Ru-Based Water Oxidation Catalysts
Development and Mechanistic Studies

Andrey Shatskiy

Academic dissertation for the Degree of Doctor of Philosophy in Organic Chemistry at Stockholm University to be publicly defended on Wednesday 5 December 2018 at 10.00 in Magnélisalen, Kemiska övningslaboratoriet, Svante Arrhenius väg 16 B.

Abstract
Oxidation of water constitutes one of the most challenging processes in artificial photosynthesis, which aims at storing solar energy in the form of chemical bonds of high-energy fuels. To facilitate this process, efficient and durable water oxidation catalysts have to be developed and integrated into the complete photosynthetic cells. Importantly, the intricate complexity of such devices requires the catalyst not only to be highly efficient and robust, but also operate through a well-defined mechanism.

This thesis describes the development and mechanistic studies of new water oxidation catalysts based on ruthenium. The first part of the thesis describes the synthesis of a dinuclear ruthenium-based catalyst active for both chemical and light-driven water oxidation. This catalyst displayed a pronounced influence of the acetonitrile co-solvent on the redox properties, which was studied in detail by electrochemical methods. In the second part, a new benzimidazole-based mononuclear catalyst was evaluated. The activity of the catalyst was studied for chemical and light-driven water oxidation, and insight into the operating mechanism was provided with the help of density functional theory calculations. In the third part of the thesis, a new mononuclear ruthenium-based catalyst was prepared and evaluated for electrochemically-driven water oxidation. This catalyst displayed activity similar to that of the current state-of-the-art water oxidation catalyst, while eliminating its main drawback, that is incomplete activation. The redox properties of the new catalyst were studied in detail by electrochemical and spectroscopic techniques, providing insight into the origins of its improved performance. Finally, in the fourth part of the thesis, a heterogeneous nanoparticulate catalyst immobilized on a solid support is described. The catalyst displayed high activity and stability during chemical and light-driven water oxidation, which was attributed to the small average particle size and efficient anchoring of the catalyst to the heterogeneous support via an oxidatively-stable linker.

Keywords: ruthenium, catalysis, water oxidation, artificial photosynthesis.

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This thesis describes the development and mechanistic studies of new water oxidation catalysts based on ruthenium. The first part of the thesis describes the synthesis of a dinuclear ruthenium-based catalyst active for both chemical and light-driven water oxidation. This catalyst displayed a pronounced influence of the acetonitrile co-solvent on the redox properties, which was studied in detail by electrochemical methods. In the second part, a new benzimidazole-based mononuclear catalyst was evaluated. The activity of the catalyst was studied for chemical and light-driven water oxidation, and insight into the operating mechanism was provided with the help of density functional theory calculations. In the third part of the thesis, a new mononuclear ruthenium-based catalyst was prepared and evaluated for electrochemically-driven water oxidation. This catalyst displayed activity similar to that of the current state-of-the-art water oxidation catalyst, while eliminating its main drawback, that is incomplete activation. The redox properties of the new catalyst were studied in detail by electrochemical and spectroscopic techniques, providing insight into the origins of its improved performance. Finally, in the fourth part of the thesis, a heterogeneous nanoparticulate catalyst immobilized on a solid support is described. The catalyst displayed high activity and stability during chemical and light-driven water oxidation, which was attributed to the small average particle size and efficient anchoring of the catalyst to the heterogeneous support via an oxidatively-stable linker.
En av få möjliga lösningar på mänsklighetens energiproblem är omvandling av solenergi till bränsle. Detta kan ske genom att med hjälp av solel på klassiskt sätt elektrolysera vatten så att vätgas och syrgas bildas. Syrgasen får återgå till atmosfären och vätgasen kan direkt användas som bränsle eller reageras med exempelvis koldioxid till flytande bränslen som metanol eller bensin. Alternativt kan man försöka imitera växternas fotosyntes och bygga en solcell som direkt splitterar vatten till vätgas och syrgas. I bågge alternativen lagras solenergi i form av kemiska bindningar i bränslen med hög energi.

I vårt arbete har vi främst studerat artificiell fotosyntes. För att möjliggöra denna process måste man utveckla effektiva och stabila katalysatorer för oxidation av vatten och integrera dessa i en komplett cell för vattensplittring. Eftersom en cell av denna typ kommer att vara mycket komplex måste katalysatorerna inte bara vara effektiva och robusta utan också operera med en väl definierad mekanism.

Denna avhandling beskriver utveckling av nya ruteniumkatalysatorer för oxidation av vatten, samt studier av mekanismerna för dessa reaktioner. Första delen av avhandlingen beskriver syntesen av en dinukleär katalysator, som kan oxidera vatten med hjälp av både kemiska oxidationsmedel och ljus. I den andra delen av avhandlingen studerades en ny, effektiv mononukleär ruteniumkatalysator som är baserad på imidazol som ligand. Både kemisk och ljuddriver vattenoxidation studerades och den kompliserade mekanismen kunde klarläggas med hjälp av kvantkemiska beräkningar. I den tredje delen av avhandlingen beskrivs syntesen och egenskaperna hos en exceptionellt aktiv mononuklär ruteniumkatalysator. Den har en aktivitet som är mellan tio och hundra gånger högre än katalysatorn i den naturliga fotosyntesen, vilket innebär att varje katalysatormolekyl genererar mellan 4 000 och 40 000 molekyler syrgas på en sekund, en svindlande hastighet. Slutligen, i den fjärde delen av avhandlingen beskrivs syntesen av en heterogen katalysator baserad på nanopartiklar av ruteniumoxid på en yta av mesoporös silika.
List of Publications

This thesis is based on the following publications, which are referred to in the text by their Roman numerals. The author contribution to each paper is stated in Appendix A. The full text reprints of the publications were made with permission from the publishers (Appendix B).

I. Catalyst-Solvent Interactions in a Dinuclear Ru-Based Water Oxidation Catalyst
   Shatskiy, A.; Lomoth, R.; Abdel-Magied, A. F.; Rabten, W.; Laine, T. M.; Chen, H.; Sun, J.; Andersson, P. G.; Kärkäs, M. D.;* Johnston, E. V.;* Åkermark, B.*
   *Dalton Trans. 2016, 45, 19024–19033

II. Chemical and Photochemical Water Oxidation Mediated by an Efficient Single-Site Ruthenium Catalyst
   Abdel-Magied, A. F.; Shatskiy, A.; Liao, R.-Z.; Laine, T. M.; Arafa, W. A. A.; Siegbahn, P. E. M.; Kärkäs, M. D.;* Åkermark, B.;* Johnston, E. V.*
   *ChemSusChem 2016, 9, 3448–3456

III. Highly Active Ruthenium-Based Water Oxidation Catalyst with an Easy Access to the Catalytically Active Species
   *Submitted manuscript

IV. Water Oxidation Mediated by Ruthenium Oxide Nanoparticles Supported on Siliceous Mesocellular Foam

† These authors contributed equally
Publications not included in this thesis:

**Cyclic Allylic Carbonates as a Renewable Platform for Protecting Chemistry in Water**
Olsén, P.;* Morvan, J.; Sawadjoon, S.; Shatskiy, A.; Johnston, E. V.;* Åkemark, B.*
*Green Chem.* **2018**, *20*, 3186–3190

**Mesoporous Ruthenium Oxide: A Heterogeneous Catalyst for Water Oxidation**

**Substituent Effects in Molecular Ruthenium Water Oxidation Catalysts Based on Amide Ligands**
Abdel-Magied, A. F.;† Arafà, W. A. A.;‡ Laine, T. M.; Shatskiy, A.; Kärkäs, M. D.;* Åkemark, B.;* Johnston, E. V.*

**Water Oxidation Catalyzed by Molecular Di- and Nonanuclear Fe Complexes: Importance of a Proper Ligand Framework**
*Dalton Trans.* **2016**, *45*, 13289–13293

**Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of Propargylic Ketones**
Shatskiy, A.; Kivijärvi, T.; Lundberg, H.; Tinnis, F.; Adolfsson, H.*
Abbreviations

Abbreviations and acronyms recommended by the American Chemical Society are used in the thesis. These and nonstandard or specific for the field abbreviations and acronyms are listed herein.

APT atom-proton transfer
ATR-FTIR attenuated total reflection–Fourier transform infrared spectroscopy
bda\(^2\)\(^-\) 2,2′-bipyridine-6,6′-dicarboxylate
bdc 2,2′-bipyridine-4,4′-dicarboxylic acid
BDD boron doped diamond
BET Brunauer-Emmett-Teller
bpm 2,2′-bipyrimidine
bpy 2,2′-bipyridine
bpz 2,2′-bipyrazine
CAN ceric ammonium nitrate
CB conduction band
CPE controlled potential electrolysis
CV cyclic voltammetry (voltammogram)
deeb diethyl 2,2′-bipyridine-4,4′-dicarboxylate
DFT density functional theory
DIPEA \(N,N\)-diisopropylethylamine
DMAP 4-dimethylaminopyridine
DPV differential pulse voltammetry (voltammogram)
EPR electron paramagnetic resonance
ESI-HRMS electrospray ionization–high-resolution mass spectrometry
Fc ferrocene
Fd ferredoxin
FOWA foot-of-the-wave analysis
\(\text{H}_2\text{bpa}^{2-}\) 2,2′-bipyridine-6,6′-bis(hydrogenphosphonate)
HAADF-STEM high-angle annular dark-field scanning transmission electron microscopy
Hbpc\(^2\)\(^-\) 2,2′-bipyridine-6-hydrogenphosphonate-6′-carboxylate
Hcbc$^2^-$ 2-(2-carboxyphenyl)-1$H$-benzo[d]imidazole-4-carboxylate
HEC hydrogen evolution catalyst
I2M interaction of two metal-oxo units
$i$-APT intramolecular atom-proton transfer
ICP-OES inductively coupled plasma–optical emission spectroscopy
IS ionic strength
isq isoquinoline
ITO indium tin oxide
LED light-emitting diode
mcbp$^2^-$ 2,6-bis(1-methyl-4-(carboxylate)benzimidazol-2-yl)pyridine
MCF mesocellular siliceous foam
Mebimpy 2,6-bis(1-methylbenzimidazol-2-yl)pyridine
MLCT metal-to-ligand charge transfer
MSE mercury–mercurous sulfate electrode
NADP$^+$ nicotinamide adenine dinucleotide phosphate
NADPH reduced nicotinamide adenine dinucleotide phosphate
NHE normal hydrogen electrode
npm 4-$t$-butyl-2,6-di(1′,8′-naphthyrid-2′-yl)pyridine
OEC oxygen evolving complex
OTTLE cell optically-transparent thin layer electrochemical cell
P680 primary electron donor in PSII
P700 primary electron donor in PSI
PCET proton-coupled electron transfer
pda$^{2^-}$ 1,10-phenanthroline-2,9-dicarboxylate
pdc$^2^-$ 2,6-pyridinedicarboxylate
PEC photoelectrochemical cell
PEM proton exchange membrane or polymer electrolyte membrane
Pheo pheophytin
pic 4-picoline
PPU 1-(pyridin-3-yl)-3-(3-(triethoxysilyl)propyl)urea
PSI photosystem I
PSII photosystem II
PV photovoltaic cell
RRDE rotating ring-disk electrode
RuBisCo ribulose-1,5-bisphosphate carboxylase/oxygenase
SC-XRD single crystal X-ray diffraction analysis
SET  solution electron transfer
SWV  square wave voltammetry (voltammogram)
tda$^{2-}$  2,2′:6′,2″-terpyridine-6,6″-dicarboxylate
TFE  2,2,2-trifluoroethanol
TfOH  triflic acid
TOF  turnover frequency
TON  turnover number
tpc$^{-}$  2,2′:6′,2″-terpyridine-6-carboxylate
tpy  2,2′:6′,2″-terpyridine
TyrZ  tyrosine residue 161 (Tyr161) of the D1 subunit in PSII
VB  valance band
WNA  water nucleophilic attack
WOC  water oxidation catalyst
XPS  X-ray photoelectron spectroscopy
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1. Introduction

The use of fossil fuels has played a key role in shaping our society’s lifestyle, allowing substantial economic and population growth over centuries. However, during the last century it has become clear that the use of fossil fuels creates significant ecological problems due to buildup of the atmospheric CO₂ concentration. Following the 19th century industrial revolution, the CO₂ level has increased approximately 1.4 times up to the current value of 409 ppm. The increased concentration of CO₂, together with the other greenhouse gases, has also resulted in a rise of the global average temperature by ca. 1°. Concurrently, this lead to various global ecological and humanitarian problems, such as retreat of glaciers, rise of the sea level, floods, multiplication of heat waves and droughts, and acidification of the ocean. Multiple models predict that further increase in the atmospheric CO₂ concentration and the following rise of global average temperature will intensify these problems. Therefore, it is of paramount importance to develop new technologies for the utilization of carbon-free or carbon-neutral renewable energy sources in the near future.

One of the prominent sources of renewable energy available to humanity is the energy of the Sun. The harvestable solar energy reaching Earth’s surface was estimated to be ca. 16 000 TW, greatly exceeding the current global energy consumption of 18 TW. Recently, photovoltaics power has become commercially competitive. However, significant drawbacks of the photovoltaics-generated electrical power are unpredictable power output and a mismatch between the maximum power output (midday) and the grid load during the day (evening), as well as uneven power output throughout the year. At the same time, cost-efficient technologies for storing electrical energy on large scale are yet to be developed. A possible solution to these problems would be to use the solar energy for production of fuels, which can be easily stored, transported with no losses, and utilized using the existing infrastructure. Fortunately, Nature provides us with the perfect model of how this process can be accomplished.

1.1. Natural Photosynthesis

The photosynthetic machinery in plants, algae, and cyanobacteria is able to harvest solar energy and store it in the form of chemical bonds. During this
process CO$_2$ is reduced to high energy carbohydrates, while water is oxidized to molecular oxygen (Eq. 1.1).\textsuperscript{11}

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2$$ \hspace{1cm} (1.1)

The key steps in natural photosynthesis include light harvesting, charge separation, electron transfer, oxidation of water, as well as utilization of the generated reducing equivalents and proton gradient for reduction of NADP$^+$ to NADPH, which in turn is used for reduction of CO$_2$. A simplified outline of these steps is presented in Figure 1.1. The oxidation half-reaction is mediated by a cofactor-protein complex photosystem II (PSII), embedded in the thylakoid membrane. In PSII, visible light is adsorbed by the P680 chromophore, and a charge-separated state is generated when an electron is transferred from the excited P680* to a pheophytin electron acceptor (Pheo). The generated pheophytin anion-radical then passes the electron to photosystem I (PSI) via a chain of electron-transfer mediators, including cytochrome $b_{6}f$ complex, that is responsible for creating a proton gradient across the thylakoid membrane. In PSI, the electron is passed to the oxidized form of the P700 chromophore, which upon excitation transfers the electron to ferre-

![Figure 1.1: General Z-scheme for the natural and artificial photosynthesis (water splitting). For artificial photosynthesis formation of the charge-separated state is initiated by an electron excitation from the valence band (VB) to the conduction band (CB) of a semiconductor, or by excitation of a molecular photosensitizer (PS→PS*) followed by an electron transfer to the CB of a semiconductor.](image-url)
doxin (Fd) that binds to NADP⁺ reductase and mediates reduction of NADP⁺ to NADPH. The latter is then used by the RuBisCo enzyme for CO₂ fixation reaction. The oxidized chromophore (P680⁺⁺), formed upon the charge separation in PSII, is a strong oxidant with the formal redox potential \( E^{\circ} \approx 1.21 \) V (all potentials in this thesis are specified vs. NHE unless otherwise noted) and is thermodynamically able to oxidize water at physiological pH \( E^{\circ}(O_2/H_2O) = 0.85 \) V at pH 6.5).

The water oxidation reaction in natural photosynthesis is catalyzed by the oxygen evolving complex (OEC) — a Mn₄CaO₅ cluster, stabilized by one imidazole (from histidine) and six carboxylate ligands (from aspartates and glutamate) of the CP43 and D1 subunits of PSII (Figure 1.2a). The catalytic cycle of water oxidation by the OEC, the so-called Kok cycle, includes four consecutive oxidations of the Mn₄CaO₅ cluster, accompanied by abstraction of four protons from water molecules coordinated to the Mn ions, and followed by O–O bond formation and O₂ liberation (Figure 1.2b). Importantly, a tyrosine residue (TyrZ) of the D1 subunit of PSII mediates the electron transfer from the OEC to P680⁺⁺, while proton transfer from an adjacent histidine residue to TyrZ⁺⁺ (electron-proton transfer) allows avoiding high-energy intermediates. Similarly, three of the one-electron oxidations of the Mn₄CaO₅ cluster are accompanied by a proton transfer to carboxylate groups of the two adjacent aspartate residues, avoiding charge build-up and directing the released protons to the proton exit channel.

Figure 1.2: a) X-ray structure of the oxygen-evolving complex (OEC) in its amino acid environment. b) Simplified catalytic cycle of water oxidation by OEC (Kok cycle) demonstrating five distinct oxidation states S₀–S₄ of OEC. The crystal structure is reprinted with permission from the publisher (Macmillan Publishers Ltd.: Nature 2011, 473, 55–60).

† In this thesis a biochemical convention for the term “formal potential” \( (E^{\circ}) \) is adapted, where it is a “conditional constant” that relates to specific conditions, including pH. In electrochemical literature the formal potential only considers the activity coefficients of the relevant species, while there is no generally recommended symbol for the redox potential of a couple under non-standard conditions.
1.2. From Natural to Artificial Photosynthesis

The described natural photosynthetic machinery provides us with an indispensable structural and functional model for conversion of solar energy into fuels. Artificial photosynthetic systems are therefore envisioned to operate through similar key steps as in natural photosynthesis, namely: light harvesting, charge separation, electron/hole transport, and oxidation and reduction half-reactions (Figure 1.1). Unlike the natural photosynthesis, artificial photosynthetic systems allow for a more flexible choice of the different components and arrangement of these components in various architectures (Figure 1.3).

Three principal arrangements are: 1) a photovoltaic cell connected to an electrolyzer, 2) an integrated photoelectrochemical cell (PEC) with buried solid- or liquid-junction photoelectrodes, and 3) a particle suspension reactor. Although the initial reports highlighted the intrinsic advantages of the type 2 devices, recent studies have demonstrated that high solar-to-fuel conversion efficiencies at low cost can also be reached with type 1 devices. Type 3 devices are believed to be potentially the most cost-efficient, but also require more challenging technological developments.

Regardless of the cell architecture, the oxidation (anodic) and reduction (cathodic) half-reactions have to be realized. For the oxidation side water is considered to be a preferable substrate, as it is virtually the most abundant source of electrons on Earth and its oxidation produces only non-toxic molecular oxygen (Eq. 1.2). For the reduction side the most straightforward transformation is reduction of the protons produced during water oxidation to molecular hydrogen (Eq. 1.3). Alternatively, CO₂ can be reduced to various high-energy products, such as HCO₂H, CO, H₂C₂O₄, CH₃OH, and CH₄.

Figure 1.3: Three principal architectures of water splitting devices. Types 1 and 2: WOC is immobilized on an anode or photoanode and HEC is immobilized on a cathode or photocathode. For type 1 devices the electrical bias is supplied by a photovoltaic cell (PV). Type 3: WOC and HEC are immobilized on a particulate semiconductor or a one phase photocatalyst is employed.
2H₂O → 4H⁺ + O₂ + 4e⁻ \hspace{1cm} E°' = 1.23 – 0.059·pH V \hspace{1cm} (1.2)

2H⁺ + 2e⁻ → H₂ \hspace{1cm} E°' = –0.059·pH V \hspace{1cm} (1.3)

Overall water splitting is achieved by combining the half-reactions in Eq. 1.2 and 1.3. The individual reactions are, however, challenging from a chemical point of view and require a water oxidation catalyst (WOC) and a hydrogen evolution catalyst (HEC) in order to decrease their activation energies and reach significant reaction rates at moderate overpotentials (η). The latter term in general refers to an excess applied potential (to the positive or negative side) relative to the thermodynamic redox potential of the couple under investigation. However, this term is poorly defined in the literature when applied to electrocatalytic† water oxidation (vide infra), leading to ambiguities during comparison of different catalysts.²²

1.3. Catalytic Oxidation of Water by Transition Metal Complexes

Currently, the water oxidation half-reaction is considered to be the bottleneck of the overall water splitting.²⁴ Development of stable and efficient WOCs is therefore highly desired. A number of homogeneous (molecular) and heterogeneous (see Section 1.4) transition metal-based WOCs inspired by the natural OEC have been developed over the past two decades. In particular, significant attention was drawn to the molecular catalysts as they offer high flexibility in the catalyst design and allow for straightforward solution-based mechanistic studies. Comprehensive reviews on molecular WOCs are currently available, focusing in detail on the mechanistic aspects,²²,²⁵ immobilization of the WOCs on the electrode surfaces,²⁶ and providing more general overview of the various catalytic systems.²⁷

1.3.1. Evaluation of the Catalytic Activity

For water oxidation to occur, the transition metal catalyst has to be oxidized past the thermodynamic redox potential of the H₂O/O₂ couple at a given pH (Eq. 1.2). This can be accomplished using strong chemical oxidants, such as ceric ammonium nitrate (CAN, \((\text{NH}_4)_2[\text{Ce}^{IV}(\text{NO}_3)_6]\), \(E°' = 1.75 \text{ V at pH 1}\)), oxone® (active component KHSO₅, \(E°' = 1.82 – 0.059\cdot\text{pH V}\)), sodium periodate (NaIO₄, \(E°' = 1.6 – 0.059\cdot\text{pH V}\)), or \([\text{Ru}^{II}(\text{bpy})_3]^{3+}\) (bpy = 2,2′-bipyridine, \(E°' = 1.21 \text{ V}\)).²⁸ The latter oxidant can also be photochemically generated in situ from the \([\text{Ru}^{II}(\text{bpy})_3]^{2+}\) photosensitizer during photochemical

† In this thesis the term “electrocatalysis” is used for simplicity when discussing molecular catalysts. In electrochemical literature “electrocatalysis” usually refers to catalysis by surface-active cites of a heterogeneous catalyst, while catalysis by molecularly defined species is referred to as “molecular catalysis” driven electrochemically.²³
water oxidation. In this case, the photosensitizer is excited by visible light ($\lambda_{\text{max}} = 450$ nm) to a highly reductive state ($E^{\circ'} = -0.86$ V), followed by an electron transfer to a sacrificial electron acceptor, typically sodium peroxidisulfate (Na$_2$S$_2$O$_8$). One-electron reduction of Na$_2$S$_2$O$_8$ results in formation of an SO$_4$$^{-\bullet}$ anion-radical ($E^{\circ'} = 2.4$ V), which can oxidize a second equivalent of the photosensitizer (Eq. 1.4–1.6). Typically, a large excess of the photosensitizer relative to the catalyst is used to ensure that transiently-generated SO$_4$$^{-\bullet}$ anion-radicals do not interact with the WOC.

\[
\begin{align*}
\text{[Ru}^{\text{II}}(\text{bpy})_3]^2^+ + h\nu & \rightarrow \text{[Ru}^{\text{II}}(\text{bpy})_3]^2^+^* \quad (1.4) \\
\text{[Ru}^{\text{II}}(\text{bpy})_3]^2^+^* + \text{S}_2\text{O}_8^{2^-} & \rightarrow \text{[Ru}^{\text{III}}(\text{bpy})_3]^3^+ + \text{SO}_4^{-\bullet} + \text{SO}_4^{2^-} \quad (1.5) \\
\text{[Ru}^{\text{II}}(\text{bpy})_3]^2^+ + \text{SO}_4^{-\bullet} & \rightarrow \text{[Ru}^{\text{III}}(\text{bpy})_3]^3^+ + \text{SO}_4^{2^-} \quad (1.6)
\end{align*}
\]

The evolved oxygen gas can be detected directly by manometry, gas chromatography, a Clark electrode, mass-spectrometry, fluorescent probe or RRDE (rotating ring-disk electrode) experiments, or the catalytic activity can be evaluated indirectly, e.g. by following the bleaching of the Ce$^{IV}$ oxidant UV-vis absorption.$^{30}$

Importantly, comparing the catalytic activity of WOCs evaluated with different sacrificial oxidants or oxygen-detecting techniques should be carried out with extreme caution.$^{28,31}$ A number of phenomena associated with the use of different sacrificial oxidants can affect catalysis. Each of the mentioned oxidants is stable at various pH range (pH ≤ 1 for CAN, pH < 5.5 for oxone, 2 < pH < 7.5 for NaI$_2$O$_4$, pH < 4 for [Ru$^{\text{II}}$(bpy)$_3$]$^{3^+}$) and provides varying driving force for the oxidation of the catalyst depending on the pH.$^{28}$ A significant advantage of CAN and [Ru$^{\text{III}}$(bpy)$_3$]$^{3^+}$ is that they favour outer-sphere one-electron oxidations. On the other hand, oxone and NaI$_2$O$_4$ can serve as two-electron oxidants and oxo-transfer reagents, leading to formation of an O–O bond where one of the oxygen atoms originates from water and the other oxygen atom from the oxidant.$^{32}$ Although typically acting as one-electron oxidant, an oxo-transfer mechanism has also been demonstrated for CAN.$^{33}$ The greatest disadvantage of [Ru$^{\text{II}}$(bpy)$_3$]$^{2^+}$/[Ru$^{\text{III}}$(bpy)$_3$]$^{3^+}$ is their low stability at neutral pH, also affected by various factors, such as the concentration of the reaction mixture components and the employed buffer.$^{34}$

Alternatively, the catalytic activity of WOCs can be evaluated electrochemically under conditions more relevant for incorporation of the WOCs into water splitting devices. In this case the working electrode is adjusted to significantly positive potentials and acts as an electron acceptor. Sweeping the potential of the working electrode between less positive and more positive values at constant rate and recording the current passed through the cell (cyclic voltammetry, CV) allows analysis of the obtained voltammetric $i$–$E$ response according to a theoretical model and calculation of the apparent rate constant of the catalytic cycle. Traditionally, the Shain methodology.$^{35}$
was employed for evaluation of the electrocatalytic activity of WOCs.\textsuperscript{36} However, this methodology typically requires analysis of the limiting catalytic current under pure kinetic conditions (KS kinetic zone\textsuperscript{37}), which usually cannot be reached for the electrocatalytic water oxidation due to various side processes.

An improved methodology, foot-of-the-wave analysis (FOWA), was developed by Savéant and co-workers in 2012\textsuperscript{38} and adapted for analysis of WOCs by Llobet and co-workers in 2015.\textsuperscript{39} The methodology relies on analysis of the foot of the catalytic wave in CV, where such side-phenomena as substrate consumption (local decrease in pH in the case of water oxidation), deactivation of the catalyst and electrode passivation or degradation can be minimized, which allow extraction of the intrinsic catalytic rate constant of the WOC. It has to be emphasized, however, that the analysis relies on the theoretical model, which has to be supported experimentally. Moreover, a number of conditions have to be fulfilled, including the Nernstian nature of all electron-transfer steps, irreversibility of the involved chemical steps, rate-limiting O–O bond formation step, etc. The largest uncertainty in FOWA is introduced from the inability to reliably determine the redox potential of the last redox couple of the catalyst that onsets water oxidation ($E^{\circ,\text{app}}$). In CV this couple is entirely buried under the catalytic wave and its potential is typically determined by differential pulse voltammetry (DPV).\textsuperscript{39} However, the value obtained from DPV can vary depending on acquisition parameters, accuracy in $iR$-drop compensation, as well as the working electrode history and reference electrode impedance. Due to these complications, comparing the activity for different WOCs obtained from FOWA has to be done with caution.

Importantly, the observed activity of a WOC (turnover frequency, TOF) when driven electrochemically is a function of the applied potential. At potentials that are lower than or close to the redox potential of the couple which onsets the catalysis, the TOF is limited by both the catalytic rate constant and the rate of the catalyst oxidation. At higher potentials, however, catalyst oxidation is not rate-limiting and TOF represents an intrinsic catalytic rate constant of the WOC ($k_{\text{cat}} = \text{TOF}_{\text{max}}$ for single-cite catalysts). This dependence can be displayed in the form of a log(TOF)–$\eta$ catalytic Tafel plot, widely used when studying heterogeneous electrocatalysts but only recently introduced for molecular electrocatalysts. Figure 1.4 provides an example of such a catalytic Tafel plot for two hypothetical WOCs. The plot exemplifies that even if one of the catalysts has higher catalytic rate constant, it can be outperformed by another intrinsically slower catalyst at lower overpotentials, if the latter catalyst has a lower potential of the redox couple that onsets water oxidation. In general, such dependence cannot be obtained from chemically- or light-driven catalytic experiments.
1.3.2. Landmark Ru-based Molecular WOCs

The first well-characterized molecular WOC, the so-called “blue dimer” ([bpy)₂(H₂O)Ru²⁺ORu²⁺(OH₂)(bpy)₂]⁴⁺, Figure 1.5), was described by Meyer and co-workers in 1982 and is still subjected to detailed mechanistic studies. Although this catalyst displayed low activity and stability (TON = 13.2; TOF = 0.0042 s⁻¹; CAN at pH 1.0), it laid the foundation for further research in the area.

Due to the polynuclear nature of both the “blue dimer” and the natural OEC, at the time it was considered that only polynuclear complexes are able to efficiently catalyze water oxidation. This led to development of a number of dinuclear WOCs with improved activity and stability in the 2000s. However, in 2005 Thummel and co-workers presented a seminal report featuring a mononuclear Ru-based catalyst [Ru²⁺(npm)(pic)₂(OH₂)]²⁺ (npm = 4-t-butyl-2,6-di(1’,8’-naphthyrid-2’-yl)pyridine, pic = 4-picoline), which could efficiently promote chemical (TON = 260; TOF = 0.014 s⁻¹; CAN at pH 1.0) as well as light-driven water oxidation (TON = 83; TOF = 0.12 s⁻¹; [Ru²⁺(bpy)₃]²⁺/S₂O₈²⁻ at pH 7.0). Shortly thereafter, Meyer and co-workers presented another seminal mononuclear catalyst [Ru²⁺(tpy)(bpm)(OH₂)]²⁺ (tpy = 2,2’:6’,2”-terpyridine, bpm = 2,2’-bipyrimidine) and its analogue with bpz (2,2’-bipyrazine) in place of the bpm ligand. These complexes demonstrated moderate catalytic performance (TON = 8 and TOF = 0.02 s⁻¹ for

\[ E^{\text{app}} = 1.4 \text{ V}; \text{TOF}_{\text{max}} = 10^3 \text{ s}^{-1} \]

\[ E^{\text{app}} = 1.1 \text{ V}; \text{TOF}_{\text{max}} = 10 \text{ s}^{-1} \]

\( ^8 \text{In this section initial (maximum) TOF values are specified, unless otherwise noted.} \)
[Ru\textsuperscript{II}(tpy)(bpm)(OH\textsubscript{2})\textsuperscript{2+}; CAN at pH 1.0], but provided an important model for the early mechanistic studies.\textsuperscript{48} In 2009, the same group introduced another mononuclear Ru-based WOC \([\text{Ru}^{\text{II}}(\text{Mebimpy})(\text{pic})_2(\text{OH}_2)]^{2+}\) (Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine)\textsuperscript{49} that displayed moderate catalytic activity for chemically-driven water oxidation (TON = 7.5 and TOF = 0.006 s\textsuperscript{-1}; CAN at pH 1.0), but was subjected to extensive mechanistic studies\textsuperscript{48a,50} and served as a model catalyst for development of various strategies for immobilization\textsuperscript{51} and stabilization\textsuperscript{51c,52} of WOCs on the electrode surfaces.

A large drawback of the aforementioned class of catalysts based on neutral N-donor ligands is the generally high potentials at which the species responsible for the O–O bond formation can be formed. Gratifyingly, this drawback can be overcome by introducing electron-donating negatively charged carboxylate ligands in the first coordination sphere of the metal center. Following this strategy, in 2010 Åkermark & Sun and co-workers developed a highly active dinuclear Ru-based WOC that could mediate both chemical (TON = 10 400, TOF = 1.2 s\textsuperscript{-1}; CAN at pH 1.0) and light-driven water oxidation (TON = 580, TOF = 0.83 s\textsuperscript{-1}; [Ru\textsuperscript{II}(bpy)(deeb)\textsuperscript{2+}/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−} (E\textsubscript{1/2}(Ru\textsuperscript{III/II}) = 1.54 V) at pH 7.2; deeb = diethyl 2,2′-bipyridine-4,4′-dicarboxylate).\textsuperscript{44j}

At the same time, Sun and co-workers introduced a structurally-related mononuclear WOC \([\text{Ru}^{\text{II}}(\text{bda})(\text{pic})_2]\) (bda\textsuperscript{2−} = 2,2′-bipyridine-6,6′-dicarboxylate) that displayed formation of highly unusual heptacoordinated Ru\textsuperscript{IV}–OH species under the catalytic conditions.\textsuperscript{53} The following mechanistic and activity studies demonstrated that this catalyst favors a bimolecular mechanism for the O–O bond formation, unlike all previously reported mononuclear Ru-based WOCs (vide infra). Rational modification of the axial ligands in this catalyst resulted in the development of extremely potent WOCs, such as [Ru\textsuperscript{II}(bda)(6-fluoroisoquinoline)\textsubscript{2} and [Ru\textsuperscript{II}(bda)(6-bromophthalazine)\textsubscript{2} with TON = 24 000 and 101 000, and TOF = 1 000 and 380 s\textsuperscript{-1} (using CAN at pH 1.0), respectively.\textsuperscript{54} Nevertheless, the characteristic bimolecular mechanism for this type of catalyst family greatly limits their applicability for incorporation into hybrid photoanodes. Under these conditions the catalyst is immobilized on the electrode surface, which restricts translational mobility needed for the bimolecular catalytic pathway. Instead, the immobilized

\*

\**It should be stressed, that the TOF and especially TON values presented in this section should be used for comparing performance of different catalysts with extreme caution, and the comparison preferably should be based on the detailed evaluation of all available experimental data. As an example, TONs of 8 and 260 were reported for chemical water oxidation with CAN by catalysts \([\text{Ru}^{\text{II}}(\text{tpy})(\text{bpm})(\text{OH}_2)]^{2+}\) and \([\text{Ru}^{\text{II}}(\text{npm})(\text{pic})_2(\text{OH}_2)]^{2+}\), respectively. However, the catalytic experiments for these catalysts were conducted with 30 and 5 000 equiv. of CAN, respectively. As a result, quantitative formation of oxygen based on the amount of the used CAN was observed for \([\text{Ru}^{\text{II}}(\text{tpy})(\text{bpm})(\text{OH}_2)]^{2+}\), while only 21% oxygen yield was observed for \([\text{Ru}^{\text{II}}(\text{npm})(\text{pic})_2(\text{OH}_2)]^{2+}\), implying that the performance of the former catalyst based on TON is certainly underestimated.
Ru(bda)-type catalyst was shown to operate via a higher energy monomolecular mechanism, leading to its decomposition to RuO$_2$. Most recently, Concepcion and co-workers presented two Ru(bda)-related WOCs, in which one or both of the carboxylate groups in the bda$^{2-}$ ligand were substituted by phosphonate groups, resulting in complexes $[\text{Ru}^{II}(\text{Hbpc})(\text{pic})_{2}]^{0}$ and $[\text{Ru}^{II}(\text{H}_{2}\text{bpa})(\text{L})_{2}]$ (Hbpc$^{2-} = 2,2'$-bipyridine-6-hydrogenphosphonate-6'-carboxylate; H$_2$bpa$^{2-} = 2,2'$-bipyridine-6,6'-bis-(hydrogenphosphonate); L = pic or isoquinoline (isq)). Despite the similarity to the coordination geometry of Ru(bda), both of these catalysts were shown to operate via a monomolecular mechanism for the O–O bond formation, and

Figure 1.5: Structures of the Ru-based WOCs discussed in Sections 1.3.2 and 1.3.3.
the monocarboxylate \([\text{Ru}^{II}(\text{Hbpc})(\text{isq})_2]\) complex could carry out chemically-driven water oxidation with a TOF as high as 100 s\(^{-1}\) (CAN at pH 1.0).

Another recent Ru(bda)-inspired WOC operating via a monomolecular pathway was developed by Llobet and co-workers.\(^{39a}\) In this catalyst, the bpy ligand core of the bda\(^{2-}\) ligand was substituted with tpy, resulting in a dicaboxylate complex \([\text{Ru}^{II}(\text{tda})(\text{py})_2]\) \((\text{tda}^{2-} = 2,2':6',2''\text{-terpyridine}-6,6''\text{-dicarboxylate})\). Initially this complex was found to be catalytically inactive, however, stoichiometric oxidation of this complex to the Ru\(^{IV}\) state triggered formation of an extremely active catalyst \([\text{Ru}^{IV}(\text{O})(\text{tda})(\text{py})_2]\), that could promote electrochemical water oxidation with \(\text{TOF}_{\text{max}} = 8000\, \text{s}^{-1}\) (from FOWA at pH 7.0).

### 1.3.3. Mechanistic Aspects

From a mechanistic point of view, catalytic water oxidation by transition metal complexes can be divided into three essential steps: 1) formation of an active catalyst from the precursor complex, 2) oxidative activation of the catalyst to a high-valent state beyond the thermodynamic potential necessary for water oxidation, and 3) O–O bond formation followed by liberation of molecular oxygen.

**Formation of the active catalyst**

Activation is necessary for the coordinatively saturated catalysts that do not possess a water molecule coordinated to the metal center in the isolated state. Activation of such complexes can proceed via a ligand–\(\text{H}_2\text{O}\) exchange, where the labile ligand is usually either a negatively-charged counter-ion (such as halogen) or a neutral monodentate N-donor molecule (such as pyridine). Examples of complexes that require such activation are the halogen-containing \([\text{Ru}^{II}(\text{tpy})(\text{bpy})(\text{X})]^+\) \((\text{X} = \text{Cl}, \text{Br}, \text{I})\) and the dicarboxylate complex \([\text{Ru}^{II}(\text{pdc})(\text{pic})_3]\) \((\text{pdc}^{2-} = 2,6\text{-pyridinedicarboxylate}, \text{Figure 1.5})\). Alternatively, coordinatively saturated Ru-based complexes can be activated by displacement of a carboxylate group of the equatorial ligand by water. Such displacement is usually favored at the Ru\(^{III}\) oxidation state of the complex and has been observed for Ru(bda) and related catalysts, such as Ru(Hbpc).

**Oxidative activation**

Oxidative activation of a WOC is needed to form sufficiently electrophilic Ru-oxo species that can mediate the O–O bond formation. In order to generate such species (typically Ru\(^{IV}\) or Ru\(^{V}\)) two or three electrons have to be abstracted from the initial reduced state of the catalyst (typically Ru\(^{II}\)). For the polypyridine complexes, such as \([\text{Ru}^{II}(\text{bpy})_3]^{2+}\), this process is highly unfavourable due to the charge build-up and already the Ru\(^{III/II}\) transition is observed at a relatively high potential of 1.21 V, independent of the pH. The polypyridine Ru-aqua complexes have a similar standard (at pH 0) redox potentials for the Ru\(^{III/II}\) couple, however, at elevated pH
(pK_a(Ru^{III}) < pH < pK_a(Ru^{II})) the potential of the couple is decreased, as the charge build-up is avoided by deprotonation of the coordinated water concomitant with electron transfer (proton-coupled electron transfer, PCET). This process allows decreasing the redox potential by 0.059 V per pH unit, according to the Nernst equation. Furthermore, the redox potentials of the Ru-based WOCs can be reduced by introducing electron-rich donor groups in the ligand framework such as carboxylates, or by introducing more distant electronic perturbations. Unfortunately, this typically only allows controlling the potential of the Ru^{III/II} couple while more relevant couples for the catalytic activity (Ru^{IV/III} and Ru^{V/IV}) are significantly less affected, which is «frustrating from a catalytic perspective».

The oxidative activation of WOCs is typically not rate-limiting during chemically-driven catalytic experiments in the presence of excess oxidant. On the other hand, during electrochemical water oxidation the Ru^{IV/III} couple often demonstrates sluggish heterogeneous electron transfer kinetics and can limit the catalytic activity.

O–O bond formation and O₂ liberation

The two main mechanisms for O–O bond formation by Ru-based WOCs are: 1) nucleophilic attack of water on a high-valent Ru-oxo species (water nucleophilic attack, WNA), and 2) radical coupling of two Ru-oxo species (interaction of two metal-oxo species, I2M). An outline of both mechanisms is presented in Figure 1.6.

A majority of the described Ru-based WOCs, both polynuclear and mononuclear, have been reported to follow the WNA mechanism. Typically, the nucleophilic attack of water is favored for the Ru^{V=O} species, resulting in formation of a Ru^{II–OOH} hydroperoxide intermediate. Alternatively, Ru^{IV=O} species with sufficiently high potential of the Ru^{IV/III} couple can participate in O–O bond formation, as was observed for the [Ru^{II}(npm)(pic)₂(OH₂)]^{2+} catalyst. The O–O bond formation via WNA

Water nucleophilic attack (WNA):

Atom-proton transfer (APT):

Intramolecular APT (i-APT):

Interaction of two metal-oxo species (I2M):

Figure 1.6: Schematic outline for the O–O bond formation mechanisms typical for the Ru-based WOCs.
was found to be the rate-limiting step for most of the described WOCs. However, this reaction could be greatly accelerated by the simultaneous abstraction of a proton from the nucleophilic water molecule (atom-proton transfer, APT). Such proton transfer can then be mediated by a base present in solution or introduced into the ligand framework of the catalyst (intramolecular APT, i-APT).  

A radical coupling mechanism for the O–O bond formation was mainly demonstrated for the Ru(bda)-based catalysts, for which the Ru°=O species has considerable radicaloid character and is better described as a Ru°–O’ intermediate. Interestingly, computational studies suggest that the O–O bond formation via I2M does not have any intrinsic activation energy and the observed activation barrier is associated with preorganization of the dinuclear transition state. Formation of such dinuclear state can be promoted by non-covalent intermolecular interactions between two molecules of the catalyst, or by covalently linking two catalytic units. It should be noted, however, that the O–O bond formation mechanism for the Ru(bda)-type catalysts is very sensitive to geometrical perturbations and the closely related catalyst [Ru°(pda)(pic)₂] (pda²⁻ = 1,10-phenanthroline-2,9-dicarboxylate) operates via a WNA mechanism, while linking of two [Ru°(bda)(pic)]²⁺ catalytic units by a rigid dinucleating xanthene-derived axial ligand inhibits the catalytic activity.

The reduced Ru-peroxo intermediates generated after O–O bond formation are usually quickly transformed into high-valent Ru-peroxo species under the catalytic conditions. The latter species is then responsible for the concomitant O₂ liberation and two-electron reduction of the metal center, which completes the catalytic cycle (Figure 1.7).

Figure 1.7: General outline of the catalytic cycle of water oxidation through WNA and I2M mechanisms for the O–O bond formation.
Catalyst deactivation

One of the crucial considerations during design of transition metal–based molecular WOCs is their stability under the catalytic conditions. In many cases decomposition of molecular WOCs results in formation of catalytically active metal oxide nanoparticles or clusters, casting doubts on the activity and mechanistic studies of the molecular complexes. The decomposition of molecular WOCs is typically triggered by ligand oxidation and/or ligand substitution followed by leaching of the metal to the solution, or by formation of polynuclear oxo-bridged species. A robust WOC should therefore be based on a ligand that lacks oxidatively labile functional groups, such as amines, primary or secondary alcohols, phenols, and benzylic CH groups, and efficiently stabilizes the metal center(s) at the relevant oxidation states, precluding the unwanted ligand-exchange reactions.

1.4. Catalytic Oxidation of Water by Inorganic (Heterogeneous) Catalysts

Heterogeneous catalysts and photocatalysts for oxidation of water have been extensively studied over the past 50 years, following the seminal work by Fujishima and Honda, who demonstrated the splitting of water over TiO$_2$ as both light-absorber and catalyst. A large number of heterogeneous WOCs have been developed thereafter based on oxides of noble as well as Earth-abundant 1st-row transition metals. Unfortunately, mechanistic and activity studies of such catalysts present a true challenge, especially if the intrinsic activity is to be evaluated independent of the catalyst morphology and fabrication technique. A benchmarking procedure for electrocatalytic water oxidation by heterogeneous catalysts was recently developed by Jaramillo and co-workers, addressing the above challenges and aiding more reliable comparison of different catalysts. On the other hand, chemically-driven catalytic experiments are currently less refined and are mainly used as a fast way for initial comparison between activities of different catalysts.

1.5. Remaining Challenges and Outlook

Importantly, some of the presented molecular WOCs already surpass the activity of the natural OEC (TOF$^{\text{OEC}} \approx 50$–$400 \text{ s}^{-1}$). Furthermore, it is important to realize that although the photosynthesis in living organisms appears continuous, the components of the photosynthetic machinery in PSII have to be repaired every 15–30 min due to irreversible photoinhibition, which limits the intrinsic stability of the OEC. In this regard, some of the developed WOCs also outperform the natural photosynthetic machinery.
Nevertheless, the OEC remains the only catalyst, which can carry out water oxidation at a record low overpotential of 70 mV,\textsuperscript{74b} setting the key goal for future research in the area.

As was discussed in Section 1.3.1, multiple problems regarding the evaluation of WOCs catalytic activity have to be addressed to reliably compare the activity of different catalysts and gain better understanding of the structure-activity relationships. Evaluation of the electrocatalytic activity of WOCs presents a particular challenge, as most of the known catalysts operate at high overpotentials. At such potentials the commonly employed carbon-based working electrodes (such as glassy carbon) can be oxidized, which alters the electrochemical response and obscures data analysis. More oxidatively stable electrode materials are currently available, including boron doped diamond (BDD) and indium tin oxide (ITO). However, the use of these electrode materials is limited by their high cost, dependency of their properties on the pre-treatment procedure, and particularly by the slow heterogeneous electron transfer kinetics,\textsuperscript{75} making them poorly suitable for kinetic studies of fast catalysts. Decreasing the operating overpotential of WOCs is therefore highly desired for more reliable mechanistic and activity studies using conventional carbon-based electrode materials.

Another intensively pursued goal in the area is development of more stable molecular WOCs based on Earth-abundant 1st-row transition metals. It is, however, necessary to mention that technoeconomic analysis of type 2 water splitting devices (Figure 1.3) demonstrates that with currently available technologies the catalyst cost makes only a minor contribution to the total cost of the device.\textsuperscript{76} Assuming the use of IrO\textsubscript{x} for the oxygen evolution and Pt for the hydrogen evolution reactions, both catalysts make up for only 2–3\% of the total cost, while the PV and PEM account for 30–40\% of the cost. Therefore, decreasing the catalyst cost will be more important for future devices with decreased cost of the other components, while at the current stage catalysts with higher stability and activity at lower overpotentials are needed for improving solar-to-fuel conversion efficiency and stimulating further development of the other components required for water splitting devices.

1.6. Objectives of the Thesis

This thesis is focused on the development of novel Ru-based WOCs and evaluation of their redox properties and catalytic activity. In particular, the redox properties of the synthesized complexes were studied by electrochemical and spectroscopic techniques. Qualitative and quantitative analysis of the obtained data provided insight into the mechanistic details under the
relevant conditions and the catalytic activity of the complexes was studied for chemical, photochemical, and electrochemical water oxidation. Furthermore, a heterogeneous nanoparticulate RuO₂ WOC has been developed and evaluated for chemical and photochemical water oxidation.
2. Catalyst-Solvent Interactions in a Dinuclear Ru-Based Water Oxidation Catalyst (Paper I)

2.1. Introduction

A Ru-based WOC [Ru\textsuperscript{II}(pdc)(pic)\textsubscript{3}] (1, Figure 2.1) was reported in 2010 by Sun and co-workers.\textsuperscript{77} This catalyst demonstrated reasonable activity for chemical (driven by CAN),\textsuperscript{77,78} photochemical (with the use of [Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+}-type photosensitizers),\textsuperscript{77,79} and electrochemical water oxidation when immobilized on an electrode surface\textsuperscript{80} or incorporated into a complete water splitting PEC.\textsuperscript{81}

Catalyst 1 displayed low solubility in water and MeCN had to be used as a co-solvent to allow solution-based mechanistic and catalytic studies. However, the use of MeCN induced formation of new species where MeCN is coordinated to the Ru center, as demonstrated for other Ru-based WOCs.\textsuperscript{82} This introduced an $E_rC_l|E_rC_i$ square scheme for the Ru\textsuperscript{II}$\rightarrow$Ru\textsuperscript{III} and Ru\textsuperscript{III}$\rightarrow$Ru\textsuperscript{II} transitions of the complex, which was observed electrochemically and supported by $^1$H NMR and ESI-MS studies.\textsuperscript{77} In this square scheme fast displacement of one of the carboxylate groups by MeCN takes place at the Ru\textsuperscript{II} oxidation state of the complex, while the reverse reaction is favored upon oxidation of the complex to the Ru\textsuperscript{III} oxidation state. The catalytically active species is proposed to form upon substitution of the axial 4-picoline ligand by water when the complex is oxidized to the Ru\textsuperscript{III} state. A more

![Figure 2.1: Structures of the previously synthesized WOCs 1, 2, and 3.](image)
thorough investigation of the catalyst demonstrated that a catalytically active dinuclear oxo-bridged complex is formed under the catalytic conditions at pH 1, however, not excluding that the initial mononuclear catalyst can also drive water oxidation under restricted translational mobility. Åkermark and co-workers demonstrated that the activity of 1 can be increased by substitution of one or both of the carboxylate groups in the pdc ligand by carboxamide groups (complexes 2 and 3, respectively; Figure 2.1). Unlike carboxylates, carboxamide groups can be further functionalized while maintaining coordination ability. In the current work, the carboxamide group in catalyst 2 was used to link the catalyst to an identical catalytic unit via a benzene linker, resulting in the dinuclear complex 4 (Figure 2.2). Similar to catalyst 1, MeCN had to be used as a co-solvent to fully solubilize 4 in aqueous media, leading to formation of species where MeCN is coordinated to the metal center. Herein, we describe the redox properties of catalyst 4, focusing in detail on how coordination of MeCN to Ru affects the redox properties of the catalyst. Furthermore, the catalytic activity of 4 for chemically- and light-driven water oxidation is evaluated in comparison to catalysts 1 and 2.

2.2. Results and Discussion

2.2.1. Synthesis and Characterization

The proposed dinucleating ligand 6,6’-((1,3-phenylenebis(azanediyl))bis(carbonyl))dipicolinic acid was synthesized from the readily available 2,6-pyridinedicarboxylic acid (Figure 2.2). One of the carboxy groups was protected as a methyl ester and the other carboxy group was used for formation of an amide bond with m-phenylenediamine, furnishing the desired ligand upon ester hydrolysis. The ruthenium complex was formed by slow addition

![Figure 2.2: Synthetic route for the dinuclear Ru complex 4.](image-url)
of the ligand solution containing NEt₃ as base to a solution of the metal precursor [Ru(DMSO)₄Cl₂] in order to prevent formation of tethered and poly-nuclear complexes. Subsequent addition of excess 4-picoline resulted in formation of complex 4, which was purified by column chromatography and isolated in the Ru II oxidation state. The structure of the complex was confirmed by 1D and 2D NMR, single crystal X-ray diffraction analysis (SC-XRD), ESI-MS, elemental analysis, UV-vis, and IR.

¹H NMR of complex 4 in CD₃OD initially displayed highly broadened and shifted peaks, typical for a paramagnetic d⁵ Ru III species. However, upon addition of only 0.05 equiv. of a reducing agent (ascorbic acid) a clear diamagnetic spectrum was observed, indicating that the isolated complex is at the Ru II oxidation state but either contains small amount of Ru III species or is slowly oxidized by air. The ¹H NMR spectrum was assigned based on the 1D and 2D NMR experiments (Figure 2.3). The integrity of the complex composition at the Ru II state in aqueous media was confirmed by ¹H NMR in CD₃CN/D₂O (3:1) with or without addition of 4-picoline.

The solid-state structure of complex 4 was investigated by SC-XRD, confirming the structure proposed by NMR analysis (Figure 2.4). The complex displayed high symmetry close to that of the C₂ point group, consistent with the high apparent symmetry of the complex observed by ¹H NMR. The two metal centers adapted distorted octahedral geometry with Ru–N and Ru–O bond lengths similar to those of the parent catalysts 1 and 2. The only notable difference was an elongation of the Ru–N_C(O)NH bond by 0.1 Å for 4 relative to 2, as expected for a Ru–N bond with a more electron-poor carboxamide nitrogen atom connected to a benzene ring.
2.2.2. Mechanistic Studies

The electrochemical properties of complex 4 were studied by CV, DPV, and square wave voltammetry (SWV) using a one-compartment three-electrode cell with glassy carbon disk working electrode \((d = 1 \text{ mm})\) and Pt wire counter electrode. Saturated calomel electrode (SCE) was used as the reference electrode for measurements in aqueous media and Ag wire pseudo-reference electrode (isolated by a salt bridge and calibrated against \(\text{Fc}^+/\text{Fc} \) couple) was used for measurements in \(\text{CH}_2\text{Cl}_2\). The potentials obtained vs. SCE were converted to vs. NHE by addition of 0.24 V. Positive feedback \(iR\)-compensation was used for CV experiments at high scan rates \((\nu > 1 \text{ V s}^{-1})\) and solution resistance was determined by the circuit stability test \((R \approx 150 \text{ } \Omega)\).

The CV of a solution of catalyst 4 in aprotic solvent \((\text{CH}_2\text{Cl}_2)\) demonstrated two pairs of close-lying chemically reversible one-electron diffusional waves with the half-wave potentials \(E_{1/2} = -0.28, -0.19, 1.02, \text{ and } 1.20 \text{ V vs. } \text{Fc}^+/\text{Fc (as calculated from DPV)}\), which were assigned to \(\text{Ru}^{III}\text{Ru}^{II}/\text{Ru}^{II}\text{Ru}^{II}, \text{Ru}^{III}\text{Ru}^{III}/\text{Ru}^{II}\text{Ru}^{II}, \text{Ru}^{IV}\text{Ru}^{III}/\text{Ru}^{III}\text{Ru}^{III} \text{ and } \text{Ru}^{IV}\text{Ru}^{IV}/\text{Ru}^{IV}\text{Ru}^{III} \) transitions, respectively (Figure 2.5). The small difference \((0.09 \text{ V})\) between the first two redox couples is indicative of weak electronic coupling between the metal centers, while larger difference \((0.18 \text{ V})\) between the last two couples suggests increased coulombic repulsion between the metal centers at higher oxidation states of the complex.

†† Half-wave potentials \(E_{1/2}\) were calculated from DPV peak potentials \(E_p\) according to equation \(E_{1/2} = E_p + \Delta E/2\), where \(\Delta E = 0.05 \text{ V}\) is the employed pulse amplitude.

Figure 2.4: ORTEP plot of complex 4 with ellipsoids at 30% probability. Solvent molecules and hydrogen atoms were omitted for clarity. Color codes: Ru — magenta, O — red, N — blue, C — black.
Thereafter, the electrochemical properties of 4 were studied in aqueous triflic acid (0.1 M TfOH, pH 1) containing 10% MeCN, that is at the same conditions as used for catalytic experiments with CAN (vide infra). Cyclic voltammograms of 4 at these conditions demonstrated typical diffusional waves at low scan rates ($v = 0.005$–$0.2$ V s$^{-1}$), while at higher scan rates ($v = 0.5$–$100$ s$^{-1}$) symmetrical waves were observed, typical for adsorbed species. The adsorption behaviour was also supported by dependence of the background-subtracted anodic peak current of the Ru$^{	ext{II}}$Ru$^{	ext{III}}$/Ru$^{	ext{II}}$Ru$^{	ext{I}}$ couple of 4 on the scan rate to the power of $0.82 \approx 1$ (the powers of 0.5 and 1 are expected for diffusional and adsorbed waves, respectively).

The background-subtracted high scan rate CVs with alternating vertex potentials of 1.015 or 1.240 V were used for further studies (Figure 2.6). The experimentally obtained background current strongly deviated from the background current observed in CVs of complex 4 and had to be simulated by fitting a multiexponential function with linear component to the experimental data. Fitting the resulting background-subtracted faradaic current to the adsorbed CV wave function allowed extraction of the anodic and cathodic peak areas and determination of the surface concentration of complex 4, giving a value of $5.7 \times 10^{-11}$ mol cm$^{-2}$, which corresponds to 69% of a dense monolayer assuming $2 \times 10^{-14}$ cm$^2$ per molecule.

The dominant anodic and cathodic waves in Figure 2.6 were assigned to the Ru$^{	ext{III}}$Ru$^{	ext{II}}$/Ru$^{	ext{II}}$Ru$^{	ext{I}}$ couple ($E_{1/2} = 0.48$ V) based on comparison to the average potential of the Ru$^{	ext{III}}$Ru$^{	ext{II}}$/Ru$^{	ext{II}}$Ru$^{	ext{II}}$ and Ru$^{	ext{III}}$Ru$^{	ext{III}}$/Ru$^{	ext{II}}$Ru$^{	ext{II}}$ couples (0.47 V) observed in CH$_2$Cl$_2$. The complete coalescence of the two couples into a single two-electron wave is presumably due to near complete inhibition of the coulombic interactions between the metal centers in the polar acidic medium.

**Figure 2.5:** CV (three cycles recorded at 0.05 V s$^{-1}$, black) and DPV (red) of a 1 mM solution of complex 4 in DCM with 0.1 M TBAPF$_6$ (tetraethylammonium hexafluorophosphate) as supporting electrolyte.
Unlike for CVs in CH₂Cl₂, an additional anodic peak with $E^{(2)}_{pa} \approx 0.8$ V was observed in the CVs of complex 4 in aqueous TfOH containing MeCN. This peak remained irreversible at low scan rates, but turned into a partly reversible wave with $E_{1/2} = 0.837$ V at high scan rates. Such behaviour is characteristic of a reversible electron transfer followed by an irreversible chemical reaction ($E,C_i$ mechanism). Based on comparison to catalyst 1, the observed electrochemical response can be explained by initial coordination of MeCN to the metal centers of 4 at the Ru²⁺Ru³⁺ state (Figure 2.7, reaction 1), while oxidation of the complex to the Ru³⁺Ru³⁺ state triggers displacement of the coordinated MeCN by the pendant carboxylate groups (Figure 2.7, reaction 2). Such change in the first coordination sphere of the metal centers is reasonable, given the better stabilization of the Ru³⁺ species by the hard carboxylate oxygen, while MeCN provides better stabilization for the Ru²⁺ species via π-backdonation. Accordingly, the potential of the Ru³⁺Ru³⁺/Ru²⁺Ru²⁺ couple is shifted to more positive potentials for MeCN-coordinated species and to more negative potentials for carboxylate-coordinated species.

**Figure 2.6:** CVs of a 0.1 mM solution of complex 4 in 0.1 M TfOH (pH 1) with addition of 10% MeCN: experimental data (third CV cycle, blue), simulated background current (black), and background-subtracted voltammograms (red). CVs with vertex potential of 1.015 or 1.240 V recorded at 1 or 100 V s⁻¹ are presented.
The described reactions establish a square scheme for the Ru$^{III}$/Ru$^{II}$ transitions in complexes 1 and 4 (Figure 2.7). Notably, in this square scheme coordination of MeCN to the Ru$^{II}$ metal center occurs quantitatively for 1, while for complex 4 an equilibrium between species with and without coordinated MeCN is established. The latter equilibrium for 4 is shifted towards carboxylate-coordinated species with $K^{(1)} \approx 0.5$, based on the ratio of the anodic peak currents in the first CV scans of 4, while the relative scan rate–independence of $K^{(1)}$ implies slow equilibrium with $k < 1 \times 10^{-2}$ s$^{-1}$ for dissociation of MeCN.

An additional anodic process with $E_{pa}^{(3)} \approx 1.1$ V was observed in the CVs of complex 4 when the potential range was extended up to 1.240 V. Similar to the second anodic wave, this process was attributed to the transfer of two electrons coupled to an irreversible chemical reaction that is outrun at high scan rates, resulting in formation of a quasi-reversible wave with $E_{1/2} = 1.06$ V. This process was assigned to the Ru$^{IV}$/Ru$^{IV}$/Ru$^{III}$/Ru$^{II}$ couple followed by exchange of the equatorial 4-picoline ligands by water, that is formation of the catalytically active species (Figure 2.7, reaction 3). Such ligand exchange is frequently observed at the Ru$^{III}$ oxidation state for related Ru-based WOCs.$^{77,91}$ However, reversibility of the Ru$^{III}$/Ru$^{III}$/Ru$^{II}$ wave for complex 4 even at low scan rates indicates kinetic stability of the complex at the Ru$^{III}$/Ru$^{III}$ oxidation state. We therefore propose that the 4-picoline–water ligand exchange for 4 occurs at the Ru$^{IV}$/Ru$^{IV}$ oxidation state.

Pseudo-first order rate constants for reactions 2 and 3 were calculated from the dependence of the anodic peak potentials $E_{pa}^{(2)}$ and $E_{pa}^{(3)}$ on the applied scan rate based on the $E_r C_1$ kinetic model (Figure 2.8).$^{35b}$ According to this model, Eq. 2.1 and 2.2‡‡ describe the dependence of the peak potential on the scan rate for adsorbed and diffusional $n$-electron couples, respectively. As-

‡‡ In these equations $n$ is the number of transferred electrons, $k$ is the pseudo-first order rate constant for $C_1$, $R$ is the gas constant, $T$ is the temperature, and $F$ is the Faraday constant.
assuming an adsorbed and two-electron nature of both couples, the slope of 0.029 for the $E_p$–log($\nu$) plots was expected and the observed slopes from Figure 2.8 were in reasonable agreement with this value (0.027 and 0.029 for $E_{pa}^{(2)}$ and $E_{pa}^{(3)}$, respectively). According to Eq. 2.2, slopes close to 0.029 could also correspond to one-electron diffusional couples, however, this would be inconsistent with the observed dependence of the anodic peak current on the scan rate (vide supra). The pseudo-first order rate constants $k^{(2)} = 1 \times 10^3$ s$^{-1}$ and $k^{(3)} = 4 \times 10^1$ s$^{-1}$ for reactions 2 and 3 were then calculated according to Eq. 2.1 using the intercept of the $E_p$–log($\nu$) plots at log($\nu$) = 0. Furthermore, these rate constants were also calculated from the dependence of the forward-to-reverse peak current ratios on the scan rate,92 resulting in reasonably close values of $k^{(2)} = 2 \times 10^2$ s$^{-1}$ and $k^{(3)} = 4 \times 10^1$ s$^{-1}$.

$$E_p = E_{1/2} + \frac{2.3RT}{nF} \log \left( \frac{RT}{nF} \right) + \frac{2.3}{nF} \log(k) - \frac{2.3RT}{nF} \log(\nu) \quad (2.1)$$

$$E_p = E_{1/2} - \frac{RT}{nF} 0.78 + \frac{1.15RT}{nF} \log \left( \frac{RT}{nF} \right) + \frac{1.15RT}{nF} \log(k) - \frac{1.15RT}{nF} \log(\nu) \quad (2.2)$$

The pH-dependence of the redox couples involved in the described square scheme was studied by SWV and UV-vis spectroscopy. A Pourbaix diagram was constructed from the peak potentials in SWV at pH 0–7 (Figure 2.9), demonstrating that the Ru$^{II}$/Ru$^{III}$/Ru$^{II}$Ru$^{II}$ redox couples for species with and without coordinated MeCN are essentially pH-independent at pH > 2 and pH > 1, respectively. The observed slopes of −4 and −2 mV per pH unit are in agreement with the previously reported behaviour of the nominally pH-independent redox couples of adsorbed transition metal complexes.$^{82,d,93,94}$ At lower pH, the slopes of −38 and −34 mV per pH unit were observed in the Pourbaix diagram, while the slope of −30 mV per pH unit is expected for two-electron one-proton redox couples according to Eq. 2.3. These values are reasonably close, indicating that at low pH one of the car-

---

**Figure 2.8:** Dependence of the anodic (black squares) and cathodic (black circles) peak potentials $E_{pa}^{(2)}$ (a) and $E_{pa}^{(3)}$ (b) on the scan rate.
Boxylate groups in both forms of complex 4 is protonated and the Ru\textsuperscript{II}Ru\textsuperscript{II}→Ru\textsuperscript{III}Ru\textsuperscript{III} transition is proton-coupled. The pK\textsubscript{a} values of ca. 2 and 1 were extracted from the Pourbaix diagram for complex 4 with and without coordinated MeCN, respectively, and the latter value was also validated by spectrophotometric pH-titration. The obtained data was subsequently used to construct a refined square scheme for complex 4, involving two proton-coupled electron transfer processes (Figure 2.10).

\[ E_{1/2} = E_{1/2}^o - 0.059 \frac{n_{H^+}}{n_e} \text{pH} \]  \hspace{1cm} (2.3)
2.2.3. Catalytic Activity

CV of complex 4 at pH 7 demonstrated a significant electrocatalytic current at $E > 1.4$ V, while reduction of the generated oxygen during the cathodic scan was observed at ca. $-0.35$ V (Figure 2.11). Unfortunately, the complex behaviour of the electrocatalytic wave due to the mixed adsorption–diffusion mass transport for complex 4 at moderate scan rates precluded quantitative analysis of the electrocatalytic activity. The catalytic activity of complex 4 was therefore studied with the use of CAN as sacrificial oxidant at pH 1, or with photochemically generated [Ru$^{III}$(bpy)$_2$(bdc)]$^{3+}$ at pH 7 (where bdc = 2,2'-bipyridine-4,4'-dicarboxylic acid; see Section 1.3.1 for details).

In order to make a reliable comparison of the catalytic activity for complex 4 and the parent catalysts 1 and 2, these catalysts were also synthesized according to the previously published procedures and the catalytic activities for all complexes were evaluated under identical conditions (Figure 2.12). Half as low concentration of catalyst 4 compared to catalysts 1 and 2 was employed to compensate for the dinuclear nature of the catalyst.

Catalyst 1 displayed slightly higher TON and a similar TOF compared to that of catalyst 4 when oxygen evolution was driven by CAN (Table 2.1). At these conditions catalyst 2 demonstrated a significantly reduced activity, presumably due to decreased stability and/or increased redox potentials of the complex at pH 1, where the carboxamide ligand can be protonated. Addition of more CAN to the catalytic mixture of 4 after 75 min of catalysis resulted in no further oxygen evolution, indicating that the observed decrease in the reaction rate over time is due to catalyst decomposition rather than degradation or depletion of the oxidant.$^{88,95}$

![Figure 2.11: CV of a 0.1 mM solution of complex 4 in phosphate buffer (0.1 M, pH 7) containing 10% MeCN. Five CV cycles were recorded in the presence (black) and absence (red) of the catalyst.](image-url)
Table 2.1. Catalytic activity of catalysts 1, 2 and 4 for water oxidation when driven by CAN or visible light.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TON (after 60 min)</th>
<th>Maximum TOF (min⁻¹)</th>
<th>O₂ yield (% after 60 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CAN</td>
<td>Light</td>
<td>CAN</td>
</tr>
<tr>
<td>1</td>
<td>980</td>
<td>80</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
<td>50</td>
<td>1.3</td>
</tr>
<tr>
<td>4</td>
<td>700</td>
<td>73</td>
<td>70</td>
</tr>
</tbody>
</table>

During the light-driven water oxidation experiments catalysts 1 and 4 displayed nearly identical TONs, while the TON for catalyst 2 was ca. 1.5 times lower. Surprisingly, all catalysts demonstrated a constant rate for oxygen evolution before reaching the maximum TON. The nearly identical steady-state TOFs for all catalysts could indicate formation of a single catalytically active species under the employed conditions, e.g. by hydrolysis of the carboxamide bonds in catalysts 2 and 4, leading to formation of catalyst 1. However, this would be inconsistent with the lower maximum TON for catalyst 2 compared to catalysts 1 and 4. Therefore, it is more likely that under the employed conditions oxygen evolution is limited by the rate of photochemical generation of the [Ru(III)(bpy)₂(bdc)]³⁺ oxidant.
2.3. Conclusions

A novel dinuclear Ru-based water oxidation catalyst 4 was synthesized and characterized both in the solid state and in solution under conditions relevant for chemical and photochemical water oxidation. Interactions of the catalyst and the employed co-solvent (MeCN) were studied in detail by electrochemical and spectroscopic techniques. Importantly, several of the reported WOCs require a co-solvent to be fully solubilized in water, which is necessary for carrying out the catalytic activity studies. These interactions greatly increase the complexity of the analytical data, potentially leading to its misinterpretation. The current study demonstrates qualitative and quantitative analysis of such data, providing an aid for evaluation of the redox properties for other WOCs. The catalytic activity of the new catalyst was evaluated in comparison to the activities of the structurally-related catalysts 1 and 2. As a result, comparable TONs and TOFs were obtained, demonstrating viability of the employed approach for linking of two catalytic units via a coordinating carboxamide ligand.
3. Chemical and Photochemical Water Oxidation Mediated by an Efficient Single-Site Ruthenium Catalyst (Paper II)

3.1. Introduction

A number of Ru WOCs containing 1H-benzimidazole-based ligands has recently been prepared by the Åkermark group. In these catalysts, the 1H-benzimidazole functionality was demonstrated to act as a robust negatively-charged N-donor ligand that is able to stabilize the metal center at high oxidation states, a feature that is crucial for water oxidation catalysis. The benzimidazole functionality could also act as a proton-transfer mediator, allowing ligand-based PCET that would lower the potentials of the relevant redox couples of the catalysts. Moreover, the redox non-innocence of the 1H-benzimidazole has been demonstrated and proposed to improve the stability of these WOCs.

In the current work, a related Ru-based WOC was prepared, inspired by the previously reported catalyst [RuIII(hpbc)(pic)3] (5, \( \text{H}_3\text{hpbc} = 2-(2\text{-hydroxyphenyl})-1H\text{-benzo}[d]\text{imidazole}-7\text{-carboxylic acid}, \) Figure 3.1). The phenolic functionality in \( \text{H}_3\text{hpbc} \) was substituted with benzoate, resulting in the new tridentate ligand \( \text{H}_3\text{cbc} \) (2-(2-carboxyphenyl)-1H-benzo[d]imidazole-4-carboxylic acid). The corresponding Ru-complex \( [\text{RuIII(Hcbc)(pic)}_3]^+ \) was then synthesized and evaluated for chemical and photochemical water oxidation and mechanistic insights into the catalytic cycle of water oxidation by 5 was provided through DFT calculations.

![Figure 3.1: Structures of the previously synthesized complex 5 and the newly evaluated complex 6.](image)

5

6
3.2. Results and Discussion

3.2.1. Synthesis and Characterization

The proposed H$_3$cbc ligand was synthesized in one step via reductive cyclization between 2-amino-3-nitrobenzoic acid and 2-carboxybenzaldehyde (Figure 3.2). The corresponding Ru$^{III}$ complex 6 ([Ru$^{III}$Hcbc](pic)$_3$Cl) was subsequently synthesized by refluxing a methanolic solution of H$_3$cbc, [Ru(DMSO)$_4$Cl$_2$] and NEt$_3$, followed by addition of 4-picoline. The complex was isolated from the reaction mixture by precipitation with water and purified by preparative thin-layer chromatography. The structure of complex 6 was confirmed by $^1$H NMR (after in situ reduction to the Ru$^{II}$ state with ascorbic acid), IR, ESI-HRMS, and elemental analysis.

The electrochemical properties of complex 6 were investigated by CV and DPV using a one-compartment three electrode cell, as described in Chapter 2 (all potentials were converted to vs. NHE). The solution-based studies were conducted in either 0.1 M TfOH (pH 1.0) or 0.1 M phosphate buffer (pH 6.0 or 7.2). Due to limited solubility of the catalyst in water, 2,2,2-trifluoroethanol (TFE) was employed as a co-solvent.

At pH 7.2, the CV of complex 6 displayed an electrocatalytic wave for water oxidation with an onset potential of ca. 1.04 V. In DPV, four peaks were observed and assigned to the Ru$^{II/III}$ (0.06 V), Ru$^{IV/III}$ (0.51 V and 0.68 V), and Ru$^{V/IV}$ (1.04 V) redox couples, based on comparison to the redox potentials obtained from the DFT calculations (vide infra).

3.2.2. Catalytic Studies

The catalytic activity of complex 6 for chemically-driven water oxidation was studied at pH 1.0 and pH 7.2 using CAN and [Ru(bpy)$_3$]$^{3+}$ as sacrificial oxidants, respectively (Figure 3.3a–d). When driven by CAN at pH 1.0, complex 6 displayed moderate stability with a maximum TON of 360 (at [6] = 1 µM), while the initial rate of oxygen evolution displayed linear dependence on both catalyst and oxidant concentrations. From these measurements, a moderate pseudo-first order catalytic rate constant was calculated ($k \approx 0.04$ s$^{-1}$, at [CAN] = 100 mM). At neutral pH when driven by [Ru(bpy)$_3$]$^{3+}$ the catalyst demonstrated similar TONs at [6] = 0.33–3.3 µM, while the TON could be significantly increased up to 3100 upon dilution of
the catalyst to [6] = 0.033 µM. Similar to experiments with CAN, a linear dependence of the rate of oxygen evolution on the catalyst concentration was found and a pseudo-first order catalytic rate constant of 0.03 s⁻¹ was calculated.

Furthermore, the activity of catalyst 6 for light-driven water oxidation was studied at neutral pH with the use of [Ru(bpy)₃]²⁺ as photosensitizer and Na₂S₂O₈ as the sacrificial electron acceptor (Figure 3.3e, see Section 1.3.1 for details.

**Figure 3.3:** Oxygen evolution by complex 6 (varying concentrations) during the catalytic experiments with 100 mM CAN (a), 10 mM [Ru(bpy)₃]³⁺ (c), and light-driven experiments with 0.6 mM [Ru(bpy)₃]²⁺ and 20 mM Na₂S₂O₈ (e). The catalytic experiments were performed at pH 1.0 (0.1 M TfOH) for CAN and at pH 7.2 for [Ru(bpy)₃]³⁺ oxidant/photosensitizer with 2.5% TFE as co-solvent. Dependence of the initial rate of O₂ evolution on the catalyst concentration is shown for catalytic experiments with CAN (b) and [Ru(bpy)₃]³⁺ (d).
for details). As for the chemically-driven water oxidation, an increase of the TON of the catalyst was observed when decreasing its concentration, resulting in a maximum TON of 330 at pH 7.2 and 600 at pH 6.0 ([6] = 0.33 µM). The observed increase in the TON upon dilution of the catalyst for all experiments is in line with previous observations for other WOCs and is likely due to the decrease in the rate of the bimolecular decomposition pathways. In case of the light-driven water oxidation at pH 6.0, the increased TON can also be explained by the increased stability of the employed photosensitizer at these conditions. Summary of the maximum TONs of catalyst 6 and the related catalysts 1 and 5 is provided in Table 3.1.

### Table 3.1. Comparison of maximum TON for chemically- or light-driven water oxidation by catalysts 1, 5, and 6.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Maximum TON under optimized conditions (concentration of the catalyst, µM)</th>
<th>[Ru(bpy)]3+/Na2S2O8/light</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAN [Ru(bpy)]3+/[Ru(bpy)]2+/Na2S2O8/light</td>
<td>980 (4)</td>
<td>80 (40)</td>
</tr>
<tr>
<td>1a</td>
<td>4000 (0.033)</td>
<td>–</td>
</tr>
<tr>
<td>5b</td>
<td>3100 (0.033)</td>
<td>330 (0.33)</td>
</tr>
<tr>
<td>6</td>
<td>360 (1)</td>
<td>–</td>
</tr>
</tbody>
</table>

a: from Ref. 97; [RuIII(bpy)2(bdc)]2+ was used as a photosensitizer.
b: from Ref. 96a.

Similar to the related polypyridyl WOCs, catalyst 6 has to undergo a picoline-water exchange in order to enter into the catalytic cycle. The catalytically active Ru-aqua species [RuIII(Hcbe)(pic)2(OH2)]+ (m/z 604.0282, 7d or 7e, vide infra) could be detected in the neutral aqueous solution of catalyst 6 by ESI-MS, implying that the picoline-water exchange could occur already at the RuIII oxidation state of the catalyst. Furthermore, analysis of the catalytic reaction mixture of 6 with [Ru(bpy)]3+ as sacrificial oxidant revealed a peak with m/z 601.1095, which could be assigned to a high oxidation state Ru-oxo intermediate [RuVI(Hcbe)(pic)2(O)2 + H+]+ (10d or 10e, vide infra).

3.2.3. Computational Studies

DFT calculations using continuum solvation model were performed in order to gain insight into the redox properties and the ligand exchange reactions for catalyst 6 under the catalytic conditions (neutral pH). The picoline-water exchange for complex 6 at RuIII oxidation state can involve either equatorial or axial picoline, resulting in formation of [(Hcbe)RuIII(pic)2(OH2)]+ species 7b or 7c, respectively (Figure 3.4). Similar to complex 5, both reactions are endergonic, while exchange of the equatorial picoline is thermodynamically favourable by 3.5 kcal mol−1. Consequently, formation of complex 7b with pK_a = 8.9 for the coordinated water is expected to be favourable under the
The reduction potentials for species 6, 7b, and 7c were calculated with \( E(\text{Ru}^{III/II}) = -0.08, -0.11, \) and \(-0.01 \) V, respectively, that is similar to the experimentally observed \( E_p(\text{Ru}^{III/II}) = 0.06 \) V (Table 3.2). The above calculations suggest that species 6 and 7b are likely to be dominant in solution under the studied conditions.

A one-electron oxidation of RuIII-aqua species 7b and 7c was found to be coupled to the release of two protons, resulting in formation of RuIV-oxo species 8b and 8c, respectively. The calculated reduction potentials for these species, 0.77 and 0.62 V, were in reasonable agreement with the experimentally observed values of 0.68 and 0.51 V. Complexes 8b and 8c were found to be close in energy, while based on the spin density distribution the RuIV=O bond in these species is better described as a Ru-oxyl radical (RuII–O•). The same (partly) radicaloid character of the Ru-oxo species was also observed for the other intermediates at higher oxidation states.

Table 3.2. Experimental and calculated redox potentials for the Ru-species derived from complex 6.

<table>
<thead>
<tr>
<th>Redox couple</th>
<th>Experimental redox potentials (V vs. NHE)</th>
<th>Calculated redox potentials (V vs. NHE) for species:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>RuIII/II</td>
<td>0.06</td>
<td>-0.08</td>
</tr>
<tr>
<td>RuIV/III</td>
<td>0.51, 0.68</td>
<td>1.20</td>
</tr>
<tr>
<td>RuVI/IV</td>
<td>1.04</td>
<td>-</td>
</tr>
<tr>
<td>RuVI/V</td>
<td>-</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The following one-electron oxidation of 8b and 8c to the formal RuV oxidation state species 9b and 9c was calculated to occur at 1.12 and 1.11 V, respectively. The one-electron oxidation for complex 8b at neutral and basic pH is concomitant with the transfer of a proton (PCET) from the Hecb2− ligand, based on the \( pK_a = 6.8 \) of complex 9b. On the other hand, oxidation of 8c to 9c at neutral pH is not proton-coupled, as the later species were calculated to have significantly higher \( pK_a = 8.9 \). Given the similar values of the calculated oxidation potentials for 8b and 8c, it is reasonable that a single DPV peak with \( E_p = 1.04 \) V was observed experimentally for the RuVI/IV couple. Further one-electron oxidation of 9b and 9c to the formal RuVI oxidation state species 10b and 10c was calculated to occur at 1.40 and 1.50 V, respectively, which is in contradiction to the experimentally observed value of 1.04 V for the onset potential of the electrocatalytic water oxidation.

As was mentioned in Section 3.2.2, ESI-HRMS measurements suggest that RuIII(OH)2 and RuVI(O)2 species could be formed under the catalytic conditions. Therefore, coordination of a second water molecule to the metal center was investigated computationally for the Ru(OHn) complexes at different
oxidation states. Addition of a second water molecule to the dominant \( \text{Ru}^{III}(\text{OH}_2) \) species 7b to form \( \text{Ru}^{III}(\text{OH}_2)(\text{OH}) \) species 7d is concomitant with dissociation of the benzoate ligand from the metal center and formation of a hydrogen bond between the coordinated water and the pendant carboxy group. However, this process was found to be unfavourable (endergonic by 7.0 kcal mol\(^{-1}\)). At higher oxidation states, a similar displacement of the carboxylate group takes place while the reaction is more thermodynamically favourable: close to isogonic at \( \text{Ru}^{IV} \) and exergonic at the \( \text{Ru}^{V} \) and \( \text{Ru}^{VI} \) oxidation states. Both \( \text{Ru}^{IV} \)- and \( \text{Ru}^{V} \)-aqua species can therefore favour formation of the Ru-diaqua complexes during catalysis, however, we tentatively propose that under the catalytic conditions oxidation of the complex to the \( \text{Ru}^{V} \) state at ca. 1.1 V outruns coordination of the second water molecule to the \( \text{Ru}^{IV} \)-aqua species, and the \( \text{Ru}^{V} \)-diaqua complex is formed. Among the two isomers of this complex, 9d with two axial picolines is 4.1 kcal mol\(^{-1}\) lower in energy than 9e, in which the two picolines occupy axial and equatorial positions. Formation of 9d is then followed by a one-electron one-proton oxidation, resulting in formation of the \( \text{Ru}^{VI}(\text{O})_2 \) species 10d with a reduction potential of 0.91 V. The latter value is lower than the \( \text{Ru}^{VI}/\text{Ru}^{V} \) redox potential for Ru-aqua complexes 10b/9b and is in better agreement with the observed onset potential of electrocatalytic water oxidation. This supports that the \( \text{Ru}^{VI}(\text{O})_2 \) species is the key intermediate in the catalytic cycle and is likely responsible for the O–O bond formation.

Figure 3.4: Selected optimized structures for the \( \text{Ru(OH}_n \) and \( \text{Ru(OH}_n)_2 \) species, involved in water oxidation by catalyst 6. Spin densities for selected atoms are in grey italic. For the structures in the lower row the energy in kcal mol\(^{-1}\) relative to the structures in the upper row are specified.
3.2.4. Proposed Catalytic Cycle

A catalytic cycle for water oxidation by complex 6 was proposed based on the presented experimental and computational results (Figure 3.5). The isolated complex 6 enters the catalytic cycle upon equatorial picoline–water exchange and formation of the Ru^{III}(OH_2) species 7b. This intermediate undergoes two consecutive one-electron oxidation steps, coupled to abstraction of two protons upon oxidation to the Ru^{IV}(O) species 8b and of one proton upon oxidation to the Ru^{V}(O) species 9b. The later species is then transformed into the Ru^{V}(O)_2 species 9d upon displacement of the benzoate ligand by a second water molecule. Finally, complex 9d undergoes one-electron one-proton oxidation to the Ru^{VI}(O)_2 species 10d, followed by O–O bond formation and release of O_2 upon one-electron oxidation of the initially formed hydroperoxide species.

3.3. Conclusions

A new Ru-based water oxidation catalyst (6) was prepared and its activity for chemically- and light-driven catalytic water oxidation was investigated. Under the studied conditions, the catalyst demonstrated similar performance to the related WOCs 1 and 5. A catalytic cycle for water oxidation by 6 was proposed based on the experimental results and DFT calculations, suggesting that the catalyst operates via an unusual catalytic route, which includes for-
Formation of a Ru-diaqua species. Formation of this complex is likely favoured due to the highly-strained nature of the developed Hbc²⁻ ligand that allows for stabilization of the Ru-diaqua species by hydrogen bonding between one of the coordinated water molecules and the pendant carboxylate group.
4. Highly Active Ruthenium-Based Water Oxidation Catalyst with an Easy Access to the Catalytically Active Species (Paper III)

4.1. Introduction

A new family of Ru-based complexes containing pentadentate equatorial ligands has recently been introduced by Llobet and co-workers. The first member of this family of complexes, [Ru\textsuperscript{II}(tda)(py)\textsubscript{2}] (11, Figure 4.1), initially demonstrated no activity for electrocatalytic water oxidation. However, the catalytically active form of this complex could be generated by oxidation of 11 to the Ru\textsuperscript{IV} state, which is followed by slow coordination of water to the metal center at neutral medium or more rapid coordination at higher pH.

![Figure 4.1: Structures of the previously reported complexes 11 and 12, and the complexes described in the current work (13\textsuperscript{II}, 13\textsuperscript{III}, and 14).](image)
The resulting catalyst [Ru\textsuperscript{IV}(O)(tda)(py)\textsubscript{2}] (12, Figure 4.1) demonstrated a record-high activity for electrocatalytic water oxidation with a TOF\textsubscript{max} ≈ 50 000 s\textsuperscript{-1} at pH 10 (determined by FOWA) and high longevity under bulk electrolysis conditions when immobilized on an electrode surface (TON ≈ 1 000 000).\textsuperscript{99} Moreover, catalyst 12 could carry out light-driven water oxidation in solution with a [Ru\textsuperscript{II}(bpy)\textsubscript{3}]\textsuperscript{2+}-type photosensitizer\textsuperscript{100} or when introduced in a hybrid photoanode.\textsuperscript{101} The impressive performance of the catalyst was attributed to the decreased redox potentials of the complex due to the ability of the tda\textsuperscript{2−} ligand to facilitate formation of seven-coordinated Ru-species, while a pendant carboxylate group accelerated the rate-limiting O–O bond formation step via i-APT. Nevertheless, a significant drawback of the catalyst is the incomplete activation of complex 11, rendering \(\frac{2}{3}\) of the Ru complex inactive during catalysis. The incomplete activation also obscured mechanistic and activity studies, and reduced performance of the hybrid photoanodes based on 11/12 due to the decrease in catalyst loading upon activation.\textsuperscript{101}

In the current work we sought to address the incomplete activation of 11 by preparing the related complex 13, which is based on a tda\textsuperscript{2−}-inspired ligand. In the new ligand two of the pyridines in tda\textsuperscript{2−} were substituted by 1-methylbenzimidazoles, similar to the previously described Mebimpy ligand (see Section 1.3.3). Coordination of the proposed ligand to Ru at high oxidation states was expected to furnish heptacoordinated complexes, where the equatorial ligand is coordinated to the metal center in a κ-N\textsuperscript{3}O\textsuperscript{2} fashion, similar to complex 11 at the Ru\textsuperscript{III} and Ru\textsuperscript{IV} states (Figure 4.2). For complex 13, however, the heptacoordinated species would have highly strained geometry due to the relative position of the carboxylate groups and formation of distorted six-membered rings. Such distortion was expected to weaken the Ru–O bonds in the complex, allowing easier dissociation of one of the carboxylate groups and formation of the catalytically active Ru-aqua species 14. Herein, a detailed spectroscopic and electrochemical study of complex 13 at Ru\textsuperscript{II} and Ru\textsuperscript{III} states (13\textsuperscript{III} and 13\textsuperscript{II}, respectively) and the active catalyst 14 is presented.
4.2. Results

4.2.1. Synthesis and Characterization

The proposed H₂mcbp (mcbp²⁻ = 2,6-bis(1-methyl-4-(carboxylate)-benzimidazol-2-yl)pyridine) ligand was synthesized starting from 3-fluoro-2-nitrobenzoic acid, which was protected as a methyl ester and transformed into the corresponding nitroaniline via ipso-substitution of the fluorine by methylamine (Figure 4.3). The following reductive cyclization with 2,6-pyridinecarboxaldehyde furnished the desired ligand upon hydrolysis of the methyl ester. The RuII complex (13II, [RuII(mcbp)(py)₂]) was synthesized by prolonged heating of a EtOH/water solution containing H₂mcbp, pyridine, [Ru(DMSO)₄Cl₂], and NEt₃, followed by slow cooling of the reaction mixture which allowed direct isolation of 13II as X-ray quality crystals. The structure of 13II was confirmed by 1D and 2D NMR, SC-XRD, ESI-HRMS, EPR, ATR-FTIR, UV-vis and elemental analysis. The corresponding RuIII complex 13III ([RuIII(Hmcbp)(py)₂](ClO₄)₂) was subsequently synthesized by oxidation of 13II with 1 equivalent of CAN, followed by recrystallization of the crude product from an aqueous TFE/TfOH mixture in the presence of NaClO₄. The structure of the complex was confirmed by ¹H NMR, SC-XRD, EPR, ATR-FTIR, UV-vis, and elemental analysis. Moreover, the complex at the RuIII oxidation state was also isolated as X-ray quality crystals with OTf⁻ as well as PF₆⁻ counterions (13III(OTf)₂ and 13III(PF₆)₂). Unfortunately, all attempts to isolate the complex at the RuIV oxidation state were unsuccessful, presumably due to slow oxidation of the employed organic co-solvents by the RuIV species.

¹H NMR of a solution of complex 13II in DMSO-d₆ displayed a diamagnetic spectrum typical for a d⁶ RuII species. Initially a mixture of at least two components was observed, but a clear ¹H NMR spectrum could be obtained in the presence of D₂SO₄. The integrity of the complex at these conditions was confirmed by HPLC-ESI-MS, while formation of DMSO-coordinated species was ruled out based on insignificant changes between the potentials of the RuIII/II couple of 13III in aqueous solutions, DMSO, and a DMSO/D₂SO₄ mixture.
mixture. The $^1$H NMR spectrum was then fully assigned with the aid of $^{13}$C NMR, $^1$H-$^1$H COSY and HSQC experiments, confirming the proposed structure (Figure 4.4). $^1$H NMR of complex 13$^{II}$ displayed a typical paramagnetic spectrum for a d$^5$ Ru$^{III}$ species with broadened and shifted signals. Addition of excess ascorbic acid resulted in full reduction of the complex to the diamagnetic Ru$^{II}$ state with the $^1$H NMR spectrum identical to that of complex 13$^{II}$.

Single crystal X-Ray analysis

The solid-state structures of complex 13 at the Ru$^{II}$ and Ru$^{III}$ oxidation states were evaluated by SC-XRD analysis (Figure 4.5). Complex 13$^{II}$ displayed distorted octahedral geometry with a κ-N$^3$O coordination mode of the mcbp$^2-$ ligand and the Ru–N(O) bond lengths were similar to those observed for catalyst 11 and related complexes. The X-ray structures of complexes 13$^{III}$ and 13$^{III}$($PF_6$)$_2$ displayed a disorder of the carboxylate groups into two positions and the structure of 13$^{III}$($OTf$)$_2$, which did not display such a disorder, is used for further discussion. The Hmcbp$^-$ ligand in 13$^{III}$($OTf$)$_2$ adapts a κ-N$^3$O coordination mode with 3.02 Å interatomic distance between the metal center and the uncoordinated protonated carboxylate group, which is in contrast to the tda$^2-$ ligand in [Ru$^{III}$($tda$)(py)$_2$]$^+$ that is coordinated to the metal center in a κ-N$^3$O$^2$ fashion. Consequently, a highly distorted octahedral geometry is observed for 13$^{III}$($OTf$)$_2$ with a large O–Ru–N outer equatorial angle of 125°. It is important to mention that such a low-symmetry structure for 13$^{III}$($OTf$)$_2$ may not be preserved in solution at neutral pH, where the fully deprotonated ligand can adapt a κ-N$^3$O$^2$ binding mode or display fast coordination/dissociation of the two carboxylate groups.
4.2.2. Electrochemical and Spectroscopic Studies at pH 2–7

The redox properties of the isolated complexes were investigated by CV, DPV, controlled potential electrolysis (CPE), spectroelectrochemistry, UV-vis, and EPR (recorded at 4 K with an X-band spectrometer). The electrochemical measurements were typically performed in phosphate buffer solutions (0.1 ionic strength) using a one-compartment three-electrode cell with glassy carbon disk working electrode \((d = 1 \text{ mm})\), mercury–mercurous sulfate reference electrode (MSE, Hg/Hg\(_2\)SO\(_4\), sat. K\(_2\)SO\(_4\)) and platinum disk counter electrode. CPE was performed in a two-compartment cell with a large area working electrode (glassy carbon or reticulated vitreous carbon) and the reference electrode in one compartment and a platinum mesh counter electrode in the other compartment. Spectroelectrochemical measurements were performed using an optically-transparent thin layer electrochemical (OTTLE) cell with platinum mesh working and counter electrodes and an Ag wire pseudo-reference electrode. During spectroelectrochemical measure-

\[13^{\text{II}} \quad 13^{\text{III}}\text{(OTf)}_2\]
ments the potential of the working electrode was swept with 0.002 V s\(^{-1}\) scan rate between the desired values while recording the UV-vis spectra of the solution in contact with the working electrode. All potentials were converted from vs. MSE to vs. NHE by adding 0.650 V.

**Redox properties of complex 13\(\text{II}\)**

The CV of complex 13\(\text{II}\) at pH 2.0 displayed two quasi-reversible one-electron waves with \(E_{1/2} = 0.767\) V and 1.357 V, assigned to the Ru\(\text{III/II}\) and Ru\(\text{IV/III}\) couples, respectively (Figure 4.6). The one-electron nature of the couples was supported by the peak separation in CV (\(\Delta E_p = 0.059\) V for Ru\(\text{III/II}\) and 0.068 V for Ru\(\text{IV/III}\)), peak width at half-height in DPV (\(W_{1/2} = 0.096\) V for Ru\(\text{III/II}\) and 0.094 V for Ru\(\text{IV/III}\)), and CPE at 1.05 V for the Ru\(\text{III/II}\) couple, upon which transfer of 1.0 electrons was observed. Spectroelectrochemical measurements of 13\(\text{II}\) at pH 2.0 demonstrated complete

![Figure 4.6: CV (black) and DPV (dashed red) of 0.2 mM solution of complex 13\(\text{II}\) in 0.1 IS P-buffer (pH 2.0, 5.0 and 7.0). Three CV cycles were recorded and the last cycle is presented.](image)

\(\text{§§ In theory, for diffusional } n\text{-electron reversible couples } \Delta E_p = 0.059/n \text{ V and } W_{1/2} = 0.094/n \text{ V.}\)
chemical reversibility of the Ru$^{III/II}$ and Ru$^{IV/III}$ couples. During the anodic scan, bleaching of the MLCT band of the Ru$^{II}$ species ($\lambda_{\text{max}} = 495$ nm) was observed upon oxidation of the Ru$^{II}$ complex to the Ru$^{III}$ state, followed by formation of a Ru$^{IV}$ species with two isosbestic points (313 and 399 nm) at higher potentials. The reverse CV scan resulted in replenishment of the UV-vis spectra of both the Ru$^{III}$ and Ru$^{II}$ species. Interestingly, in dry MeCN the potential of the Ru$^{III/II}$ couple for 13$^\text{II}$ was shifted in the cathodic direction by K. P. V, but gradually returned to the potential values observed in aqueous solutions upon addition of water, highlighting the importance of the hydrogen-bonding interactions for influencing the redox properties of complex 13.

Upon increasing the pH, an unexpected pH-dependence of the redox potentials for the Ru$^{III/II}$ and Ru$^{IV/III}$ couples of 13 was observed with the slopes of $-0.019$ and $-0.030$ V per pH unit, respectively, while the slopes of $-0.059 \cdot m$ V per pH unit were expected according to Eq. 2.3. This behaviour can be explained by the close-lying pK$\alpha$ values for complex 13 at the Ru$^{II}$, Ru$^{III}$, and Ru$^{IV}$ oxidation states. In this case, the pH-dependence of the observed redox potentials can be described by Eq. 4.1, where $E^\circ$(Ru$^{ox/\text{red}}$) is the standard redox potential of a redox couple under investigation at pH = 0.

$$E^\circ(\text{Ru}^{ox/\text{red}}) = E^\circ(\text{Ru}^{ox/\text{red}}) - 0.059 \cdot \log \left( \frac{[\text{H}^+]}{[\text{H}^+] + K_a^{\text{ox}}} \right)$$

(4.1)

Fitting Eq. 4.1 to the experimental data obtained from CV (for Ru$^{III/II}$ couple) and DPV (for Ru$^{IV/III}$ couple) revealed that complex 13 is protonated at low pH with pK$\alpha$ = 4.0, 3.3, and 2.1 for the Ru$^{II}$, Ru$^{III}$, and Ru$^{IV}$ species, respectively. Based on the crystal structures of 13 and previous observations for the related carboxylate complexes the protonation is likely to happen at the pendant carboxylate group of the mcbp$^{2-}$ ligand.

At pH > 5 an electrocatalytic wave was observed in the CV of 13 at high potentials, which increased in intensity upon increasing the pH. Upon repetitive cycling at pH 7.0 a growth of the catalytic wave was observed, concomitant with formation of a new anodic wave with $E_{\text{pa}} \approx 0.95$ V. This behaviour is consistent with formation of the electrocatalytically active Ru-aqua species when 13 is oxidized to the Ru$^{IV}$ state already on the time-scale of the CV measurements with 0.05 V s$^{-1}$ scan rate (vide infra).

**Redox properties of complex 13$^{III}$**

As expected, the CV of complex 13$^{III}$ at pH 2.0 displayed identical voltammetric response to that of the Ru$^{II}$ complex 13$^{II}$. The oxidation state of the metal center in 13$^{III}$ was confirmed by CPE, UV-vis, $^1$H NMR, and EPR. CPE of 13$^{III}$ at 0.45 V resulted in transfer of 0.82 electrons and its UV-vis spectrum was identical to that of the Ru$^{III}$ species generated from the Ru$^{II}$
complex 13II during spectroelectrochemical measurements. The presence of paramagnetic RuIII species was further confirmed by 1H NMR and EPR.

Surprisingly, complex 13III was found to be unstable upon increasing pH and stopped flow UV-vis measurements were used to monitor the change in solution composition over time upon pH jump from 2.0 to 7.0 (Figure 4.7). During the course of 250 min after the pH jump an MLCT band with $\lambda_{\text{max}} = 479$ nm appeared, identical to that of the RuII complex 13II at pH 7.0, but with twice as low concentration compared to the initial RuII species. Furthermore, during the reaction complete disappearance of the RuII species was observed by EPR, while formation of new redox couples could be observed by CV. These couples were assigned to the catalytically active Ru-aqua species, based on comparison to the voltammograms of stoichiometrically generated complex 14 (vide infra).

The above observations suggest a net disproportionation reaction of the RuIII species into RuII and RuIV=O species.*** This transformation is further supported by the nearly complete overlap between the UV-vis spectrum of the solution of 13III at 250 min after a pH jump and the sum of the UV-vis spectra of complexes 13II and 14 (normalized to the half concentration of 13III, Figure 4.7b). The direct disproportionation of the RuIII species is, however, unlikely due to the large difference between the potentials of the RuIII/II and RuIV/III couples of complex 13 ($\Delta E_{1/2} \approx 0.6$ V). Therefore, we propose that at pH 7.0 the RuIII species are slowly transformed into the RuIII–OH species (Eq. 4.2). In the RuIII and RuIII–OH mixture, the latter is easier to oxidize since $E_{\text{pa}}$(RuIV=O/RuIII–OH) = 0.95 V is sufficiently lower than $E_{1/2}$(RuIV/III) = 1.32 V and the solution electron transfer (SET) reaction takes place ac-

*** The protonation state of the Ru-aqua species is assigned based on the Pourbaix diagram of complex 14 (see Section 4.2.3).
cording to Eq. 4.3. The reverse reaction, that is reduction of RuIV=O by RuII species, is thermodynamically possible since \( E_{pc}(\text{RuIV}=\text{O}/\text{RuII}–\text{OH}) \approx E_{pc}(\text{RuIV}/\text{III}) \approx 0.7 \text{ V} \), but the overall equilibrium is shifted towards the products of the forward reaction due to the large difference between \( E_{pa}(\text{RuIV}=\text{O}/\text{RuIII–OH}) \) and \( E_{1/2}(\text{RuIV}/\text{III}) \) values. Importantly, although the described transformations include coordination of water to the metal center of 13 already at the RuII oxidation state, this reaction is sufficiently slow and does not affect the electrochemical response from 13II at pH 7.0 on the timescale of the CV and spectroelectrochemical measurements. At lower pH the described transformations become less favourable as both of them require abstraction of a proton, while the driving force for the SET reaction decreases due to the decreasing difference between \( E_{pa}(\text{RuIV}=\text{O}/\text{RuIII–OH}) \) and \( E_{1/2}(\text{RuIV}/\text{III}) \).

\[
\begin{align*}
\text{RuII} + \text{H}_2\text{O} & \rightleftharpoons \text{RuII}–\text{OH} + \text{H}^+ \quad (4.2) \\
\text{RuIII} + \text{RuIII–OH} & \rightarrow \text{RuII} + \text{RuIV}=\text{O} + \text{H}^+ \quad (4.3)
\end{align*}
\]

4.2.3. Evaluation of the Catalytically Active RuIV=O Species (14)

**Stoichiometric generation of complex 14**

Similar to the measurements at pH 2.0, spectroelectrochemical measurements of complex 13II at pH 7.0 between 0.52 V and 1.06 V demonstrated complete chemical reversibility of the RuIII/II couple with an observed \( E_{pc} \approx 0.65 \text{ V} \). When extending the studied potential range to the values where oxidation of 13 to the RuIV state can take place (1.00 to 1.40 V) a similar voltammetric response was obtained with one cathodic wave at a close potential (\( E_{pc} \approx 0.70 \text{ V} \), Figure 4.8a). However, the change in the UV-vis spectrum during the latter measurements was dramatically different (Figure 4.8b–e). Formation of the RuIV species could be observed during the anodic CV scan from 1.00 to 1.40 V, but the RuIII species were not replenished upon the cathodic scan from 1.40 to 1.00 V. Instead, the UV-vis spectrum continued to change with the same trend as upon the RuIII→RuIV transition. The cathodic scan from 1.00 to 0.50 V then demonstrated formation of new species, and the UV-vis spectra corresponded to neither RuII nor RuIII species observed previously at pH 7.0. We attribute these changes in the UV-vis spectra to formation of a RuIV species during the anodic scan above 1.00 V (Eq. 4.4), followed by fast transformation into the RuIV=O species (Eq. 4.5), which are reduced to the RuIII–OH species at significantly lower potentials (Eq. 4.6).

\[
\begin{align*}
\text{RuIII} – \text{e}^- & \rightarrow \text{RuIV} \quad (4.4) \\
\text{RuIV} + \text{H}_2\text{O} & \rightarrow \text{RuIV}=\text{O} + 2\text{H}^+ \quad (4.5) \\
\text{RuIV}=\text{O} + \text{H}^+ + \text{e}^- & \rightarrow \text{RuIII–OH} \quad (4.6)
\end{align*}
\]
For further studies, the catalytically active Ru IV=O complex 14 was generated stoichiometrically by CPE of a pH 7.0 solution of 13II at 1.40 V (Figure 4.9). During the electrolysis, accumulation of the catalytically active species 14 resulted in a rise of the catalytic current that reached a plateau upon complete transformation of 13II into 14. Thereafter, the electrolysis was terminated and the pH or concentration of the solution were adjusted to the desired values for further studies.

**Figure 4.8:** Spectroelectrochemical measurements of a 0.4 mM solution of complex 13II at pH 7.0. a) CV of complex 13II recorded with the use of the OTTLE cell with 0.002 V s⁻¹ scan rate. b-e) Change in the UV-vis spectra during spectroelectrochemical measurements in the specified potential ranges.
A comparison of the CVs of complex $13^{II}$ before and after CPE revealed full transformation of the initial complex to complex $14$ (Figure 4.10). Three new redox processes were observed: an irreversible couple with $E_{pa} = 0.952$ V and $E_{pc} = 0.709$ V, a lower intensity irreversible couple with $E_{pa} = 0.606$ V and $E_{pc} = 0.430$ V, and a quasi-reversible one-electron couple with $E_{1/2} = 0.202$ V ($\Delta E_p = 0.071$ V). The high intensity irreversible couple was assigned to the Ru$^{IV}$=O/Ru$^{III}$–OH transition based on the spectroelectrochemical measurements (Figure 4.11). During these measurements complete chemical reversibility of the Ru$^{IV}$=O/Ru$^{III}$–OH couple was observed with $\lambda_{max} = 307$ nm for the Ru$^{III}$–OH and $\lambda_{max} = 316$ nm for the Ru$^{IV}$=O species, highlighting the stability of the catalytically active complex $14$ under the employed conditions. Unfortunately, spectroelectrochemical characterization
of the lower intensity couples was prohibited by the narrow working potential window of the employed OTTLE cell. These couples were tentatively assigned to the Ru$^{	ext{III}}$–OH/Ru$^{	ext{II}}$–OH$_2$ transitions of two different isomers of the complex based on the charge balance with the Ru$^{	ext{IV}}$=O/Ru$^{	ext{III}}$–OH couple. Importantly, the electrochemical response of the stoichiometrically generated complex 14 is in line with formation of the Ru-aqua species observed during wide potential range CV measurements of complex 13$^{	ext{II}}$ and disproportionation of complex 13$^{	ext{II}}$, as described in the previous sections.

The Pourbaix diagram of complex 14 was constructed using CV and DPV data at pH 1–10 (Figure 4.13b). All Ru$^{	ext{III}}$–OH/Ru$^{	ext{II}}$–OH$_2$ and Ru$^{	ext{IV}}$=O/Ru$^{	ext{III}}$–OH couples displayed pH-dependence close to −0.059 V per pH unit at the studied pH range. This pH-dependence supports that water is coordinated to the metal center of the involved species, as the carboxylate groups of the mcbp$^2$ ligand are expected to be fully deprotonated at pH > 4 for all oxidation states of the complex. The Ru$^{	ext{V}}$=O/Ru$^{	ext{IV}}$=O couple was found to be pH-independent at neutral and basic pH with $pK_{\text{aH}} = 5.1$ for the Ru$^{	ext{IV}}$=O species.
Furthermore, complexes \( \text{Ru(II)} \) and \( \text{Ru(III)} \) were studied in buffered aqueous solutions by \( ^1H \) NMR and EPR. The \( ^1H \) NMR spectrum of \( \text{Ru(II)} \) in a pD 7.0 solution could be fully assigned based on the comparison to the \( ^1H \) NMR spectrum in DMSO/D\( _2 \)SO\( _4 \) mixture. Following CPE of complex \( \text{Ru(II)} \) for generation of Ru-aqua species \( \text{Ru(III)} \), the \( ^1H \) NMR spectrum displayed poorly resolved or broadened peaks, most likely due to the presence of paramagnetic \( \text{Ru(III)}-\text{OH} \) species. This species could be observed by EPR, displaying less symmetrical EPR spectrum compared to the spectrum of the non-aqua \( \text{Ru(II)} \) complex \( \text{Ru(III)} \) at pH 7.0. Reduction of complex \( \text{Ru(III)} \) with ascorbic acid furnished a \( ^1H \) NMR spectrum identical to that of the initial complex \( \text{Ru(II)} \). This suggests that on the timescale of the NMR measurements (ca. 3 min between addition of ascorbic acid and acquisition of the NMR data) water dissociates from the \( \text{Ru(II)}-\text{OH}_2 \) species, although this species is kinetically stable on the shorter timescale of the CV measurements. The \( ^1H \) NMR spectra of complex \( \text{Ru(III)} \) before and after reduction with ascorbic acid also displayed low intensity contaminant peaks. However, these peaks did not correspond to free pyridine, which is an expected product from decomposition of complexes \( \text{Ru(II)} \) and \( \text{Ru(III)} \).

**Catalytic activity of \( \text{Ru(III)} \) for water oxidation**

The CV of complex \( \text{Ru(III)} \) recorded up to 1.45 V displayed a characteristic elevated electrocatalytic current compared to complex \( \text{Ru(II)} \) (Figure 4.12a). Unlike for complex \( \text{Ru(II)} \), no changes in the redox couples was observed upon repetitive CV cycling except for a slight anodic shift due to the pH drop after reaching the potentials of electrocatalytic water oxidation. Moreover, no reverse loop for the catalytic current was observed, supporting that the active catalyst \( \text{Ru(III)} \) was generated stoichiometrically during CPE.

The electrocatalytic activity of \( \text{Ru(III)} \) for water oxidation was subsequently studied by FOWA, assuming rate-limiting O–O bond formation via WNA.

---

**Figure 4.12:** a) Three CV cycles of a 0.2 mM solution of \( \text{Ru(II)} \) before (black) and after CPE (red) at 1.40 V at pH 7.0. In the inset graph only the last CV cycle is presented. b) CVs of a 0.2 mM solutions of electrochemically generated complex \( \text{Ru(III)} \) at pH 7, 8, and 9.
The \( i-E \) response at the foot of the catalytic wave (\( E = 1.2-1.32 \) V) in the CV of 14 was analyzed according to Eq. 4.7, where \( i_p \) is the peak current of the catalytically active species taken from the anodic peak with \( E_{pa} = 0.95 \) V, \( k_{WNA} \) is the pseudo-first order catalytic rate constant, and \( E^{\circ,app} \) is the potential of the redox couple that onsets water oxidation (\( E^{\circ,app} = E^{\circ}(\text{Ru}^{V=O}/\text{Ru}^{IV=O}) = 1.40 \) V, obtained from the DPV measurements). The slope of the \( i/i_p \) vs. 1/(1 + \( \exp(F(E^{\circ,app} - E)/RT) \)) plot was then used to calculate \( k_{WNA} \) according to Eq. 4.7. The catalytic rate constant was found to be concentration- and scan rate–independent, which is in line with the proposed WNA mechanism for the rate-limiting step. For this mechanism, the relationship between the catalyst TOF and the applied overpotential is described by Eq. 4.8, according to which the TOF reaches its limiting value \( \text{TOF}_{\text{max}} = k_{WNA} \) at \( \eta \to \infty \). As a result of the above analysis, \( \text{TOF}_{\text{max}} \) values of \( 1.4 \pm 0.4 \times 10^3 \), \( 9.3 \pm 0.3 \times 10^3 \), and \( 4.2 \pm 1.5 \times 10^4 \) s\(^{-1} \) were calculated for complex 14 at pH 7.0, 8.0, and 9.0, respectively (Figure 4.12b). For the parent catalyst 12 similar \( \text{TOF}_{\text{max}} \) values were reported (8\times10^3, 2.5\times10^4, and 5\times10^4 s\(^{-1} \) at pH 7.0, 8.0, and 10.0, respectively).

\[
\frac{i}{i_p} = 4 \cdot 2.24 \frac{\sqrt{RT}}{F_{V}} k_{WNA} \frac{1}{1 + \exp\left(F(E^{\circ,app} - E)/RT\right)}
\]

(4.7)

\[
\text{TOF} = k_{WNA} \frac{1}{1 + \exp\left(F(E^{\circ,app} - E_{H_2O/O_2} - \eta)/RT\right)}
\]

(4.8)

The electrocatalytic activity of 14 was also studied on a longer timescale at pH 7.0 by CPE at 1.45 V. The amount of the evolved oxygen during electrolysis was monitored by a gas-phase Clark electrode and 98% faradaic efficiency was observed after CPE for 30 min. A TON = 9.3 was calculated for this experiment, based on the total amount of the catalyst in the anode compartment. Importantly, the CV of the solution before and after CPE demonstrated identical voltammetric response (after adjusting pH of the solution after CPE back to pH 7.0), supporting the stability of complex 14 under the catalytic conditions.

4.3. Discussion

Given the similar activity of catalysts 12 and 14 for electrocatalytic water oxidation, it is valuable to compare their redox properties along with the redox properties of the corresponding non-activated complexes 11 and 13. As evident from the simulated Pourbaix diagrams of the non-activated com-
plexes (Figure 4.13), both Ru$^{III/II}$ and Ru$^{IV/III}$ couples of complex 13 are shifted anodically by ca. 0.2–0.3 V compared to complex 11. The anodic shift could be attributed to the difference between the electronic properties of the N–N–N ligand cores in tda$^{2−}$ and mcbp$^{2−}$ ligands (tpy for complex 11 and Meimpy for complex 13). However, an opposite trend in the redox potentials was observed for the related complexes [Ru(tpy)(py)$_3$]$^{2+}$ and [Ru(Meimpy)(pic)$_3$]$^{2+}$, where the Ru$^{III/II}$ couple for the Ru(Meimpy) complex is shifted cathodically by ca. 0.25 V relative to the Ru(tpy) complex. This observation supports that the elevated redox potentials for complex 13 are indeed due to the reduced stabilization of the metal center by the more loosely coordinated mcbp$^{2−}$ ligand. This is also in line with the obtained crystal structure of complex 13$^{III}$, where the Hmcbp$^−$ ligand coordinates to the metal center in a κ-N$^3$O fashion, whereas the tda$^{2−}$ ligand adapts a κ-N$^3$O$^2$ coordination mode for complex 11 in the Ru$^{III}$ and Ru$^{IV}$ oxidation states.

![Simulated Pourbaix diagrams](image)

**Figure 4.13:** Simulated Pourbaix diagrams for non-activated (grey) and activated (red) Ru(mcbp) (a, 13 and 14) and Ru(tda) (b, 11 and 12) complexes. The pH-dependent thermodynamic potential for water oxidation is indicated by blue line.
The described weakening of the Ru–O bonds allows for easier access to the catalytically active Ru-aqua species for complex 13 compared to complex 11. Coordination of water to the metal center could be observed already at the RuII oxidation state for 13, whereas complex 11 was kinetically stable at this oxidation state. Moreover, a large difference between the rates of the catalysts’ activation was observed for the complexes at the RuIV oxidation state. For complex 11, a 10 h CPE at pH 7.0 was required to transform only 1/3 of the initial complex into the corresponding Ru-aqua species, whereas for complex 13 full activation could be achieved already on the timescale of the spectroelectrochemical measurements (ca. 4 min). Importantly, the slow and incomplete activation of 11 limits the performance of the 11-based hybrid photoanodes, where leaching of the complex from the electrode surface during its activation decreased the final catalyst loading. We expect this problem to be completely eliminated for hybrid photoanodes based on complex 13.

Comparing the Pourbaix diagrams of the activated catalysts 12 and 14 reveals a striking similarity of their redox properties. Herein, it is important to mention that assignment of the CV waves for catalyst 14 observed at pH 7.0 was extremely challenging due to overlap with the waves of the RuII/III and RuIV/III couples of the still present non-activated complex 11. In the previous work, the newly formed anodic \( E_{pa} \approx 0.9 \) V and cathodic \( E_{pc} \approx 0.7 \) V waves of 12 were assigned to the RuIV=O/RuIII–OH and RuIII–OH/RuII–OH2 couples, respectively. However, based on comparison with the voltammetric response from catalyst 14, these waves are likely to correspond to a single irreversible RuIV=O/RuII–OH couple, while the RuIII–OH/RuII–OH2 couple is entirely buried under the RuIII/RuII wave from complex 11. The presented Pourbaix diagrams also reveal peculiar coincidentally indistinguishable pK_a values for the RuIII–OH2 and RuIV=OH species, while no pK_a values could be observed for the protonation of the carboxylate groups of both the tda2− and mcbp2− ligands (likely due to their close values). Nevertheless, this behavior was also observed for the Ru-aqua species of the related [RuII(bda)(pic)2] and [RuII(tpc)(pic)2]+ (tpc = 2,2′:6′,2″-terpyridine-6-carboxylate) complexes, indicating that diminishing difference between the pK_a values is characteristic for such Ru-aqua species.

A catalytic cycle for catalyst 14 was devised based on combination of the obtained experimental data and the catalytic cycle established for catalyst 12 with the help of DFT calculations (Figure 4.14). Before entering the catalytic cycle, the isolated RuII complex 13 undergoes two one-electron oxidation steps to form the RuIV species, which is rapidly transformed into the catalytically active RuIV=O species 14. This species undergoes one-electron oxidation to form the key RuV=O intermediate, which is responsible for the rate-limiting O–O bond formation via WNA. As established for catalyst 12, the non-chelating carboxylate group of the equatorial ligand assists the O–O bond formation by simultaneous abstraction of a proton from the nucleo-
philic water molecule (i-APT mechanism). The formed Ru\textsuperscript{III}–OO\textsubscript{H\textsubscript{2}} species undergoes one-electron/one-proton oxidation to the Ru\textsuperscript{IV}–OO\textsubscript{H} species, for both of which the hydroperoxide protons are stabilized by the hydrogen bonding with the non-chelating carboxylate group of the mcbp\textsuperscript{2}\textsuperscript{+} ligand. The latter species then releases molecular oxygen, concomitant with reduction of the metal center to the Ru\textsuperscript{II} state, followed by association of water and formation of the Ru\textsuperscript{II}–OH\textsubscript{2} species. Finally, this species undergoes the two one-electron/one-proton oxidation steps, resulting in formation of the Ru\textsuperscript{IV}=O species, and completes the catalytic cycle.

4.4. Conclusions
Ru complex 13 based on a new pentadentate equatorial ligand was developed and isolated in the Ru\textsuperscript{II} and Ru\textsuperscript{III} oxidation states. The geometric considerations during the ligand design enabled complete transformation of complex 13 into the active catalyst 14, which was not possible for the parent catalyst 12. The redox properties of complexes 13, 13\textsuperscript{II}, and 14 were studied.
in detail by the electrochemical and spectroscopic techniques. The activity of catalyst 14 for the electrocatalytic water oxidation was evaluated, demonstrating similar TOF$_{\text{max}}$ values to that of the state-of-the-art catalyst 12.
5. Water Oxidation Mediated by Ruthenium Oxide Nanoparticles Supported on Siliceous Mesocellular Foam (Paper IV)

5.1. Introduction

Heterogeneous catalysts for water oxidation have been extensively studied in the past decades and have found commercial applications, e.g. in the PEM (polymer electrolyte membrane) water splitting cells. Heterogeneous WOCs based on both noble and abundant 1st-row transition metals have been developed, however, noble metal–based catalysts, such as RuO$_2$ and IrO$_2$, still largely outperform WOCs based on earth-abundant transition metals in terms of intrinsic activity and stability, in particular under acidic conditions. Nevertheless, given the high cost of RuO$_2$ and IrO$_2$, further improvement in their performance is of high value.

Recently, Åkermark and co-workers demonstrated that a Pd-based nanoparticulate catalyst immobilized on an amino-functionalized mesocellular siliceous foam (MCF) can efficiently catalyze both chemically- and light-driven water oxidation. In the current work, we sought to prepare a related nanoparticulate RuO$_2$-based WOC, stabilized by immobilization on a functionalized MCF. In this catalyst, an organic linker is grafted onto the MCF surface to facilitate loading of the metal precursor on the support, followed by reduction of the precursor to form the nanoparticulate catalyst. A new oxidatively-stable pyridine-based linker was developed in order to avoid side-reactions during the precursor loading and catalysis, which are to be expected for the commonly used MCF linkers based on primary amines. Using the new linker, an active RuO$_2$ WOC was prepared and evaluated for chemically- and light-driven water oxidation.

5.2. Results and Discussion

5.2.1. Synthesis and Characterization

The desired nanoparticulate RuO$_2$ catalyst was prepared according to the synthesis outlined in Figure 5.1. The pyridine-based linker 1-(pyridin-3-yl)-3-(3-(triethoxysilyl)propyl)urea (PPU) was synthesized from triethoxy(3-
isocyanatopropyl)-silane and 3-aminopyridine, which slowly react in CH₂Cl₂ at room temperature, producing the desired linker in quantitative yield. The MCF support was synthesized according to a previously published procedure. Subsequently, a mixture of PPU and MCF was refluxed in toluene for 48 h, resulting in grafting of the linker onto the heterogeneous support through condensation between the triethoxysilyl groups of PPU and silanol groups present on the MCF surface. The PPU-functionalized MCF (PPU-MCF) was loaded with Ru³⁺ by stirring a mixture of RuCl₃ and PPU-MCF overnight at room temperature in a pH 9 aqueous solution. The resulting Ru³⁺-PPU-MCF catalyst precursor was reduced to the Ru⁰ state by NaBH₄ in water. The reduced catalyst precursor then provided the desired RuO₂-PPU-MCF catalyst upon exposure to air.

The synthesized catalyst was characterized by IR, inductively coupled plasma–optical emission spectroscopy (ICP-OES), analysis of the N₂ adsorption/desorption isotherms, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and X-ray photoelectron spectroscopy (XPS). Grafting of PPU on the heterogeneous support was confirmed by IR, where a characteristic C=O stretching band from the PPU linker could be observed at ṽ = 1640 cm⁻¹. The nitrogen loading of 4.55 and 2.56 wt% was determined by ICP-OES for the PPU-MCF and RuO₂-PPU-MCF, respectively, while 7.26 wt% loading of RuO₂ was measured for the nanoparticulate catalyst. The porous structures of pristine PPU-MCF and the RuO₂-loaded catalyst were evaluated by analysis of the N₂ adsorp-

![Figure 5.1: Synthesis of the RuO₂-PPU-MCF nanoparticulate catalyst.](image-url)
tion/desorption isotherms. An average pore and window size of 19.6 and 12.4 nm was determined for the RuO$_2$-PPU-MCF. The BET (Brunauer-Emmett-Teller) surface area analysis demonstrated a specific surface area and pore volume of 341.15 m$^2$ g$^{-1}$ and 1.55 cm$^3$ g$^{-1}$, respectively. The particle size distribution was evaluated by HAADF-STEM. As evident from Figure 5.2, most of the RuO$_2$ particles in the synthesized catalyst are of subnanometer size (0.6–1.0 nm), which is considerably smaller than for other RuO$_2$ nanoparticulate WOCs immobilized on mesoporous silica.$^{105}$ The oxidation state of Ru in the catalyst was confirmed by XPS, where a characteristic for RuO$_2$ peak at ca. 463 eV was observed, corresponding to the Ru 3p$^{3/2}$ transitions.$^{106}$

5.2.2. Catalytic Activity

The catalytic activity of RuO$_2$-PPU-MCF was evaluated for chemically-driven water oxidation with the use of CAN as the terminal oxidant (Figure 5.3a) and for light-driven water oxidation with the use of [Ru(bpy)$_3$]$^{2+}$-type photosensitizers and Na$_2$S$_2$O$_8$ as sacrificial electron acceptor (Figure 5.3b, see Section 1.3.1 for details). Upon addition of water to a solid mixture of CAN and RuO$_2$-PPU-MCF, immediate evolution of oxygen was detected by the on-line mass-spectrometry and was followed over 24 h. The rate of oxygen formation decreased during the first three hours of catalysis and reached a nearly constant value thereafter. Under these conditions the catalyst demonstrated a TON $\approx$ 10 (after 24 h) and an initial TOF $\approx$ 24 h$^{-1}$ (both values are calculated relative to the total amount of Ru in the catalyst, determined by ICP-OES). The catalyst recovery study was performed on a scaled up reaction ($\times$4, 5 h reaction time). The catalyst was separated from the reaction mixture by centrifugation and analysed by XPS, demonstrating essen-

![Figure 5.2: a) HAADF-STEM image of the RuO$_2$-PPU-MCF catalyst. b) The particle size distribution for the RuO$_2$ nanoparticles in the catalyst. The number-average particle size was calculated to be 1.1 nm.](image)
ti
tally identical spectrum to that of the freshly prepared catalyst. Leaching of Ru from the MCF support to the reaction media was investigated by ICP-OES, however, only trace amounts of Ru close to the detection limit could be observed (<5% of the total amount of Ru).107

Catalytic light-driven experiments with [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} as photosensitizer resulted in a TON ≈ 4 after 100 min and an initial TOF ≈ 11 h\textsuperscript{-1}. The recovered catalyst was analysed by HAADF-STEM, demonstrating nearly unchanged morphology and particle size distribution after catalysis. The use of a photosensitizer with higher Ru\textsuperscript{II}/Ru\textsuperscript{III} redox potential ([Ru(bpy)\textsubscript{2}(deeb)]\textsuperscript{2+}; \(E_{1/2}(\text{Ru}^{II}/\text{III}) \approx 1.40\) V) resulted in lower maximum TON ≈ 1, which is opposite to the trend observed for the molecular WOCs.44i-k,96b,108 The decrease of the maximum TON for the light-driven experiments with [Ru(bpy)\textsubscript{2}(deeb)]\textsuperscript{2+} was also observed for the Pd-MCF catalyst,\textsuperscript{104} and can be explained by slower diffusion of the photosensitizer through the MCF pores due to the polar ethylcarboxylate groups on the deeb ligands.

5.3. Conclusions

As evident from Table 5.1, the activity of the developed catalyst for light-driven water oxidation compares well to the activity of previously reported noble metal–based nanoparticulate WOCs supported on silica and greatly exceeds the activity of 1\textsuperscript{st}-row transition metal–based heterogeneous WOCs under similar conditions. The employed synthetic approach allowed synthe-
sis of a well-distributed nanoparticulate catalyst with a small (ca. 1.1 nm) average particle size. On the other hand, the previously employed direct approach of loading the pre-synthesized nanocatalyst onto the solid support resulted in high degree of agglomeration and larger average size of the catalyst particles.\textsuperscript{105b,c} The developed catalyst also demonstrated high stability during both chemically- and light-driven catalytic experiments. Evidence for the structural integrity of the catalyst during 5 h of chemically-driven water oxidation with CAN under acidic conditions was demonstrated. The later observation is particularly important, as RuO\textsubscript{2} WOCs synthesized without annealing are highly unstable in the presence of CAN, which results in oxidation to the catalytically inactive RuO\textsubscript{4}.\textsuperscript{109}

### Table 5.1. Comparison of catalytic activity for light-driven water oxidation at neutral pH for RuO\textsubscript{2}-PPU-MCF and previously reported catalysts.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TON</th>
<th>TOF\textsubscript{5}, h\textsuperscript{-1}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO\textsubscript{2}-PPU-MCF</td>
<td>4.0</td>
<td>7.9</td>
<td>This work</td>
</tr>
<tr>
<td>Pd-MCF</td>
<td>5.0</td>
<td>7.9</td>
<td>104</td>
</tr>
<tr>
<td>RuO\textsubscript{2}-SBA-15</td>
<td>4.0</td>
<td>24.1</td>
<td>105c</td>
</tr>
<tr>
<td>Mesoporous Mg-Co\textsubscript{3}O\textsubscript{4}</td>
<td>&gt;0.30</td>
<td>0.6</td>
<td>110</td>
</tr>
<tr>
<td>LaCoO\textsubscript{3}</td>
<td>0.70</td>
<td>5.0</td>
<td>111</td>
</tr>
<tr>
<td>LiCoMnO\textsubscript{4}</td>
<td>0.055</td>
<td>0.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>Li\textsubscript{1.1}Co\textsubscript{2}O\textsubscript{4}</td>
<td>0.10</td>
<td>0.6</td>
<td>&quot;</td>
</tr>
<tr>
<td>Li\textsubscript{2}Co\textsubscript{2}O\textsubscript{4}</td>
<td>0.50</td>
<td>3.2</td>
<td>&quot;</td>
</tr>
<tr>
<td>LaMnO\textsubscript{3}</td>
<td>0.20</td>
<td>1.7</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mn\textsubscript{2}O\textsubscript{3}</td>
<td>0.23</td>
<td>1.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>MgMn\textsubscript{2}O\textsubscript{4}</td>
<td>0.060</td>
<td>3.2</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: For all catalysts [Ru(bpy)_3]\textsuperscript{2+} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} were used as photosensitizer and sacrificial electron acceptor, respectively.

\textsuperscript{b}: Herein, the “average” TOF is indicated, as calculated from the maximum TON.
Appendix A

The author’s contribution to Papers I–IV is as following:

**Paper I:** Performed the synthesis (except for complexes 1 and 2), experimental part (except X-ray analysis) and data analysis, wrote major part of the manuscript, and prepared the supplementary information.

**Paper II:** Supervised the work by Dr. Ahmed Abdel-Magied, performed part of the catalytic activity studies, and wrote part of the manuscript.

**Paper III:** Conceived the project, performed the synthesis, experimental part (except ESI-HRMS and X-ray analysis) and data analysis, wrote the manuscript, and prepared the supplementary information.

**Paper IV:** Performed the catalytic activity studies and wrote part of the manuscript.
Appendix B

Reprints of Papers I–IV were made with permission from the publishers:

I. **Catalyst-Solvent Interactions in a Dinuclear Ru-Based Water Oxidation Catalyst**
   Shatskiy, A.; Lomoth, R.; Abdel-Magied, A. F.; Rabten, W.; Laine, T. M.; Chen, H.; Sun, J.; Andersson, P. G.; Kärkäs, M. D.; Johnston, E. V.; Åkermark, B.
   *Open Access, Published by The Royal Society of Chemistry*

II. **Chemical and Photochemical Water Oxidation Mediated by an Efficient Single-Site Ruthenium Catalyst**
    *Open Access, Published by Wiley-VCH Verlag GmbH & Co. KGaA*

III. **Highly Active Ruthenium-Based Water Oxidation Catalyst with an Easy Access to the Catalytically Active Species**
    *Submitted manuscript*

IV. **Water Oxidation Mediated by Ruthenium Oxide Nanoparticles Supported on Siliceous Mesocellular Foam**
    *Open Access, Published by The Royal Society of Chemistry*
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References


