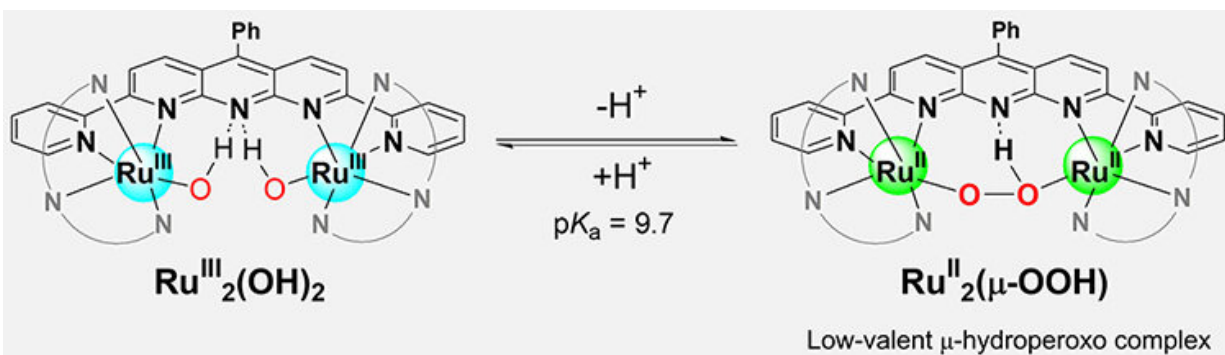


The first observation of oxygen-oxygen bond formation by a low-valent RuIII complex

February 11 2022



Mechanism of proton dissociation-induced O-O bond formation via intramolecular coupling low-valent RuIII/OH centers. Credit: Niigata University

Currently, the world's energy demand mainly depends on fossil fuels being a limited resource. The consumption of fossil fuels leads to emission of carbon dioxide (CO_2) that is one of the major greenhouse gases contributing to global warming and climate changes. We need to urgently establish sustainable energy societies based on renewable energy sources. On the other hand, nature has perfected an ultimate solar energy conversion system, photosynthesis, where high-energy molecules such as carbohydrates are efficiently produced from CO_2 and water using solar energy. Inspired by the natural photosynthesis, scientists have been developing artificial systems capable of converting solar energy into valuable fuels. In artificial photosynthetic systems, water oxidation is an

essential process to acquire electrons for reduction reactions such as hydrogen production and CO₂ fixation, but is considered to be a bottleneck due to its complexity and sluggish kinetics.

"Water oxidation is a critical process in artificial photosynthesis, and efficient water oxidation catalysts (WOCs) are needed to construct effective artificial photosynthetic systems. The catalytic water oxidation consists of a set of complicated multiple steps. Particularly, oxygen-oxygen (O-O) [bond formation](#) is commonly assumed to be the highly energy demanding and difficult step in the catalytic cycle. So, the understanding of O-O bond formation is very important for creating efficient WOCs," said Professor Masayuki Yagi who conducts research on energy storage materials and technology at the Department of Materials Science and Technology, Faculty of Engineering/Graduate School of Science and Technology, Niigata University.

A metal complex is a molecule that contains one or more metal ions centers, surrounded by a series of ligands coordinated to the metal core. Metal complexes are promising materials for WOCs due to the advantages of the fine-tuning of their catalytic activities by rational [ligand](#) design. It is commonly accepted that the O-O bond formation step cannot proceed without generation of highly-oxidized (high valent) metal complexes. In the case of water oxidation catalyzed by ruthenium (Ru) complexes, the high-valent Ru^{IV} or ^V has been believed to be required for this step so far. Therefore, if the O-O bond formation could be promoted by metal complexes in a low valence state, water oxidation would be induced by low overpotentials.

Prof. Yagi's research team at the Niigata University are developing novel [metal complexes](#) that serve as WOCs and investigating the mechanism for [water oxidation](#). They have been successful in observing the O-O bond formation induced by a low-valent Ru^{III} complex, which has been published in the *Proceedings of the National Academy of Sciences* on 21

December.

In this study, Prof. Yagi's team have demonstrated that the O-O bond formation via intramolecular coupling of vicinal OH ligands on Ru^{III}-OH units of a dinuclear complex has been induced by dissociation of one proton of the two OH ligands in the core. "We have synthesized a dinuclear Ru^{III} complex (Ru^{III}₂(OH)₂) with organic ligands, which act as bridging scaffold to place the two OH ligands in close proximity. When Ru^{III}₂(OH)₂ was dissolved in alkaline aqueous media, the intramolecular O-O bond formation was induced by deprotonation of one of the OH ligands of Ru^{III}₂(OH)₂ centers via coupling of the OH and deprotonated O⁻ ligands, conjugated with two-electron transfer from two Ru^{III} centers to their ligands to generate Ru^{II}₂(μ-OOH). This is the first observation of the O-O bond formation at the low-valent Ru^{III} centers. Our research study provides a crucial clue to develop efficient WOCs operating under low overpotentials, since the high-valent state of the catalyst are not necessarily attained for O-O bond formation in the present mechanism," explained Prof. Yagi.

The research team has characterized the O-O bond of Ru^{II}₂(μ-OOH) by using advanced spectroscopic techniques. Computational calculations of Ru^{II}₂(μ-OOH) suggested that the hydrogen bond interaction between H⁺ of the μ-OOH ligand and central nitrogen atom of the organic bridging ligand is a key factor for the intramolecular O-O bond formation by the low-valent Ru^{III} complex. Prof. Yagi said, "based on our new finding of the O-O [bond](#) formation mechanism, we will develop innovative WOCs in order to realize artificial photosynthesis in near future."

More information: Yuki Tanahashi et al, Mechanism of H⁺ dissociation-induced O-O bond formation via intramolecular coupling of vicinal hydroxo ligands on low-valent Ru(III) centers, *Proceedings of the National Academy of Sciences* (2021). [DOI: 10.1073/pnas.2113910118](https://doi.org/10.1073/pnas.2113910118)

Provided by Niigata University

Citation: The first observation of oxygen-oxygen bond formation by a low-valent RuIII complex (2022, February 11) retrieved 26 June 2024 from <https://phys.org/news/2022-02-oxygen-oxygen-bond-formation-low-valent-ruiii.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.