J|A|C|S
COMMUNICATIONS

Isolated Seven-Coordinate Ru(IV) Dimer Complex with $[HOHOH]^-$ Bridging Ligand as an Intermediate for Catalytic Water Oxidation

Lele Duan, Andreas Fischer, Yunhua Xu, and Licheng Sun*

Department of Chemistry, School of Chemical Science and Engineering, Royal Institute of Technology (KTH), 100 44 Stockholm, Sweden

Received April 29, 2009; E-mail: lichengs@kth.se

In pursuit of clean and sustainable energy sources, more and more efforts are being spent on solar energy conversion into a fuel by light-driven water splitting to H_2 and O_2,[1−3] which would potentially meet the urgent energy demands of our society. However, the catalytic water oxidation to molecular oxygen is still the bottleneck of the entire process.[2,4]

Among the few water oxidation catalysts,[5−12] ruthenium-based catalysts have shown catalytic activity with high turnover numbers.[5−11] Several ruthenium aqua complexes generated by Meyer, Llobet, and their co-workers[13−15] were reported to be active in the oxidation of water, and the catalytic mechanisms have been studied both electrochemically and theoretically, mainly relying on the six-coordinate ruthenium models.[5b,16−21] On the other hand, a number of nonaqua ruthenium complexes synthesized by Thummel and co-workers[7,22−24] exhibited also high activities toward water oxidation. Recently, Meyer et al. and Thummel et al. proposed a tentative mechanism for water oxidation in which seven-coordinate ruthenium intermediates are involved.[5b,7] Unfortunately, none of the proposed intermediates has been isolated or spectroscopically characterized so far, which hinders the understanding of the reaction process, in particular, with regard to the question of how water molecules interact with ruthenium catalysts. Therefore, the most challenging task in this research field is to identify the important intermediates or active species of the water oxidation catalysts.

The scarcity of reaction intermediates is mainly because of the isolation problem of high valent Ru complexes due to their unstability. To capture the high valent ruthenium intermediates, negatively charged ligands would be a good choice for the complexation because they can stabilize the higher oxidation states of metal ions.[25] Recently, we have reported a dinuclear ruthenium complex with a biscarboxylato ligand, showing that the introduction of a negatively charged ligand dramatically lowers the oxidation potential of Ru(II) to Ru(III).[26] Herein, we would like to report the synthesis of a mononuclear ruthenium complex Ru(II)L(pic)$_2$ (**1**) (2,2′-bipyridine-6,6′-dicarboxylic acid, H_2L; 4-picoline, pic) with a biscarboxylato ligand and the successful isolation of a very uncommon seven-coordinate Ru(IV) dimeric complex μ-(HOHOH)-$[Ru(IV)L(pic)_2]_2(PF_6)_3 \cdot 2H_2O$ (**2**), which is an intermediate in the water oxidation reaction catalyzed by complex **1** (see structures in Figure 1). Our experimental observation can provide several new insights for understanding the catalytic water oxidation mechanism, which is urgently needed to systematically improve the performance of ruthenium-based catalysts as well as to uncover the secrets of OEC in Photosystem II.

Overnight reflux of an acetonitrile solution of H_2L, $Ru(DMSO)_4Cl_2$, and triethylamine, followed by addition of 4-picoline, afforded mononuclear Ru(II) complex **1** in 30% isolated yield. The ^{1}H NMR spectrum of **1** in $CDCl_3$ shows signals at 8.14−8.10 and 7.66 ppm from the L^{2-} ligand and signals at 7.59, 6.81, and 2.20 ppm assigned to the 4-picoline ligands. These ^{1}H NMR results indicate a symmetric structure of complex **1**, which is consistent with the proposed structure in Figure 1.

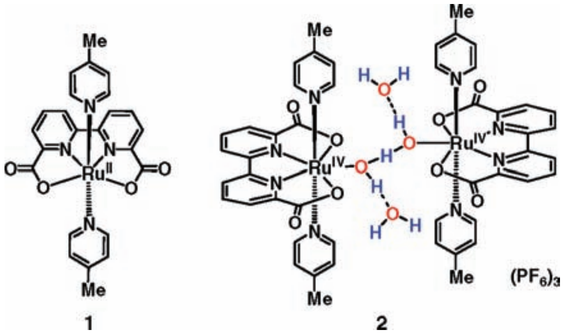

Figure 1. Molecular structures of complexes **1** and **2**.

The crystal structure determination reveals that complex **1** features a six-coordinate ruthenium complex with distorted octahedral coordination (Figure 2). It is noticeable that the angle of O2−Ru1−O3 is expanded to 122.99°, which is much bigger than the ideal 90° of an octahedron configuration.

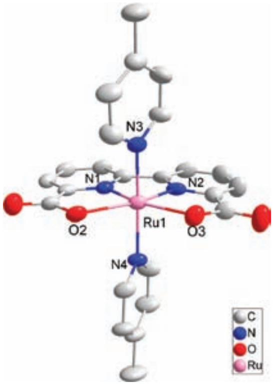

Figure 2. X-ray crystal structure of complex **1** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

In dichloromethane, complex **1** shows one reversible redox wave with $E_{1/2} = -0.06$ V versus Fc/Fc$^+$, which is assigned to the Ru^{II}/Ru^{III} process (Figure S1). Due to the strong electron donating ability of carboxylates, the oxidation potential of complex **1** is 0.91 V lower than that of the related complex $[Ru(II)(L')(pic)_2]^{2+}$ (L′ = 2,9-di(pyrid-2′-yl)-1,10-phenanthroline), with $E_{1/2} = 0.85$ V versus Fc/Fc$^+$ (1.24 V vs SCE) reported by Thummel's group.[23] The relatively low oxidation potential of complex **1** encouraged us to attempt to isolate high valent intermediates formed during its catalytic water oxidation.

10.1021/ja9034686 CCC: $40.75

The catalytic water oxidation of complex **1** was therefore demonstrated chemically. When complex **1** was added to an aqueous triflic acid solution (pH 1.0) containing a Ce(IV) oxidant ($Ce(NH_4)_2(NO_3)_6$), molecular oxygen was generated as monitored by a Clark-type oxygen electrode (Figure S2). At a low concentration (2.0×10^{-6} M) of catalyst **1**, a strong response was observed from the oxygen electrode, indicating a high catalytic activity for water oxidation. From the amount of O_2 evolved in this very dilute solution, the turnover number of **1**, $[O_2]/[\mathbf{1}]$, was calculated to be at least 120. Kinetic measurements showed that the decay of Ce(IV) is zero order for Ce(IV) under our condition and second order for complex **1** with the rate constant being 7.83×10^5 $M^{-1}s^{-1}$ (Figures S3−S6), indicating that a binuclear catalytic process is involved in water oxidation by **1**.

To investigate the mechanism of water oxidation by complex **1**, we attempted to isolate related intermediates after several catalytic turnovers while the system was still active. To a solution of complex **1** (11.9 mg, 0.022 mmol) in a mixture of acetonitrile (0.3 mL) and aqueous triflic acid (pH 1.0, 4 mL), 20 equiv of Ce(IV) (240 mg, 0.44 mmol) were added in several portions. The color of the solution changed from dark red to light yellow, accompanied by evolution of a large amount of O_2 bubbles. When the gas evolution ceased, excess aqueous NH_4PF_6 was added to the solution, which resulted in the formation of an orange precipitate. The ^{1}H NMR of this orange solid in acetonitrile-d_3 shows broad peaks (Figure S7), indicating the paramagnetic character of this orange solid. To rule out the possibility that the formation of the paramagnetic species is due to the decomposition of the orange solid, ^{1}H NMR spectrum was recorded at low temperature (−40 °C). However, no other species was observed (Figure 3, upper). According to the high resolution mass spectrometry (HR-MS), this orange solid was found to be $[Ru(III)L(pic)_2]^+$, the Ru(III) species corresponding to the structure of **1** (found m/z^+, 530.0553; calcd, 530.0528; Figure 4).

When the amount of Ce(IV) oxidant was increased to ca. 60 equivalents, and after addition of excess aqueous NH_4PF_6 followed by keeping overnight, the reaction solution gave a dark red precipitate instead of the orange one. According to the ^{1}H NMR spectrum, two obviously different patterns of proton resonances were observed at −40 °C (Figure 3, lower). One set (broad peaks) is consistent with the paramagnetic $[Ru(III)L(pic)_2]^+$ species; the other set is diamagnetic and shows all the proton peaks of ligands L^{2-} (8.84, 8.56, and 8.13 ppm) and pic (7.46, 7.10, and 2.28 ppm) in a ratio of 1:2, indicating that the ligands in this new species are the same as in **1**. Compared with the ^{1}H NMR spectrum of complex **1** (Figure S11), the peaks of the L^{2-} ligand are significantly shifted to downfield, reflecting a higher oxidation state of the ruthenium center. When the temperature was increased to room temperature, the previously observed diamagnetic ^{1}H NMR signals disappeared and only the signals from the paramagnetic $[Ru(III)L(pic)_2]^+$ species were left (Figure S8). This is most likely due to the conversion of this higher oxidation state ruthenium species to the $[Ru(III)L(pic)_2]^+$. Accordingly, purification of this higher oxidation state Ru species was hindered by its relatively low stability under neutral conditions and at room temperature. To further analyze the structure of this dark red solid, HR-MS measurements were performed, resulting in the observation of two major products. One is the $[Ru(III)L(pic)_2]^+$ species that was identical to the Ru(III) species discussed above and the other has an m/z^+ value of 547.0510 (Figure 4). This mass value fits exactly to the structure of complex $[Ru(IV)L(pic)_2(OH)]^+$ (calcd m/z^+: 547.0555), indicating that the oxidation state of ruthenium is +IV. Now the question is how the OH^- coordinates to the Ru(IV) ion. The large bite angle of O2−Ru1−O3 (122.99°), observed for complex **1**, suggested that another ligand might coordinate on this equatorial site without big structural change of the existing ligands. Therefore, we propose that this higher oxidation state ruthenium species $[Ru(IV)L(pic)_2(OH)]^+$ has an OH^- as the seventh ligand (18 electrons in total).

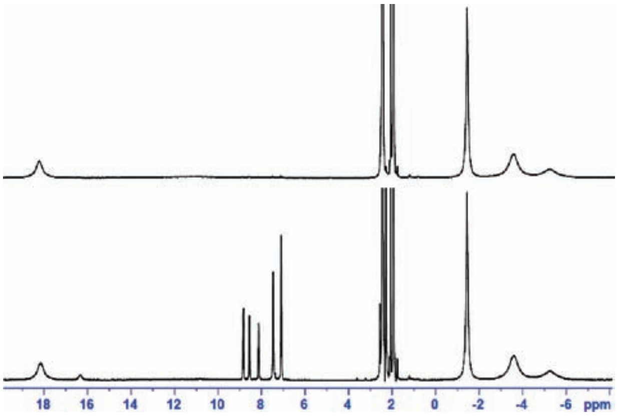

Figure 3. ^{1}H NMR (400 MHz) spectra of the orange precipitate (upper) and the dark red precipitate (lower) in CD_3CN at −40 °C.

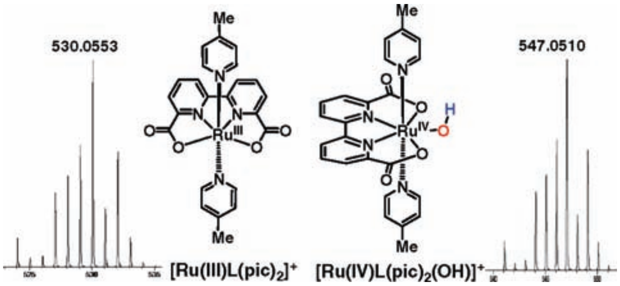

Figure 4. Structures of the $[Ru(III)L(pic)_2]^+$ and the $[Ru(IV)L(pic)_2(OH)]^+$ species with their corresponding HR-MS spectra.

To our delight, this proposal was verified by X-ray crystallography. A dark red single crystal suitable for X-ray analysis was grown at room temperature during the precipitation process. Complex **2** is composed of two $Ru(IV)L(pic)_2$ units that are linked by an $[HOHOH]^-$ group (Figure 5). Three $[PF_6]^-$ counterions balance the charge and two solvent water molecules hydrogen-bonded to the $[HOHOH]^-$ group are present in the structure. Additionally, acetonitrile is present in the lattice. The two Ru(IV) units in the dimer are symmetric with the central H atom of the bridging ligand in the inversion center. Each Ru(IV) ion is seven-coordinated and centered in a highly distorted pentagonal bipyramidal configuration with the O2−N1−N2−O4 dihedral angle of 23.13°. To accommodate the 7-fold coordination, the Ru atom is slightly pushed away from the bipyridyl unit of the L^{2-} ligand. As a result, the Ru−N bonds are lengthened to 2.085 Å for Ru1−N1 and 2.091 Å for R1−N2, while the Ru−O bonds are shortened to 2.033 Å for Ru1−O2 and 2.043 Å for Ru1−O4. Angles in the pentagonal base are all close to the ideal value of 72°. The bridging ligand $[HOHOH]^-$ coordinates ruthenium centers via the O atoms as the seventh ligands and the proton sitting exactly in the middle between two OH^- ligands, presenting the answer of how water molecules bond to the catalysts during water oxidation. Noticeably, the hydrogen bond of H−O···H···O−H in $[HOHOH]^-$ bridge is about 0.2 Å shorter than that of O3−H···O6, reflecting a strong hydrogen bonding network. Similar short and symmetric O···H···O bonds have been observed in other dinuclear metal complexes, with one example of dinuclear ruthenium complexes.[27] Each of the two solvent water molecules hydrogen bonds to one of the O atoms of the bridging ligand, potentially acting as a base to remove the proton released from the catalytic center. In the meantime, hydrogen bonding involving the 6- and 6′-carboxylato groups and water molecules stabilizes the dimer as shown in Figure S9.

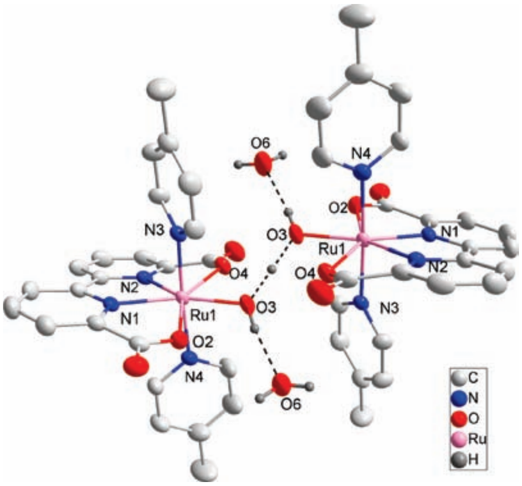

Figure 5. Crystal structure of complex **2** with thermal ellipsoids at 50% probability. Hydrogen atoms except the H−O type are omitted for clarity.

The isolated dark red precipitate was still active toward water oxidation by using Ce(IV) as oxidant in an aqueous triflic acid solution (pH 1.0; Figure S10), indicating that complex **2** is indeed an intermediate involved in the catalytic water oxidation processes.

Several important features from this work are worth to mention. First, ligand exchange is obviously not necessary in the octahedral coordinate complex **1** for attack of water to Ru ion to occur. In other words, no ligand needs to be released to provide the "open site". Water can attack directly to the six-coordinate Ru(IV) center, forming a seven-coordinate Ru(IV)−OH dimeric species with simultaneous release of one proton. Second, an important observation from our system is that the formation of the seven-coordinate Ru(IV)−OH species does not require any major structural change of its six-coordinate precursor. By slightly opening up the O−Ru−O bite angle, Ru(IV) ion can accept a water molecule as the seventh ligand. This provides a low reorganization energy pathway for efficient water oxidation. The third feature of our observation is the hydrogen bonding network of the bridging [HOHOH]$^-$ ligand with two H_2O molecules between the two high valent Ru centers of complex **2** in solid state. This network might provide a proton transfer channel during the catalytic oxidation of water.

In summary, a very uncommon seven-coordinate Ru(IV) dimeric complex μ-(HOHOH)[Ru(IV)L(pic)$_2$]$_2$(PF$_6$)$_3$·2H_2O (**2**) was successfully isolated as an intermediate and characterized by X-ray diffraction. Our observation will provide the experimental evidence to exhibit the mechanistic aspects of catalytic water oxidation from another viewpoint. With this observation the catalytic water oxidation mechanism by ruthenium catalysts, either mononuclear or dinuclear, would gradually become better understood. It might also have some relevance for the mechanism of catalytic oxygen reduction in fuel cells. The most important conclusion from our work is that a seven-coordinate Ru(IV) dimer complex with bridging ligand [HOHOH]$^-$ together with two water molecules in the form of a hydrogen bonding network is involved as an intermediate in catalytic water oxidation. Our new findings will be helpful in the design of more efficient and robust ruthenium catalysts for water oxidation.

Acknowledgment. We acknowledge the Swedish Research Council, *K* & *A* Wallenberg Foundation, the Swedish Energy Agency, and China Scholarship Council (CSC) for financial support of this work. We would like to thank Dr. Yan Gao at Stockholm University for the help of HR-MS measurements, Prof. Björn Åkermark (SU) for discussions, and professors Christina Moberg and Torbjörn Norin, KTH, for proof reading and good comments on the manuscript.

Supporting Information Available: Experimental details and X-ray crystallographic files for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Eisenberg, R.; Gray, H. *Inorg. Chem.* **2008**, *47*, 1697.
(2) Balzani, V.; Credi, A.; Venturi, M. *ChemSusChem* **2008**, *1*, 26.
(3) Sun, L.; Hammarström, L.; Åkermark, B.; Styring, S. *Chem. Soc. Rev.* **2001**, *30*, 36.
(4) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.
(5) (a) Concepcion, J. J.; Jurss, J. W.; Templeton, J. L.; Meyer, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 17632. (b) Concepcion, J. J.; Jurss, J. W.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 16462.
(6) Muckerman, J. T.; Polyansky, D. E.; Wada, T.; Tanaka, K.; Fujita, E. *Inorg. Chem.* **2008**, *47*, 1787.
(7) Tseng, H.-W.; Zong, R.; Muckerman, J. T.; Thummel, R. *Inorg. Chem.* **2008**, *47*, 11763.
(8) Betley, T. A.; Wu, Q.; Van Voorhis, T.; Nocera, D. G. *Inorg. Chem.* **2008**, *47*, 1849.
(9) Sala, X.; Romero, I.; Rodríguez, M.; Escriche, L.; Llobet, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2842.
(10) Geletii, Y. V.; Botar, B.; Köerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L. *Angew. Chem., Int. Ed.* **2008**, *120*, 3960.
(11) Sartorel, A.; Carraro, M.; Scorrano, G.; Zorzi, R. D.; Geremia, S.; McDaniel, N. D.; Bernhard, S.; Bonchio, M. *J. Am. Chem. Soc.* **2008**, *130*, 5006.
(12) (a) Hull, J. F.; Balcells, D.; Blakemore, J. D.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 8730. (b) McDaniel, N. D.; Coughlin, F. J.; Tinker, L. L.; Bernhard, S. *J. Am. Chem. Soc.* **2008**, *130*, 210. (c) Kanan, M. W.; Nocera, D. G. *Science* **2008**, *321*, 1072. (d) Mullins, C. S.; Pecoraro, V. L. *Coord. Chem. Rev.* **2008**, *252*, 416, and references therein.
(13) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029.
(14) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855.
(15) Sens, C.; Romero, I.; Rodríguez, M.; Llobet, A.; Parella, T.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2004**, *126*, 7798.
(16) Chronister, C. W.; Binstead, R. A.; Ni, J.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 3814.
(17) Hurst, J. K. *Coord. Chem. Rev.* **2005**, *249*, 313.
(18) Yamada, H.; Siems, W. F.; Koike, T.; Hurst, J. K. *J. Am. Chem. Soc.* **2004**, *126*, 9786.
(19) Yang, X.; Baik, M.-H. *J. Am. Chem. Soc.* **2006**, *128*, 7476.
(20) Yang, X.; Baik, M.-H. *J. Am. Chem. Soc.* **2008**, *130*, 16231.
(21) Romain, S.; Bozoglian, F.; Sala, X.; Llobet, A. *J. Am. Chem. Soc.* **2009**, *131*, 2768.
(22) Deng, Z.; Tseng, H.-W.; Zong, R.; Wang, D.; Thummel, R. *Inorg. Chem.* **2008**, *47*, 1835.
(23) Zhang, G.; Zong, R.; Tseng, H.-W.; Thummel, R. P. *Inorg. Chem.* **2008**, *47*, 990.
(24) Zong, R.; Thummel, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 12802.
(25) Lomoth, R.; Huang, P.; Zheng, J.; Sun, L.; Hammarström, L.; Åkermark, B.; Styring, S. *Eur. J. Inorg. Chem.* **2002**, 2965.
(26) Xu, Y.; Åkermark, T.; Gyollai, V.; Zou, D.; Eriksson, L.; Duan, L.; Zhang, R.; Åkermark, B.; Sun, L. *Inorg. Chem.* **2009**, *48*, 2717.
(27) Jüstel, T.; Bendix, J.; Metzler-Nolte, N.; Weyhermüller, T.; Nuber, B.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 35.

JA9034686