 | -1.05670900 | 0.03805600 |
| H | 5.81582300 | -2.80411200 | -0.69882500 |
| H | 1.74809000 | -0.67738800 | -3.00388700 |
| H | 2.18452400 | 0.77678600 | -4.99288500 |
| H | 2.36337200 | 3.25963200 | -4.65109000 |
| H | 2.10300200 | 4.18057600 | -2.35749300 |
| H | 1.63722700 | 3.35154400 | 3.75000800 |
| H | 1.81247200 | 5.24533700 | 2.16491500 |
| H | 1.88874500 | 4.83632900 | -0.27811200 |
| H | 1.54184100 | -2.60706800 | 2.22866000 |
| Ru | -2.11322800 | -0.17378400 | -0.89555900 |
| O | -0.36650200 | -0.24040000 | -0.01442900 |
| N | -2.88287300 | -2.02296600 | -0.22537300 |
| N | -3.13105900 | 0.35192900 | 0.81039200 |
| N | -2.05282900 | 1.93681400 | -0.93389900 |
| C | -2.83495900 | -3.17378700 | -0.92029300 |
| H | -2.28638400 | -3.14028000 | -1.85894600 |
| C | -3.46457400 | -4.32994400 | -0.47709800 |
| H | -3.41102000 | -5.23564400 | -1.07561500 |
| C | -4.17279300 | -4.29238000 | 0.72024600 |
| H | -4.68336800 | -5.17814400 | 1.09154000 |
| C | -4.24648500 | -3.09396500 | 1.42678800 |
| H | -4.82570900 | -3.03888800 | 2.34500300 |
| C | -3.60864900 | -1.95964400 | 0.93402200 |
| C | -3.73383200 | -0.62268800 | 1.52760500 |
| C | -4.46065600 | -0.28942100 | 2.66993100 |
| H | -4.95830500 | -1.05443700 | 3.25998100 |
| C | -4.56923600 | 1.05189200 | 3.03230100 |
| H | -5.14381300 | 1.32912600 | 3.91302800 |
| C | -3.97837400 | 2.04118800 | 2.24931000 |
| H | -4.10464100 | 3.08900600 | 2.50872300 |
| C | -3.25802200 | 1.66240400 | 1.11682900 |
| C | -2.66242200 | 2.55899000 | 0.12053700 |
| C | -2.77029000 | 3.94762700 | 0.15063400 |
| H | -3.26976800 | 4.43762900 | 0.98278100 |
| C | -2.28301700 | 4.70140000 | -0.91329000 |
| H | -2.39519400 | 5.78337600 | -0.91254100 |
| C | -1.68782500 | 4.04885700 | -1.98993800 |
| H | -1.32950400 | 4.59769100 | -2.85743200 |
| C | -1.59034700 | 2.66289200 | -1.96501200 |
| H | -1.15566700 | 2.09740700 | -2.78703200 |
| O | -3.70115200 | 0.05313700 | -1.94946200 |
| O | -1.15636100 | -0.70326100 | -2.47908100 |
| O | -3.89824600 | -1.04021100 | -2.82760500 |
| H | -1.78938300 | -0.85194900 | -3.21300600 |
| H | -4.64513100 | -0.71326300 | -3.37439000 |

**V (Broken Symmetry Singlet)**

**E =** -2470.98549775 a.u.

| | | | |
|---|---|---|---|
| Ru | -1.44902100 | 0.19465400 | 0.12558300 |
| N | -1.32287000 | 0.71138600 | 2.16951600 |
| C | -1.17760600 | -0.38120400 | 2.98657500 |
| C | -1.11134700 | -0.22789600 | 4.36935900 |
| C | -1.20598700 | 1.04342000 | 4.93021100 |
| C | -1.36225500 | 2.14234400 | 4.09081200 |
| C | -1.41493900 | 1.93378700 | 2.71710600 |
| N | -1.88250600 | 2.09493700 | -0.70409900 |
| C | -0.96177600 | 2.97215800 | -1.14621500 |
| C | -1.29616400 | 4.20428800 | -1.68579000 |
| C | -2.64314300 | 4.55301200 | -1.77620100 |
| C | -3.59846000 | 3.66128400 | -1.30603400 |
| C | -3.20151900 | 2.43585000 | -0.76515000 |
| N | -3.55102600 | 0.32820300 | 0.31981400 |
| C | -4.34015400 | -0.60936800 | 0.88170800 |
| C | -5.72004600 | -0.48985000 | 0.94610800 |
| C | -6.31894100 | 0.64524300 | 0.40495400 |
| C | -5.51266800 | 1.61947800 | -0.17238900 |
| C | -4.12852700 | 1.45008400 | -0.20520500 |
| N | -1.80250900 | -1.05145600 | -1.54467700 |
| C | -2.12369100 | -0.68255800 | -2.79619200 |
| C | -2.41974400 | -1.60104300 | -3.79618500 |
| C | -2.39080100 | -2.95889500 | -3.48774200 |
| C | -2.06427700 | -3.35045900 | -2.19181900 |
| C | -1.77619000 | -2.38660900 | -1.22741600 |
| N | -1.31794000 | -1.61038700 | 0.96356800 |
| C | -1.17606900 | -1.68596000 | 2.31032800 |
| C | -1.13059900 | -2.94018700 | 2.92160100 |
| C | -1.25312300 | -4.08238200 | 2.13216300 |
| C | -1.44519000 | -3.97212000 | 0.75495700 |
| C | -1.48679100 | -2.70297500 | 0.17860200 |
| H | -1.00522500 | -1.09782600 | 5.01285900 |
| H | -1.16990800 | 1.16972100 | 6.00989100 |
| H | -1.45149300 | 3.15007100 | 4.48786000 |
| H | 0.07196500 | 2.65059400 | -1.02623100 |
| H | -0.51703000 | 4.88435800 | -2.02124800 |
| H | -2.94523000 | 5.50980700 | -2.19563100 |
| H | -4.65091000 | 3.92624400 | -1.35401500 |
| H | -3.83624300 | -1.48172600 | 1.29189900 |
| H | -6.30956500 | -1.27467300 | 1.41239800 |
| H | -7.39859000 | 0.77307000 | 0.43423400 |
| H | -5.96650900 | 2.51191000 | -0.59408100 |
| H | -2.14205200 | 0.38889600 | -2.98462500 |
| H | -2.68217800 | -1.25254600 | -4.79168800 |
| H | -2.63301500 | -3.70446400 | -4.24198600 |
| H | -2.05767100 | -4.40587600 | -1.92897400 |
| H | -1.02913700 | -3.03330000 | 3.99978900 |
| H | -1.23385600 | -5.06495800 | 2.59816000 |

| | | | |
|---|---|---|---|
| H | -1.58818500 | -4.86572400 | 0.15231700 |
| H | -1.53750000 | 2.76087800 | 2.02089800 |
| Ru | 2.07146300 | 0.20455500 | -0.90074000 |
| O | 0.40629900 | 0.39451400 | -0.10977700 |
| N | 2.83457300 | 2.15527800 | -0.50282800 |
| N | 3.09655500 | -0.14182000 | 0.73998700 |
| N | 1.94591500 | -1.89997000 | -0.83704600 |
| C | 2.78315400 | 3.25809000 | -1.26821000 |
| H | 2.21255700 | 3.17474200 | -2.19178100 |
| C | 3.43401000 | 4.43986500 | -0.93554100 |
| H | 3.37615600 | 5.29714800 | -1.60101400 |
| C | 4.17041100 | 4.48560500 | 0.24435200 |
| H | 4.69885500 | 5.39060600 | 0.53537700 |
| C | 4.24701800 | 3.34265400 | 1.03727800 |
| H | 4.84505400 | 3.35376900 | 1.94492000 |
| C | 3.58747600 | 2.18149300 | 0.64407600 |
| C | 3.72370500 | 0.89808200 | 1.34569600 |
| C | 4.48840800 | 0.65191700 | 2.48504100 |
| H | 5.00908600 | 1.46006100 | 2.99169900 |
| C | 4.60735800 | -0.65538600 | 2.95342700 |
| H | 5.21124100 | -0.85928500 | 3.83470600 |
| C | 3.99296300 | -1.70812700 | 2.27667100 |
| H | 4.13104800 | -2.72976600 | 2.62045900 |
| C | 3.23443400 | -1.43226500 | 1.14079500 |
| C | 2.62229500 | -2.41675900 | 0.23800900 |
| C | 2.79317200 | -3.79253800 | 0.36980600 |
| H | 3.34457100 | -4.19841600 | 1.21431700 |
| C | 2.30758800 | -4.64645300 | -0.61857700 |
| H | 2.47156700 | -5.71912600 | -0.54157000 |
| C | 1.64612400 | -4.10557300 | -1.71665600 |
| H | 1.28381200 | -4.73451400 | -2.52616700 |
| C | 1.48357400 | -2.72587600 | -1.78666600 |
| H | 0.97715800 | -2.25104700 | -2.62540200 |
| O | 3.59788400 | -0.13970400 | -2.05932100 |
| O | 1.10047000 | 0.38109800 | -2.91179700 |
| H | 0.90462100 | 1.24936200 | -3.30228800 |
| O | 3.55832800 | -0.73647700 | -3.18108700 |
| H | 1.75385700 | -0.02683800 | -3.52780900 |

**V (Triplet)**

**E =** -2470.97884000 a.u.

| | | | |
|---|---|---|---|
| Ru | -1.47523300 | 0.21145000 | 0.13022500 |
| N | -1.31995100 | 0.60117700 | 2.19588200 |
| C | -1.23860500 | -0.54407000 | 2.94814900 |
| C | -1.17077700 | -0.47592100 | 4.33750600 |
| C | -1.19722000 | 0.76375200 | 4.97205500 |
| C | -1.28795000 | 1.91676300 | 4.19820600 |
| C | -1.34625200 | 1.79253500 | 2.81437200 |
| N | -1.82982100 | 2.17496300 | -0.58856200 |
| C | -0.86829500 | 3.03608500 | -0.97465700 |
| C | -1.14741900 | 4.30762400 | -1.45020600 |

| | | | |
|---|---|---|---|
| C | -2.47855300 | 4.71503300 | -1.53333100 |
| C | -3.47400800 | 3.83994100 | -1.11859800 |
| C | -3.13299300 | 2.57220800 | -0.64035500 |
| N | -3.57886100 | 0.42621700 | 0.32770000 |
| C | -4.41121200 | -0.50495100 | 0.83517000 |
| C | -5.78541000 | -0.33027600 | 0.89882300 |
| C | -6.33183400 | 0.85627700 | 0.41606000 |
| C | -5.48070000 | 1.82445000 | -0.10470800 |
| C | -4.10503000 | 1.59744300 | -0.13996700 |
| N | -1.86448100 | -0.91768800 | -1.62272000 |
| C | -2.14141100 | -0.46473000 | -2.85648000 |
| C | -2.43748200 | -1.31153900 | -3.91831200 |
| C | -2.45820100 | -2.68518200 | -3.69167700 |
| C | -2.18070800 | -3.16364900 | -2.41318700 |
| C | -1.88766500 | -2.26906600 | -1.38602600 |
| N | -1.43496500 | -1.64574100 | 0.85716200 |
| C | -1.30027900 | -1.80558500 | 2.19704200 |
| C | -1.31020300 | -3.09484300 | 2.73191400 |
| C | -1.47652500 | -4.18051800 | 1.87383100 |
| C | -1.65199400 | -3.98139000 | 0.50393800 |
| C | -1.63736200 | -2.67989400 | 0.00402200 |
| H | -1.11627800 | -1.38680000 | 4.92868500 |
| H | -1.15902000 | 0.82449200 | 6.05734700 |
| H | -1.32233600 | 2.90306600 | 4.65334600 |
| H | 0.15117400 | 2.66803700 | -0.86186400 |
| H | -0.33760200 | 4.97206300 | -1.74128800 |
| H | -2.73732400 | 5.70419600 | -1.90389900 |
| H | -4.51435400 | 4.14990900 | -1.16082600 |
| H | -3.94831200 | -1.41866000 | 1.20153100 |
| H | -6.41084600 | -1.11277900 | 1.32006600 |
| H | -7.40526600 | 1.02853200 | 0.44712900 |
| H | -5.89319000 | 2.75693100 | -0.47966300 |
| H | -2.13039300 | 0.61688000 | -2.97900600 |
| H | -2.66138100 | -0.89603400 | -4.89733800 |
| H | -2.70122900 | -3.37643900 | -4.49576000 |
| H | -2.21260300 | -4.23260800 | -2.21481100 |
| H | -1.21557000 | -3.25724200 | 3.80248000 |
| H | -1.50074200 | -5.18938900 | 2.27972800 |
| H | -1.82292700 | -4.83168200 | -0.15163000 |
| H | -1.42002300 | 2.66455700 | 2.16796700 |
| Ru | 2.09057000 | 0.16993500 | -0.87603500 |
| O | 0.36455100 | 0.33525300 | -0.13417900 |
| N | 2.93962400 | 2.05584700 | -0.38822900 |
| N | 3.07595600 | -0.30927000 | 0.75720900 |
| N | 1.90870600 | -1.92605100 | -0.92917100 |
| C | 2.95537600 | 3.18905500 | -1.11033300 |
| H | 2.39204300 | 3.17051400 | -2.04215900 |
| C | 3.66273700 | 4.31984200 | -0.72198800 |
| H | 3.65909600 | 5.20582400 | -1.35131700 |
| C | 4.38474900 | 4.27708100 | 0.46717400 |
| H | 4.95652100 | 5.14012400 | 0.80090200 |
| C | 4.39260500 | 3.10029200 | 1.21359700 |
| H | 4.98032100 | 3.04374400 | 2.12625000 |

| | | | |
|---|---|---|---|
| C | 3.68019200 | 1.99157800 | 0.76623600 |
| C | 3.74902800 | 0.67141900 | 1.41085400 |
| C | 4.50084200 | 0.33960300 | 2.53655600 |
| H | 5.05581800 | 1.09945200 | 3.08013300 |
| C | 4.56646900 | -0.99310400 | 2.94152800 |
| H | 5.16126900 | -1.26362200 | 3.81084700 |
| C | 3.91564300 | -1.98524400 | 2.21131600 |
| H | 4.01803000 | -3.02825900 | 2.49901600 |
| C | 3.17083600 | -1.62200200 | 1.08991600 |
| C | 2.53313600 | -2.53080300 | 0.12981100 |
| C | 2.63172300 | -3.91952100 | 0.19138100 |
| H | 3.14332200 | -4.39650400 | 1.02378900 |
| C | 2.12452900 | -4.69289300 | -0.84950800 |
| H | 2.23299500 | -5.77509900 | -0.82791600 |
| C | 1.51512200 | -4.06111500 | -1.93084600 |
| H | 1.14135600 | -4.62807200 | -2.78004500 |
| C | 1.42442800 | -2.67374300 | -1.93208800 |
| H | 0.97336200 | -2.12395100 | -2.75726200 |
| O | 3.74571500 | -0.20261600 | -1.90481600 |
| O | 1.24495700 | 0.54107400 | -2.90000100 |
| H | 0.75990100 | 1.35668000 | -3.10589700 |
| O | 3.87601500 | 0.34988000 | -3.05494800 |
| H | 2.07008000 | 0.58063600 | -3.44934200 |

**V-TS (Singlet)**

**E =** -2547.39239050 a.u.

| | | | |
|---|---|---|---|
| Ru | 1.48405800 | -0.20436400 | 0.02249900 |
| N | 1.07692400 | -0.94552600 | 1.96003300 |
| C | 0.85233400 | 0.05412900 | 2.87171800 |
| C | 0.60219700 | -0.24658800 | 4.20890000 |
| C | 0.59156100 | -1.57430300 | 4.62935600 |
| C | 0.82279200 | -2.57962400 | 3.69541600 |
| C | 1.05918500 | -2.22259000 | 2.37193100 |
| N | 2.05414600 | -2.00485600 | -0.93242500 |
| C | 1.21036500 | -2.85244900 | -1.55357000 |
| C | 1.63631000 | -4.01590900 | -2.17442900 |
| C | 2.99565400 | -4.32658200 | -2.15562500 |
| C | 3.86920000 | -3.46920600 | -1.49999500 |
| C | 3.38128500 | -2.31268300 | -0.88631100 |
| N | 3.54931000 | -0.31591000 | 0.42723000 |
| C | 4.24857300 | 0.57603600 | 1.15729000 |
| C | 5.61677900 | 0.47596500 | 1.35925800 |
| C | 6.30294700 | -0.58891000 | 0.78142200 |
| C | 5.59017700 | -1.51572900 | 0.03035100 |
| C | 4.21300100 | -1.36971800 | -0.13671300 |
| N | 1.93272700 | 1.21215600 | -1.47876400 |
| C | 2.33351800 | 0.98804100 | -2.74096000 |
| C | 2.66021100 | 2.01386300 | -3.62086000 |
| C | 2.57679800 | 3.33002000 | -3.17524300 |
| C | 2.16986200 | 3.57309400 | -1.86600100 |
| C | 1.85435700 | 2.50581300 | -1.02736700 |

| | | | |
|---|---|---|---|
| N | 1.22553700 | 1.49715800 | 1.02412100 |
| C | 0.95001400 | 1.42643500 | 2.35097500 |
| C | 0.85696300 | 2.60525600 | 3.09178600 |
| C | 1.07494800 | 3.82465400 | 2.45153700 |
| C | 1.38737400 | 3.86472200 | 1.09298200 |
| C | 1.46505500 | 2.66724400 | 0.38126200 |
| H | 0.43796300 | 0.55181600 | 4.92887500 |
| H | 0.41964300 | -1.81667400 | 5.67566800 |
| H | 0.83825700 | -3.62744700 | 3.98369100 |
| H | 0.15970500 | -2.56616700 | -1.51169000 |
| H | 0.91705700 | -4.67057200 | -2.65992500 |
| H | 3.36855900 | -5.22847700 | -2.63522900 |
| H | 4.92865900 | -3.70641300 | -1.46235300 |
| H | 3.68113800 | 1.39539500 | 1.59243900 |
| H | 6.12959100 | 1.22279700 | 1.95934600 |
| H | 7.37647500 | -0.69911000 | 0.91527200 |
| H | 6.11068500 | -2.35463000 | -0.42305100 |
| H | 2.40256100 | -0.05722800 | -3.03792200 |
| H | 2.98803500 | 1.77815100 | -4.62996600 |
| H | 2.83800300 | 4.15662600 | -3.83213600 |
| H | 2.11733300 | 4.59423200 | -1.49502700 |
| H | 0.65421500 | 2.58039300 | 4.15961900 |
| H | 1.03087600 | 4.74949600 | 3.02260600 |
| H | 1.59373300 | 4.81686500 | 0.61014900 |
| H | 1.25294000 | -2.97169800 | 1.60658000 |
| Ru | -2.07968300 | -0.08902500 | -0.96845700 |
| O | -0.34512500 | -0.42075000 | -0.47938200 |
| N | -2.66111000 | -2.10625700 | -0.68228300 |
| N | -2.69192100 | 0.01302100 | 0.88143600 |
| N | -1.87266000 | 1.97555800 | -0.62786600 |
| C | -2.73093100 | -3.11331000 | -1.56709300 |
| H | -2.39558700 | -2.88426500 | -2.57747600 |
| C | -3.22207800 | -4.37218400 | -1.23754700 |
| H | -3.27608600 | -5.14903800 | -1.99576700 |
| C | -3.65250600 | -4.59880200 | 0.06613100 |
| H | -4.04949200 | -5.56806900 | 0.35930900 |
| C | -3.59057400 | -3.55724000 | 0.98983300 |
| H | -3.95044100 | -3.71304400 | 2.00375100 |
| C | -3.10478000 | -2.31275000 | 0.59871800 |
| C | -3.10491900 | -1.13272000 | 1.47592200 |
| C | -3.54114800 | -1.08155500 | 2.79921300 |
| H | -3.89070400 | -1.97756000 | 3.30527600 |
| C | -3.55908100 | 0.14459700 | 3.46273300 |
| H | -3.91697400 | 0.19660900 | 4.48849000 |
| C | -3.15493800 | 1.30844000 | 2.81066800 |
| H | -3.20223500 | 2.26698600 | 3.32169700 |
| C | -2.71977500 | 1.22471400 | 1.48850900 |
| C | -2.30872600 | 2.33716700 | 0.62155400 |
| C | -2.39339900 | 3.67913400 | 0.98303300 |
| H | -2.76945200 | 3.95992700 | 1.96430100 |
| C | -2.03743000 | 4.66392800 | 0.06325100 |
| H | -2.13763500 | 5.71580700 | 0.32245800 |
| C | -1.56906900 | 4.28261400 | -1.19072800 |

| | | | |
|---|---|---|---|
| H | -1.28905000 | 5.02004300 | -1.93910200 |
| C | -1.49446400 | 2.92723200 | -1.49556500 |
| H | -1.14774500 | 2.57244700 | -2.46438900 |
| O | -3.61253500 | 0.91057700 | -2.63152600 |
| O | -1.18315800 | -0.15430200 | -3.06611600 |
| H | -0.52196500 | -0.83693800 | -3.25664400 |
| O | -3.20672000 | 1.65561900 | -3.53187900 |
| H | -1.72588100 | -0.07040100 | -3.86932900 |
| O | -4.81041800 | -0.36377100 | -0.75445800 |
| H | -5.36205300 | 0.43366600 | -0.69026500 |
| H | -5.25551700 | -0.88228200 | -1.44500500 |

**V-TS (Triplet)**

**E =** -2547.39220924 a.u.

| | | | |
|---|---|---|---|
| Ru | 1.44411300 | -0.14729000 | -0.04294900 |
| N | 0.80778000 | -1.12301600 | 1.69689500 |
| C | 0.41676900 | -0.26265800 | 2.69304500 |
| C | 0.01700000 | -0.75231700 | 3.93546700 |
| C | 0.01843600 | -2.12409000 | 4.17174300 |
| C | 0.40947800 | -2.98655000 | 3.15006000 |
| C | 0.79925700 | -2.44701700 | 1.93008200 |
| N | 2.29867300 | -1.76651100 | -1.15072900 |
| C | 1.64820000 | -2.50704800 | -2.06784000 |
| C | 2.25900700 | -3.51965200 | -2.79155000 |
| C | 3.60756200 | -3.78622300 | -2.56282600 |
| C | 4.28453900 | -3.03632500 | -1.61029300 |
| C | 3.61468200 | -2.03099900 | -0.90863200 |
| N | 3.44013700 | -0.27572000 | 0.71269700 |
| C | 3.95059500 | 0.50331500 | 1.68700100 |
| C | 5.26491800 | 0.40870200 | 2.11736700 |
| C | 6.09683700 | -0.53370500 | 1.51726700 |
| C | 5.57864600 | -1.34511700 | 0.51531100 |
| C | 4.24620700 | -1.20584400 | 0.12379000 |
| N | 2.11023100 | 1.46702200 | -1.24330600 |
| C | 2.70944000 | 1.40795500 | -2.44455700 |
| C | 3.09357500 | 2.54612900 | -3.14397100 |
| C | 2.85359200 | 3.79408600 | -2.57480800 |
| C | 2.23434200 | 3.86228500 | -1.32923200 |
| C | 1.86943000 | 2.68931600 | -0.67219300 |
| N | 0.95233700 | 1.40285800 | 1.10121300 |
| C | 0.52337000 | 1.16277300 | 2.36797700 |
| C | 0.31640600 | 2.23248800 | 3.24197200 |
| C | 0.57801300 | 3.52682700 | 2.80104700 |
| C | 1.06287200 | 3.74393900 | 1.51012600 |
| C | 1.25855500 | 2.65443200 | 0.66392100 |
| H | -0.27326000 | -0.06377600 | 4.72587500 |
| H | -0.26718800 | -2.51261700 | 5.14692600 |
| H | 0.43811500 | -4.06308800 | 3.29786000 |
| H | 0.59690100 | -2.25522500 | -2.19586900 |
| H | 1.68951500 | -4.08966900 | -3.52077000 |
| H | 4.12338800 | -4.56897600 | -3.11399500 |

| | | | |
|---|---|---|---|
| H | 5.33409400 | -3.23715400 | -1.41567100 |
| H | 3.27202300 | 1.22864900 | 2.13104700 |
| H | 5.62545600 | 1.06274100 | 2.90672400 |
| H | 7.13438400 | -0.63795900 | 1.82609400 |
| H | 6.21597500 | -2.08697400 | 0.04276400 |
| H | 2.88595500 | 0.40974300 | -2.84074200 |
| H | 3.58200300 | 2.44895200 | -4.11000900 |
| H | 3.15299100 | 4.70468000 | -3.08896700 |
| H | 2.04750100 | 4.82954900 | -0.86829400 |
| H | -0.00550300 | 2.05992300 | 4.26630500 |
| H | 0.44482800 | 4.36815800 | 3.47749300 |
| H | 1.31921000 | 4.75059700 | 1.18847700 |
| H | 1.12792600 | -3.07642900 | 1.10514600 |
| Ru | -1.97302300 | -0.12108700 | -1.07815400 |
| O | -0.15031800 | -0.41127000 | -1.00641800 |
| N | -2.47605200 | -2.16226900 | -0.79586600 |
| N | -2.49910100 | -0.06938800 | 0.79535500 |
| N | -1.83932400 | 1.92857600 | -0.70560800 |
| C | -2.49047400 | -3.16854900 | -1.68405800 |
| H | -2.22573000 | -2.90503800 | -2.70613800 |
| C | -2.84128800 | -4.46903100 | -1.33877700 |
| H | -2.85798500 | -5.24667800 | -2.09779500 |
| C | -3.18032000 | -4.73757300 | -0.01596900 |
| H | -3.46588100 | -5.74153600 | 0.29021900 |
| C | -3.16901300 | -3.69741900 | 0.91197200 |
| H | -3.44940700 | -3.89082400 | 1.94461400 |
| C | -2.82863600 | -2.41127500 | 0.50431900 |
| C | -2.88874900 | -1.23412700 | 1.38306600 |
| C | -3.38812500 | -1.20513000 | 2.68091900 |
| H | -3.72493200 | -2.11869100 | 3.16447400 |
| C | -3.51245000 | 0.01859600 | 3.34183200 |
| H | -3.93019100 | 0.05116100 | 4.34553100 |
| C | -3.15167400 | 1.19951100 | 2.70100700 |
| H | -3.29554100 | 2.15754900 | 3.19513100 |
| C | -2.64493700 | 1.13977900 | 1.40153000 |
| C | -2.28592700 | 2.27066700 | 0.54726700 |
| C | -2.42385600 | 3.60897800 | 0.91172700 |
| H | -2.81062600 | 3.87073100 | 1.89420700 |
| C | -2.10408700 | 4.60870700 | -0.00281800 |
| H | -2.24304200 | 5.65543100 | 0.25906800 |
| C | -1.61954100 | 4.24864000 | -1.25869500 |
| H | -1.36300500 | 4.99919000 | -2.00238000 |
| C | -1.49955600 | 2.89944100 | -1.57136800 |
| H | -1.14742500 | 2.56088100 | -2.54462800 |
| O | -3.85496000 | 0.92568200 | -2.40907900 |
| O | -1.48777700 | -0.08332800 | -3.30961600 |
| H | -0.66455800 | -0.49567600 | -3.61379600 |
| O | -3.69542900 | 1.86875200 | -3.17594100 |
| H | -2.13609800 | -0.19539400 | -4.02517000 |
| O | -4.88976500 | -0.68484600 | -0.59309400 |
| H | -5.53541600 | 0.03316500 | -0.49542800 |
| H | -5.35781600 | -1.32308300 | -1.15450200 |

**VI (Doublet)**

**E =** -1407.06032769 a.u.

| | | | |
|---|---|---|---|
| Ru | -0.01546600 | 0.04067600 | -0.65651400 |
| N | -0.71443100 | -1.95579800 | -0.49007900 |
| C | -2.07095800 | -2.03247400 | -0.30343600 |
| C | -2.70458800 | -3.27160800 | -0.27294200 |
| C | -1.95400100 | -4.43437400 | -0.43821600 |
| C | -0.57885900 | -4.33510600 | -0.62468000 |
| C | 0.00879400 | -3.07313600 | -0.64595700 |
| N | 2.11621300 | -0.18582200 | -0.85416300 |
| C | 2.74610200 | -0.11646200 | -2.04421800 |
| C | 4.12560800 | -0.23128900 | -2.15404600 |
| C | 4.88048400 | -0.41966000 | -0.99912800 |
| C | 4.22956900 | -0.49241000 | 0.22823500 |
| C | 2.84080300 | -0.37351700 | 0.28439400 |
| N | 0.71269200 | -0.28886500 | 1.36493500 |
| C | -0.09190500 | -0.36649100 | 2.44558300 |
| C | 0.40067300 | -0.57318800 | 3.72378300 |
| C | 1.77689500 | -0.71922500 | 3.89499300 |
| C | 2.60795500 | -0.65209900 | 2.78335400 |
| C | 2.05842200 | -0.43919600 | 1.51857600 |
| N | -0.02430600 | 2.09080300 | -0.25657500 |
| C | 1.03803600 | 2.91892900 | -0.30320200 |
| C | 0.89889400 | 4.29558000 | -0.18763100 |
| C | -0.37386500 | 4.83065400 | -0.00651900 |
| C | -1.47424100 | 3.97417300 | 0.05656600 |
| C | -1.28725700 | 2.60383800 | -0.06764300 |
| N | -1.93157100 | 0.33083000 | -0.16819500 |
| C | -2.75564600 | -0.75137400 | -0.13006500 |
| C | -4.12051600 | -0.54721400 | 0.07007800 |
| C | -4.59398800 | 0.75428900 | 0.22651600 |
| C | -3.71848800 | 1.84382400 | 0.19661000 |
| C | -2.36311000 | 1.60926200 | -0.00696900 |
| H | -3.77968200 | -3.33299500 | -0.12244000 |
| H | -2.44258600 | -5.40605900 | -0.42452500 |
| H | 0.04012800 | -5.21651200 | -0.77088700 |
| H | 2.11144700 | 0.02636100 | -2.91588400 |
| H | 4.58919500 | -0.17747000 | -3.13574300 |
| H | 5.96297000 | -0.51211500 | -1.05102200 |
| H | 4.80495100 | -0.64073300 | 1.13781200 |
| H | -1.15838000 | -0.24519500 | 2.26841400 |
| H | -0.28450600 | -0.61504500 | 4.56625600 |
| H | 2.19786100 | -0.88834700 | 4.88360700 |
| H | 3.68115500 | -0.77194500 | 2.90200000 |
| H | 2.00853100 | 2.45265000 | -0.45334000 |
| H | 1.77929000 | 4.93043700 | -0.24313200 |
| H | -0.51401400 | 5.90532500 | 0.08869400 |
| H | -2.47289900 | 4.37996100 | 0.19834200 |
| H | -4.81047600 | -1.38645700 | 0.10101700 |
| H | -5.65768600 | 0.92488900 | 0.37841700 |
| H | -4.09976000 | 2.85339800 | 0.32585000 |

| | | | |
|---|---|---|---|
| H | 1.07526900 | -2.94245000 | -0.81458800 |
| O | -0.07617200 | -0.13447800 | -2.33349100 |

**VII (Doublet)**

**E =** -1483.47915463 a.u.

| | | | |
|---|---|---|---|
| Ru | -0.50977800 | -0.13249600 | -0.27679300 |
| N | -2.02542200 | -1.54461700 | 0.29013500 |
| C | -3.25239200 | -0.94676200 | 0.42741400 |
| C | -4.38009400 | -1.70636400 | 0.72658100 |
| C | -4.25917700 | -3.08313500 | 0.90153700 |
| C | -3.00328900 | -3.67070400 | 0.79298100 |
| C | -1.91045900 | -2.86608300 | 0.48518600 |
| N | 1.29786100 | -1.60266400 | -0.59287300 |
| C | 0.88173800 | -2.62215200 | -1.37909000 |
| C | 1.66116700 | -3.71070000 | -1.74542100 |
| C | 2.96428200 | -3.78189800 | -1.27615800 |
| C | 3.42752000 | -2.73303300 | -0.49227300 |
| C | 2.59891500 | -1.65106400 | -0.17090900 |
| N | 2.63036700 | 0.05046300 | 1.63414200 |
| C | 3.21976700 | 0.98131700 | 2.41231600 |
| C | 4.52907400 | 1.35776300 | 2.18109900 |
| C | 5.20998300 | 0.76355600 | 1.11833000 |
| C | 4.57232400 | -0.19306400 | 0.33119200 |
| C | 3.25475300 | -0.56787200 | 0.60216100 |
| N | 0.40956800 | 1.74066700 | -0.62239200 |
| C | 1.65214700 | 1.98813200 | -1.06654500 |
| C | 2.09146200 | 3.27119100 | -1.36642100 |
| C | 1.20948000 | 4.33538500 | -1.20326000 |
| C | -0.09111700 | 4.08070200 | -0.77214900 |
| C | -0.48462700 | 2.77518500 | -0.49816200 |
| N | -2.06300000 | 1.06622900 | 0.00855500 |
| C | -3.26965800 | 0.51121000 | 0.28447000 |
| C | -4.37246300 | 1.35156700 | 0.43441000 |
| C | -4.19671900 | 2.72713800 | 0.30521900 |
| C | -2.93827300 | 3.26277300 | 0.02455700 |
| C | -1.85774800 | 2.40064900 | -0.13418300 |
| H | -5.35158000 | -1.22921300 | 0.82719100 |
| H | -5.13608200 | -3.68443600 | 1.13009500 |
| H | -2.86127400 | -4.73820900 | 0.93855600 |
| H | -0.13360400 | -2.54819300 | -1.75893100 |
| H | 1.23928100 | -4.47832700 | -2.38872800 |
| H | 3.61084600 | -4.62276600 | -1.51632400 |
| H | 4.44058000 | -2.75842300 | -0.09917100 |
| H | 2.60909300 | 1.38526600 | 3.21448300 |
| H | 5.00259300 | 2.09619400 | 2.82160500 |
| H | 6.23945000 | 1.04166400 | 0.90191000 |
| H | 5.09467900 | -0.64601000 | -0.50726400 |
| H | 2.29026400 | 1.11821700 | -1.20340400 |
| H | 3.10126200 | 3.42394700 | -1.73757900 |
| H | 1.51946700 | 5.35324400 | -1.42903800 |
| H | -0.79918400 | 4.89922300 | -0.67220000 |

| | | | |
|---|---|---|---|
| H | -5.35654300 | 0.94562300 | 0.65204900 |
| H | -5.04952900 | 3.39200200 | 0.42252500 |
| H | -2.81515600 | 4.33758100 | -0.07665200 |
| H | -0.90949500 | -3.28189500 | 0.39208300 |
| O | -0.80704800 | -0.47438800 | -1.91354500 |
| O | -0.01632000 | -0.16311600 | 1.61393400 |
| H | 1.63332800 | -0.17877600 | 1.82614300 |
| H | -0.63642000 | -0.50981600 | 2.27818300 |

**VIII (Doublet)**

**E =** -1064.32847767 a.u.

| | | | |
|---|---|---|---|
| Ru | -0.00065700 | -0.86398200 | -0.08260700 |
| N | -2.08853900 | -0.53298800 | -0.02102700 |
| C | -2.38586800 | 0.80389200 | -0.01343200 |
| C | -3.70729500 | 1.23281200 | 0.01306900 |
| C | -4.73467400 | 0.28996100 | 0.03540400 |
| C | -4.41664600 | -1.06245900 | 0.03475500 |
| C | -3.07570900 | -1.43468000 | 0.00743800 |
| N | 2.06882600 | -0.48641400 | 0.02462900 |
| C | 3.06417400 | -1.38090300 | 0.02646900 |
| C | 4.40018200 | -0.98806800 | 0.02924900 |
| C | 4.70097400 | 0.36927600 | 0.02564000 |
| C | 3.66323400 | 1.30015400 | 0.01716200 |
| C | 2.34586100 | 0.85442200 | 0.01355900 |
| N | -0.02110300 | 1.08982000 | -0.02704000 |
| C | -1.23063100 | 1.71123300 | -0.01829300 |
| C | -1.25664800 | 3.10192900 | -0.00152900 |
| C | -0.04933600 | 3.80127000 | 0.00954800 |
| C | 1.17209400 | 3.12897500 | 0.01425000 |
| C | 1.17511200 | 1.73737800 | -0.00178600 |
| H | -3.94131200 | 2.29420100 | 0.01801700 |
| H | -5.77189200 | 0.61525400 | 0.05595500 |
| H | -5.18723100 | -1.82786200 | 0.05491300 |
| H | 2.76430300 | -2.42664900 | 0.01791600 |
| H | 5.18181900 | -1.74263300 | 0.02826500 |
| H | 5.73446900 | 0.70686200 | 0.02498100 |
| H | 3.88398900 | 2.36447600 | 0.00814600 |
| H | -2.20003600 | 3.64049900 | 0.00473100 |
| H | -0.06161000 | 4.88862600 | 0.02049200 |
| H | 2.10432200 | 3.68650400 | 0.03244400 |
| H | -2.77346700 | -2.47864800 | 0.00545700 |
| O | 0.12908800 | -1.19666800 | -1.75105300 |
| O | -0.05805300 | -1.23878700 | 1.78926500 |
| H | 0.76683500 | -1.23447000 | 2.30787700 |
| O | 0.18644400 | -3.13023100 | -0.02113200 |
| H | -0.03418000 | -3.64817700 | -0.81455700 |
| H | -0.20017400 | -3.58140600 | 0.74848700 |

**IX (Closed-shell singlet)**

**E =** -1063.70598270 a.u.

| | | | |
|---|---|---|---|
| Ru | -0.01902100 | -0.88033300 | -0.00001500 |
| O | 0.01332000 | -1.18937700 | 1.67258600 |
| N | -2.09420200 | -0.48773500 | -0.00002200 |
| N | 0.03183000 | 1.08112400 | -0.00005700 |
| N | 2.10649800 | -0.55277900 | 0.00000800 |
| C | -3.09681700 | -1.37143500 | -0.00007300 |
| H | -2.80900300 | -2.42001800 | -0.00004300 |
| C | -4.42663200 | -0.95849600 | -0.00009800 |
| H | -5.21911600 | -1.70157200 | -0.00014600 |
| C | -4.70637500 | 0.40314000 | -0.00005200 |
| H | -5.73494700 | 0.75565000 | -0.00005900 |
| C | -3.65605400 | 1.32078300 | 0.00000800 |
| H | -3.86369400 | 2.38768200 | 0.00004700 |
| C | -2.34521100 | 0.85855100 | 0.00000900 |
| C | -1.16382300 | 1.72998800 | 0.00001100 |
| C | -1.15237900 | 3.12146000 | 0.00008400 |
| H | -2.08192600 | 3.68368100 | 0.00016700 |
| C | 0.07251200 | 3.78808500 | 0.00005800 |
| H | 0.08933500 | 4.87543700 | 0.00010700 |
| C | 1.27587500 | 3.08407500 | -0.00001100 |
| H | 2.22182500 | 3.61811800 | -0.00001400 |
| C | 1.24538100 | 1.69211600 | -0.00004300 |
| C | 2.39852500 | 0.78394000 | -0.00003600 |
| C | 3.72142200 | 1.21325300 | -0.00006400 |
| H | 3.95556500 | 2.27464300 | -0.00011300 |
| C | 4.74856700 | 0.27097400 | -0.00003700 |
| H | 5.78586000 | 0.59673800 | -0.00006000 |
| C | 4.43188700 | -1.08216900 | -0.00000100 |
| H | 5.20340800 | -1.84699200 | -0.00000300 |
| C | 3.09058600 | -1.45588600 | 0.00001100 |
| H | 2.78846000 | -2.50022100 | -0.00002000 |
| O | -0.31526700 | -3.16025700 | 0.00025000 |
| H | -0.06209400 | -3.67418800 | 0.78633800 |
| H | -0.06173000 | -3.67410000 | -0.78577300 |
| O | 0.01336200 | -1.18970800 | -1.67256700 |