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A broad view at the complexity involved in water oxidation catalysis based on Ru-bpn complexes

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†Electronic supplementary information (ESI) available.

Abstract

A new Ru complex with the formula $[\text{Ru}(\text{bpn})(\text{pic})_2]\text{Cl}_2$ (where bpn is 2,2'-bi(1,10-phenanthroline) and pic stands for picoline) (**1** Cl_2) is introduced to investigate a true nature of active species involved in the electrochemical and chemical water oxidation mediated by a class of N4 tetradenate equatorial ligands. A comprehensive electrochemical (by using cyclic voltammetry, differential pulse voltammetry, and controlled potential electrolysis), structural (X-ray diffraction analysis), spectroscopic (UV-vis, NMR, resonance Raman,) and kinetic study is presented. **1**²⁺ undergoes a substitution reaction when it is chemically (by using NaIO_4) or electrochemically oxidize to Ru^{III} , where picoline is replaced by hydroxido ligand to produce $[\text{Ru}(\text{bpn})(\text{pic})(\text{OH})]^{2+}$ (**2**²⁺). The former complex is in an equilibrium with an oxo-bridged species $\{[\text{Ru}(\text{bpn})(\text{pic})]_2(\mu\text{-O})\}^{4+}$ (**3**⁴⁺) that is the major form of the complex in the Ru^{III} oxidation state. The dimer formation is the rate determining step of the overall oxidation process ($k_{\text{dimer}} = 1.35 \text{ M}^{-1}\text{s}^{-1}$), which is in line with electrochemical data at $\text{pH} = 7$ ($k_{\text{dimer}} = 1.4 \text{ M}^{-1}\text{s}^{-1}$). **3**⁴⁺ can be reduced to $[\text{Ru}(\text{bpn})(\text{pic})(\text{OH}_2)]^{2+}$ (**4**²⁺), showing a sort of square mechanism behavior. All species generated *in situ* at $\text{pH} 7$ have been thoroughly characterized by NMR, mass spectrometry, UV-Vis and electrochemical techniques. **1**²⁺ and **4**²⁺ are also characterized by single crystal X-ray diffraction analysis. Chemical oxidation of **1**²⁺ triggered by Ce^{IV} shows its capability to oxidize water to dioxygen.

Keywords

Ruthenium complexes, coordination chemistry, substitution reactions, redox reactions, kinetics, N4 ligands, water oxidation catalysis

Graph Abstract

Introduction

Coordination and organometallic compounds based on ruthenium are one of the most diverse and rich families of transition metal compounds.^{1, 2} This variety is related to the ability of the Ru metal center to exist in eleven different oxidation states, -2 to +8, and to accommodate a range of geometries within each oxidation state.³ Furthermore, there is nearly an endless number of ligands that can be potentially coordinated to the Ru center, including mono and polydentate ligands, which can bind in a terminal or bridging fashion. The latter have the capacity to generate polynuclear complexes, whose properties are highly dependent on the electronic coupling between metal centers through these bridging ligands.⁴ These extreme diversity of Ru complexes is reflected in a myriad of applications that range from photochemical and photophysical applications,^{5, 6} magnetochemistry,^{7, 8} bioinorganic and medicinal chemistry^{9, 10} and catalysis,¹¹ to cite a few of them.

In the catalysis field, Ru complexes have been used for many reactions, including olefin metathesis,¹² racemization of alcohols,^{13, 14} nitrile hydrolysis¹⁵ and redox catalysis.¹⁶ The latter is especially relevant given the easy access to different metal oxidation states and include hydrogenation and hydrogen transfer reactions,¹⁷ CO₂ reduction,¹⁸ alcohol oxidation,¹⁹ epoxidation^{20, 21} and water oxidation catalysis.²² Catalytic water oxidation is especially important because of its significance for the design of new energy conversion schemes based on artificial photosynthesis.²³ In the context of molecular water oxidation catalysis, Ru complexes, among several transition metals,²⁴ have been leading the field and very rugged and efficient catalysts have already been reported by some of us.^{22, 25-28} Development of these catalysts was the result of thorough spectroscopic characterization of the reaction intermediates and kinetic studies of the different catalytic steps, complemented with the detailed computational analysis.^{29, 30} The fine tuning of the complex redox properties by small ligand variation additionally helps in understanding of the catalyst performance.^{28, 31, 32} However, the complete characterization of the reaction intermediates involved in the catalytic cycle is difficult because of the different oxidation states involved that can have different chemical behavior influencing substitution kinetics, isomerization processes and even changes in the coordination number and geometry. For this reason, it is of paramount importance to properly understand and characterize the different parameters that lead to the generation of active species. Equally important is to uncover the reaction pathways that either block catalysis or lead to decomposition processes.³³

Recently a family of Ru complexes $[\text{Ru}^{\text{II}}(\text{N4})(\text{pic})_2]^{2+}$, containing tetradentate equatorial N4 ligands (Chart I) and picoline as the axial ligand, has been described for N4 = 2,2'-(1,10-phenanthroline-2,9-

diyl)bis(pyridine) (bpb)³⁴⁻³⁶ and 2,2':6',2'':6'',2'''-quaterpyridine (qpy),³⁷ respectively. These [Ru^{II}(N4)(pic)₂]²⁺ complexes in the presence of an oxidant, undergo ligand oxidation at the two external pyridyl groups forming the corresponding N4-O2 di-N-oxide ligands, 2,2'-(1,10-phenanthroline-2,9-diyl)bis(pyridine-1-oxide) (bpb-O2) and [2,2':6',2'':6'',2'''-quaterpyridine] 1,1'''-dioxide (qpy-O2). The new [Ru(N4-O2)(pic)₂]²⁺ complexes generated in this manner are powerful water oxidation catalysts and thus it is of interest to understand both the mechanism of the N-oxide formation as well as the active species responsible for catalysis.

Within this context we report here the synthesis of a new [Ru^{II}(N4)(pic)₂]²⁺ complex containing the equatorial tetradentate N4 ligand 2,2'-bi(1,10-phenanthroline) abbreviated as bpn (Chart I), [Ru^{II}(bpn)(pic)₂]²⁺, **1**²⁺, and the related family of complexes obtained under oxidative conditions. We disclose the chemistry behind a complex solution/reactivity behavior of **1**²⁺, based on kinetic, redox and spectroscopic analyses.

Experimental Section

Materials. The 2-cyano-1,10-phenanthroline³⁸, 8-amino-7-quinolinecarbaldehyde³⁹ and 2,2'-bi [1,10]phenanthroline (bpn)⁴⁰ were prepared according to the literature. Ruthenium precursor RuCl₃·3H₂O and other reagents including 1,10-phenanthroline, 8-nitro-7-quinolinecarbaldehyde, 4-methylpyridine (pic), anhydrous MgSO₄, NaHCO₃ and 30% H₂O₂, were obtained from Sigma-Aldrich and used as received. When required, solvents were dried by following the standard procedures, distilled under nitrogen and used immediately. High purity de-ionized water used for the electrochemistry experiments was obtained by passing distilled water through a nanopure Milli-Q water purification system. For other spectroscopic and electrochemical studies, HPLC-grade solvents were used.

Instrumentation and methods. The microwave synthesis was performed in a Biotage® Initiator. A 500 MHz Bruker Avance II spectrometer was used to carry out NMR spectroscopy. MALDI-TOF-MS experiments were performed on a Bruker Daltonics Autoflex equipped with a nitrogen laser (337 nm) and Mass accuracy in Reflectron mode: 10-50 ppm. ESI-Mass experiments were performed by using micromass Q-TOF mass spectrometer. IR measurements were performed on FT-ATR TR0 spectrophotometer. UV/Vis spectroscopy was performed on a Cary 50 (Varian) UV/Vis spectrophotometer in 0.1 cm quartz cuvettes. Elemental analyses were carried out on Perkin-Elmer 240C elemental analyzer. All electrochemical experiments were performed with an IJ-Cambria CHI-660 potentiostat using a three-electrode cell for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) or two-compartment

cell for controlled potential electrolysis (CPE). All potentials in this work are reported vs. NHE. $E_{1/2}$ values were estimated from CV experiments as the average of the oxidative and reductive peak potentials ($E_{p,a} + E_{p,c}$)/2 or from DPV. Glassy carbon (GC, d = 3 mm) was used as working electrode (W), Pt disk/mesh was used as counter electrode (CE) and a Hg/Hg₂SO₄ (K₂SO₄ saturated) was employed as reference electrode (RE), unless indicated differently, and potentials were converted to NHE by adding 0.65 V. The pH of the solutions was determined by a pH-meter (CRISON, Basic 20+) calibrated before measurements through standard solutions at pH= 4.01, 7.00 and 9.21.

The kinetics experiments of the oxidation of **1**²⁺ by NaIO₄ were performed in buffered solution (phosphate buffer, from now on phbf, pH 7.2) at 5 or 25 °C with the use of a biologic cryo SFM-4000 four syringe stopped-flow equipped with a 150 W xenon lamp and combined with a J&M TIDAS diode array detector (200–724 nm, integration time 0.5 ms). Complete spectra were recorded between 200 and 724 nm with the integrated J&M software BioKine V4.66. A Huber C-905 cryostat filled with silicon oil was used to maintain constant temperature (± 0.01 °C). The buffered solutions of **1**²⁺ and oxidant were mixed in a 1:1 volume ratio (113 μ L complex:113 μ L oxidant) with a total flow rate of 5.5 mL/s under pseudo-first order conditions, i.e. at least 7-fold excess of NaIO₄ over Ru complex. The spectral changes accompanying the formation and decay of the reaction intermediates as well as kinetic traces at a fixed wavelength were analyzed with the use of the SPECFIT/32 global analysis program (Version 2.10, 1993–1996, Spectrum Software Associates, P.O. Box 4494, Chapel Hill, NC 27515-4494, U.S.A.). The reported k_{obs} values were obtained from the fits of experimental data to two-exponential function using kinetic model A→B→C and they are the average of at least five measurements. Spectroelectrochemical experiments were performed by using a Cary 50 (Varian) UV/Vis spectrophotometer equipped with a UV-Vis probe, which was immersed in the working compartment during CPE experiments performed in a two-compartment electrolysis cell.

Manometric measurements were performed on a Testo 521 differential pressure manometer with an operating range of 0.1-10 kPa and accuracy within 0.5% of the measurements. The manometer was coupled to thermostatic reaction vessels for dynamic monitoring of the headspace pressure above each reaction solution. The manometer's secondary ports were connected to thermostatic reaction vessels containing the same solvents and headspace volumes as the sample vials. Each measurement for a reaction solution (2.0 mL) was performed at 298 K. In a typical experiment, 0.1 M in TA/TFE (2:1 mixture, pH 1, 1.5 mL) was added to the reaction vessel containing a solution of the catalyst (2 μ mol) under stirring, and the equivalent volume was added to the reference vessel. The pressures were equalised, a

blank solution of TA (0.5 mL) was injected into the reference cell and a TA solution containing cerium(IV) ammonium nitrate (CAN, 0.2 mmols, 0.5 mL) was then injected into the reaction vessel. Resulting a final concentration of catalyst = 1mM and concentration of CAN = 100 Mm.

The resonance Raman (rR) spectrum was acquired using a Renishaw inVia Reflex RAMAN confocal microscope (Gloucestershire, U.K.) that was equipped with a Laser Nd:YAG (DPSS) 532 nm. Spectra integration time was 10 seconds and spectra shown correspond to ten accumulations on the solid sample. Laser power used was 100 % of the nominal power (50 mW).

Synthesis of [Ru(bpn)Cl₂]Cl. To a 20 mL degassed microwave flask containing RuCl₃·3H₂O (16 mg, 0.0613 mmol) and bpn (20 mg, 0.05 mmol), 12 mL of ethanol were added and the solution was heated in a microwave oven for 2 h at 150 °C with a power of 150 W. The resulting reaction mixture was centrifuged and the black solid was collected by decanting the red solution. The black solid was dispersed in ethanol, filtered and washed with ethanol (28 mg, 0.0398 mmol, yield 65%). IR (ATR, cm⁻¹) 723, 860, 1458, 1526, 1598, 3062, 3451 (ESI Fig. S15). Anal. Calcd. for C₂₄H₁₄Cl₃N₄Ru [Ru(bpn)(Cl)₂]Cl: C, 50.9; H, 2.5; N, 9.9. Found: C, 51.0; H, 2.4; N, 9.7.

Synthesis of [Ru(bpn)(pic)₂]Cl₂, 1Cl₂. To a 20 mL degassed microwave flask containing 12 mg of [Ru(bpn)Cl₂]Cl (0.021 mM) were added 2 mL of water, 8 mL of ethanol and 2 mL of 4-picoline (20 mmol). Then it was placed in a microwave oven for 2 h at 150 °C with a power of 150 W. The resulting mixture was filtered and the solution concentrated by rotary evaporator. Then diethyl ether was added at which point a solid precipitated that was filtered and re-dissolved in MeOH and precipitated again with diethyl ether. Finally, this solid can be recrystallized from a solution with a mixture of MeOH/DCM (0.1/0.2 mL) and using Et₂O (3 mL) to slowly diffuse. A red crystalline solid was formed, which was filtered (13 mg, 0.0181 mmol, yield 85%). ¹H NMR (500 MHz, D₂O): δ= 1.89 (s, 6 H), 6.63 (d, *J*= 6.25Hz, 4 H), 7.74 (d, *J*= 6.40 Hz, 4 H), 7.99 (dd, *J*= 11.66 Hz, 4 H), 8.07ppm (dd, *J*= 4.43 Hz, 2 H), 8.51 (m, 4 H), 8.85ppm (d, *J*= 8.75, 2H), 10.01 ppm (d, *J*= 4.90, 2H). ¹³C NMR (126 MHz, MeOD): δ= 159.18, 155.30, 150.72, 150.24, 149.82, 137.97, 133.36, 130.74, 129.98, 129.55, 128.10, 126.74, 125.97, 123.12, 19.56 (ESI Fig. S1-S5). UV/Vis [*λ*_{max}, nm (ε, M⁻¹cm⁻¹): 576.97 (22636), 473.02 (4992.44), 370.01 (27952.88), 354 (20200), 311.00 (22674). Anal. Calcd. (Found) for C₃₇H₃₄Cl₄N₆O₂Ru ([Ru(bpn)(pic)₂]Cl₂·CH₂Cl₂·2H₂O): C, 53.1; H, 4.1; N, 10.0. Found: C, 52.7; H, 3.5; N, 9.9. MS (ESI⁺ positive mode, methanol) calculated for [M+Cl]⁺ *m/z* = 681.11, found: 681.1.

Electrochemical synthesis of {[Ru(bpn)(pic)₂(μ-O)}⁴⁺, 3⁴⁺. A two-compartment electrochemical cell was used for this experiment. The reference electrode and working electrode were placed in one compartment containing 1.39 mM solution of 1²⁺ (4.5 ml) in 0.1 M phbf solution at pH 7 and the counter

electrode was placed in the second compartment in complex-free 0.1 M phbf solution at pH 7. A CPE experiment was performed at $E_{app} = 1.45$ V for 1 h. For NMR characterization of product 3^{4+} , the same procedure was repeated using a deuterio aqueous solution at pD 7. ^1H NMR (500 MHz, D_2O): $\delta = 1.72$ (s, 3 H), 6.43 (d, $J = 6.20\text{ Hz}$, 2 H), 6.59 (t, $J = 4.37\text{ Hz}$, 2 H), 7.34 (d, $J = 5.15\text{ Hz}$, 2 H), 7.43 (d, $J = 6.50\text{ Hz}$, 2 H), 7.98 ppm (dd, $J = 6.95\text{ Hz}$, 4 H), 8.35 (d, $J = 8.65\text{ Hz}$, 2 H), 9.40 ppm (d, $J = 8.35$, 2H), 9.60 ppm (d, $J = 8.30$, 2H) (ESI Fig. S6-S9). UV/Vis [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 367.99 (17371.51), 575.92 (3837.30), 784.98 (2632.77) and MALDI⁺ (positive mode, methanol): calculated for $[\text{M}+3\text{Cl}]^+ m/z^+ = 1227.07$, found: 1227.4.

Electrochemical synthesis of $[\text{Ru}(\text{bpn})(\text{pic})(\text{OH}_2)]^{2+}$, 4^{2+} . A two-compartment electrochemical cell was used for this experiment. The reference electrode and working electrode were placed in one compartment containing a solution of complex 3^{4+} (prepared *in situ* as described above) in 0.1 M phbf at pH 7 and the counter electrode was placed in the second compartment in pure 0.1 M phbf solution at pH 7. A CPE electrolysis experiment was performed at $E_{app} = 0.35$ V for 2 h. The presence of complex 4^{2+} can be confirmed by CV and/or NMR spectroscopy (in the latter case the experiment was carried out in a D_2O phbf at pD 7). ^1H -NMR (500 MHz, D_2O): $\delta = 1.8$ (s, 3 H), 6.55 (d, $J = 5.95\text{ Hz}$, 2 H), 7.65 (d, $J = 6.20\text{ Hz}$, 2 H), 8.06 (m, 6 H), 8.42 (d, $J = 8.65\text{ Hz}$, 2 H), 8.59 ppm (d, $J = 8.057$, 6 H), 8.69 (d, $J = 8.65\text{ Hz}$, 2 H), 9.96 ppm (d, $J = 4.70$, 2H) (ESI Fig. S10-S14). UV/Vis [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 584 (448.85), 474 (874), 4069 (369), 3119.11 (355) and MALDI⁺ (positive mode, methanol) calculated for $[\text{M}]^+ m/z^+ = 570.09$, found: 570.01.

Single Crystal X-Ray Diffraction.

Data collection. Crystal structure determination for samples 1Cl_2 and $4(\text{CF}_3\text{SO}_3)_2$ were carried out using a Apex DUO Kappa 4-axis goniometer equipped with an APEX 2 4K CCD area detector, a Microfocus Source E025 IuS using MoK_α radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus ($T = -173\text{ }^\circ\text{C}$). Crystal structure determination for samples Full-sphere data collection was used with ω and φ scans. *Programs used:* Data collection APEX-2⁴¹, data reduction Bruker Saint⁴² V/.60A and absorption correction SADABS.⁴³

Crystal preparation. Crystals of 1Cl_2 were grown by slow diffusion of diethyl ether in a solution of 1Cl_2 dissolved in a mixture of MeOH/DCM under air. Dark red crystals of $4(\text{CF}_3\text{SO}_3)_2$ were grown by slow diffusion of diethyl ether in a mixture of 0.1 M triflic acid (TA from now on) and acetone of 4^{2+} . The crystals used for structure determination were selected using a Zeiss stereomicroscope using polarized light and prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Structure Solution and Refinement. Crystal structure solution was achieved using the computer program SHELXT.⁴⁴ Visualization was performed with the program SHELXL.⁴⁵ Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXL 2015.⁴⁶ All non-hydrogen atoms were refined including anisotropic displacement parameters. The asymmetric unit of structure of **1Cl₂** contains one molecule of the cationic metal complex, two chlorine anions and two dichloromethane molecules. For **4(CF₃SO₃)₂** the crystals obtained were of low quality and after several attempts only a suitable dataset could be collected for structure determination. The asymmetric unit contains one molecule of the metal complex, two triflate anions, 0.4 diethylether molecules and 0.40 water molecules. The metal complex molecule is disordered partially in two orientations (ratio 65:35). The triflate anions are disordered in two orientations (ratio 66:34 and 82:18 respectively). The 0.4 diethylether molecules are disordered in two positions around an inversion center (ratio 20:20). The 0.4 water molecules are disordered in three positions with a ratio of (15:15:10).

Crystal Data Deposition: CCDC # 2018088-2018089, contain the supplementary crystallographic data for **1Cl₂** and **4(CF₃SO₃)₂**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

Results and Discussion

Synthesis, structure and spectroscopy of Ru-bpn complexes

The synthetic strategy followed for the preparation of complexes **1-4** is outlined in Scheme 1. A sample of Ru^{III}Cl₃ and bpn were dissolved in EtOH and heated in a microwave (μ W) apparatus to generate the complex [Ru^{III}(bpn)Cl₂]Cl in a good yield. The latter is then treated with excess of 4-picoline (pic) in EtOH and heated again in μ W to generate [Ru^{II}(bpn)(pic)₂]Cl₂, **1Cl₂**, where the axial chlorido ligands are substituted by monodentate pic ligands, while the metal center is reduced to oxidation state II. Applying a potential of 1.45 V to **1Cl₂** dissolved in an aqueous pH 7 phbf solution (ESI Fig. S28), quantitatively generates the oxo-bridged dinuclear Ru complex, {[Ru^{III}(bpn)(pic)]₂(μ -O)}⁴⁺, **3⁴⁺**, with concomitant loss of a picoline ligand per each Ru center via the formation of a mononuclear Ru(III) intermediate species [Ru^{III}(bpn)(pic)(OH)]²⁺, **2²⁺**. The degree of protonation of the oxygen atom is obtained from the Pourbaix diagram shown in ESI Fig. S32, that agrees well with those of related complexes with similar type of ligands.^{47, 48} This reaction sequence was monitored via ¹H-NMR spectroscopy (ESI Fig. S8). Furthermore,

adding 4.5 equivalents of NaIO_4 as the oxidizing agent to a pH 7 solution of $\mathbf{1Cl}_2$, gives the same result (ESI Fig. S9). Finally, exposure of $\mathbf{3}^{4+}$ in pH 7 phbf to $E_{\text{app}} = 0.35$ V for 2 h generates quantitatively the Ru(II)-OH₂ mononuclear complex $[\text{Ru}^{\text{II}}(\text{bpn})(\text{pic})(\text{OH}_2)]^{2+}$, $\mathbf{4}^{2+}$ (ESI Fig. S29). This complex can also be obtained chemically by adding excess amount of ascorbic acid as the reducing agent to the electrochemically generated $\mathbf{3}^{4+}$ (ESI Fig. S13).

Sufficiently good crystals for X-ray diffraction were obtained for $\mathbf{1Cl}_2$ and $\mathbf{4}(\text{CF}_3\text{SO}_3)_2$ and the ORTEP plots of their cations are displayed in Fig. 1. In both cases, the Ru center adopts a slightly distorted octahedral geometry with the bpn ligand occupying the equatorial positions and the pic and aqua occupying the axial ones. Bonding distances and angles are unremarkable for Ru(II) polypyridyl type of complexes^{35, 37, 49-51} except perhaps for the N-Ru-N angles between the outer pyridyl groups of phenanthroline moieties that turn out to be 122.5° and 125.3° for $\mathbf{1Cl}_2$ and $\mathbf{4}(\text{CF}_3\text{SO}_3)_2$, respectively, and that reflect the geometrical distortion imposed by the bpn ligand.

Complexes $\mathbf{1}^{2+}$, $\mathbf{4}^{2+}$, and $\mathbf{3}^{4+}$ show diamagnetic behavior, thus they were further characterized in solution by 1D and 2D NMR spectroscopy and the spectra are presented in Fig. 2A and in the SI (ESI Fig. S1-S14). Complexes $\mathbf{1}^{2+}$ and $\mathbf{4}^{2+}$ are Ru(II) complexes with a low spin d^6 electronic configuration, whereas in $\mathbf{3}^{4+}$ the electronic coupling between two d^5 Ru(III) through the oxo bridge results in a dinuclear complex with a diamagnetic behavior at room temperature.³³ All the resonances in the ¹H-NMR spectra of $\mathbf{1}^{2+}$, $\mathbf{4}^{2+}$, and $\mathbf{3}^{4+}$ could be unambiguously assigned based on the symmetry of the complexes (Fig. 2A). Especially informative are the DOSY spectra recorded for $\mathbf{1}^{2+}$ and $\mathbf{3}^{4+}$ that are shown in Fig. 2B, where a hydrodynamic radius of 9.44 log(m²/s) and 9.50 log(m²/s) are obtained for $\mathbf{1}^{2+}$ and $\mathbf{3}^{4+}$, respectively, in agreement with the dimeric nature of the latter (9.50 log(m²/s) is reported for related dinuclear Ru complexes).³³

Complexes **1-4** were also characterized by UV-vis spectroscopy that is exhibited in Fig. 3. The mononuclear complexes show the typical MLCT in 450-600 nm region together with π - π^* ligand-based transitions in the UV region. In addition, complex $\mathbf{3}^{4+}$ shows a band at 790 nm typical of Ru(III)-oxo bridged complexes.^{52, 53}

Kinetic analysis of the substitution and dimerization process at pH 7

In order to gain further insights into the sequence of reactions that occur after the oxidation of $\mathbf{1}^{2+}$, a kinetic analysis was carried out using NaIO_4 . The rapid-scan stopped-flow mixing of the solutions of $\mathbf{1}^{2+}$ and the oxidant resulted in spectral changes, which indicate the occurrence of three consecutive reactions (Fig. 4). The first two reactions, within the shorter time scale, are characterized by the decrease of the absorbance ascribed to the Ru^{II} species, with concomitant formation of a new intermediate exhibiting a broad and low-intensity band at 680 nm (Fig. 4A). The latter is characteristic for the formation of

hydroxido substituted Ru^{III} species, i.e. Ru^{III}-OH intermediate [Ru^{III}(bpn)(pic)(OH)]²⁺, **2**²⁺, as indicated in Scheme 2. These fast reactions are followed by the third significantly slower reaction, which is accompanied by the spectral changes pointing to the formation of Ru^{III} dimer species **3**⁴⁺, as a final product (characteristic bands at 700-800 nm, Fig. 4B and ESI Fig. S16). The kinetic traces (at $\lambda = 370$ nm) recorded at various concentrations of the oxidant (at least 7-fold excess of oxidant over complex concentration was used to ensure pseudo-first order conditions) within the short time scale clearly display biphasic behavior and were well fitted to the two-exponential function (Fig. 4C) resulting in the pseudo-first order constants, k_{obs1} and k_{obs2} , for the first (oxidation) and second (substitution) reaction, respectively.

As shown in Fig. 4C, the fast step of the oxidation reaction was significantly accelerated by the higher concentrations of NaIO₄. The values of k_{obs1} increase with increasing concentrations of oxidant and the plot of k_{obs1} values vs [NaIO₄] results in the straight line with no meaningful intercept, meaning the rate of the reverse reaction is close to zero (Fig. 4C, ESI Fig. S21 and ESI Table S1). The latter indicates that the studied kinetics exhibits no contribution from the reverse reaction under the selected experimental conditions. Therefore, the pseudo-first order constant, k_{obs1} , can be expressed as follows:

$$k_{\text{obs1}} = k_1[\text{NaIO}_4] \quad (\text{Eq. 1})$$

where k_1 represents the second order constant for the formation of [Ru^{III}(bpn)(pic)₂]³⁺, **1**³⁺, (Scheme 2).

The second-order constant, k_1 , obtained from the slope of the linear fit is equal to $(2.95 \pm 0.1) \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ at 25 °C and pH 7.2. The rate of the second reaction does not show dependence on oxidant concentration resulting in the value of k_{obs2} equal to $4.98 \pm 0.22 \times 10^{-3} \text{ s}^{-1}$ at pH 7.2 and 25 °C. This result is in line with the expectation that the second reaction involves the substitution of picoline ligand in **1**³⁺ by the hydroxide group to form the intermediate **2**²⁺, also labeled as Ru^{III}-OH²⁺, (Scheme 2).

The kinetics of the last, slowest reaction related to the dimerization of **2**²⁺ and resulting in the final product **3**⁴⁺, also labeled as Ru^{III}-O-^{III}Ru⁴⁺ (Eq. 2), was explored by the method of initial rates, v_{init} , at lower temperature (5 °C) to slow down the formation of the dimer and allow the generation of a significant concentration of **2**²⁺.

The rate constant labeled as k_{dimer} represents the second order rate constant for the dimerization reaction (Eq. 2). The value of v_{init} ($4.69 \times 10^{-9} \text{ M s}^{-1}$ at 5 °C and pH 7.2) was determined from the initial part of the kinetic trace for dimerization reaction, where the absorbance changes ascribed to the formation of $\mathbf{3}^{4+}$, display linear dependence vs. time (Fig. 4D and ESI Fig. S21). In order to calculate the value of k_{dimer} the initial concentration of $\mathbf{2}^{2+}$ in the solution, $[\mathbf{2}^{2+}]_{\text{init}}$, was determined from the spectral changes accompanying the formation of $\mathbf{2}^{2+}$ and the known molecular extinction coefficient for the starting Ru^{II} complex $\mathbf{1}^{2+}$ (ESI Fig. S19, Fig. S21 and Table S2-3). It follows that the second order rate constant for the dimerization reaction is equal to $1.35 \pm 0.02 \text{ M}^{-1}\text{s}^{-1}$ at pH 7.2 at 5 °C. The value of k_{dimer} was also calculated in a similar way but with the use of spectroelectrochemical experiments in which the intermediate $\mathbf{2}^{2+}$ was generated by the applied potential of 1.45 V at 5 °C. The values of k_{dimer} obtained from the spectroelectrochemical experiments ($k_{\text{dimer}} = 1.40$ and $1.54 \text{ M}^{-1}\text{s}^{-1}$ at pH 7.2 and 9.0, respectively at 5 °C) are in line with the value found from the chemical oxidation (ESI Fig. S22 and Fig. S23). Scheme 2 summarizes the rate constants obtained for all the processes involved in the chemical oxidation of $\mathbf{1}^{2+}$ at pH 7.2.

In order to calculate the equilibrium constant for the dimerization reaction (K_e , Eq. 3) and the second-order rate constant for the reverse reaction (k_b) (Eq. 2), the equilibrium concentrations, $[\text{Ru}^{\text{III}}\text{-OH}^{2+}]_e$ and $[\text{Ru}^{\text{III}}\text{-O}^{\text{III}}\text{Ru}^{4+}]_e$, were calculated from the spectral changes after adding various concentrations of oxidant (NaIO_4) at 25 °C (see SI for the applied calculation approach).

$$K_e = [\text{Ru}^{\text{III}}\text{-O}^{\text{III}}\text{Ru}^{4+}]_e \times [\text{H}_2\text{O}] / [\text{Ru}^{\text{III}}\text{-OH}^{2+}]_e^2 \quad (\text{Eq. 3})$$

A plot of $[\text{Ru}^{\text{III}}\text{-O}^{\text{III}}\text{Ru}^{4+}]_e$ vs. $[\text{Ru}^{\text{III}}\text{-OH}^{2+}]_e^2$ gives a linear dependence (ESI Table S4 and ESI Fig. S24). The slope of this plot multiplied by the $[\text{H}_2\text{O}]$ results in $K_e = (1.7 \pm 0.1) \times 10^6$ at pH 7.2 and 25 °C. The value of k_b for the dimerization reaction can be calculated from the relationship $k_b = k_{\text{dimer}}/K_e$. Since the value of $k_{\text{dimer}} = 1.35 \text{ M}^{-1}\text{s}^{-1}$ was measured at 5 °C it was first extrapolated to 25 °C by applying Q_{10} temperature coefficient of 2 – 3. Assuming that $k_{\text{dimer}} \sim 5.4 - 12.2 \text{ M}^{-1}\text{s}^{-1}$ at 25 °C, the second-order rate constant for the reverse reaction, i.e. hydrolysis of the dimer, k_b , can be estimated to be between 3.2×10^{-6} and $7.2 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$ at this temperature. Finally, at constant $[\text{H}_2\text{O}] = 55.5 \text{ M}$, the pseudo-first order rate constant, k_{obs} , for the reverse reaction will be in the range $2\text{-}4 \times 10^{-4} \text{ s}^{-1}$ at 25 °C under selected reaction conditions.

Redox properties of 1-4 and water oxidation catalysis.

The redox properties of the complexes described in this work were investigated in organic solvents and in aqueous solutions by means of electrochemical techniques such as cyclic voltammetry (CV), differential pulse voltammetry (DPV) and CPE experiments. All potentials in this work were measured vs. mercury sulfate electrode (MSE) and reported vs. the normal hydrogen electrode (NHE).

The CV of $\mathbf{1}^{2+}$ (1 mM) recorded in trifluoroethanol (TFE) is presented in ESI Fig. S25 and shows a electrochemically quasi-reversible wave at 1.44 V ($E_{p,a} = 1.48$ V, $E_{p,c} = 1.40$ V) associated with the $\text{Ru}^{\text{III/II}}$ couple.⁵⁴ In sharp contrast, the CV of $\mathbf{1}^{2+}$ (1 mM) in aqueous solution at pH 7 shown in Fig. 5 (top, red trace), displays an irreversible process ($E_{p,a} = 1.22$ V and $E_{p,c} = 1.15$ V) that clearly indicates the electrochemical reaction coupled with homogenous chemical steps, i.e. an EC mechanism. Indeed, a CPE of $\mathbf{1}^{2+}$ at 1.45 V for 2 h quantitatively generates the dimer $\mathbf{3}^{4+}$ as indicated in the previous section. A CV of $\mathbf{3}^{4+}$ is also shown in Fig. 5 (bottom, blue trace) and demonstrates the presence of several redox processes that can be rationalized based on the operation of a square mechanism where the dimer $\mathbf{3}^{4+}$ and monomer $\mathbf{4}^{2+}$ interconvert very fast during the CV time scale upon reduction and oxidation, respectively (Scheme 1).

The CV in the bottom of Fig. 5, shows that the formation of the monomer $\mathbf{4}^{2+}$ occurs upon reductive scanning, where two waves appear that can be tentatively assigned to the $\text{Ru}^{\text{III,III/III,II}}$ and $\text{Ru}^{\text{III,II/II,II}}$ processes and whose cathodic peaks appear at 0.40 and 0.21 V, respectively (ESI Fig. S26). The reduction processes are associated with the formation of $\mathbf{4}^{2+}$ in agreement with the CPE experiment carried out at 0.35 V as indicated in the synthesis section. The one electron oxidation of $\mathbf{4}^{2+}$ wave to generate $\mathbf{2}^{2+}$, appears at $E_{p,a} = 0.92$ V and triggers the chemical step, i.e. formation of the dimer $\mathbf{3}^{4+}$. Thus, the monomer, $\mathbf{4}^{2+}$, vastly predominates at low potentials and the dimer, $\mathbf{3}^{4+}$, at high potentials.

The dimerization process of $\mathbf{2}^{2+}$ significantly prevents access to higher oxidation states such as $[\text{Ru}^{\text{V}}(\text{O})(\text{bpn})(\text{pic})]^{3+}$, needed for the water oxidation catalysis using this type of complexes.²⁹

Nevertheless, some evidence for the access to high oxidation states by the monomer, even if in very low concentrations, comes from a combined CPE and resonance Raman (rR) experiment using isotopically labeled H_2O (ESI Fig. S18 and Fig. 6). We carried out a CPE of $\mathbf{1}^{2+}$ at 1.45 V, which mainly generates the dimer. Fig. 6 shows the rR spectra, where a vibration at 844 cm^{-1} in H_2O^{16} shifts to 801 cm^{-1} in H_2O^{18} (98%). Both, the energy of the vibration and the 43 cm^{-1} isotopic shift are consistent with the vibration of the $\text{Ru}=\text{O}$ group in $[\text{Ru}^{\text{IV}}(\text{O})(\text{bpn})(\text{pic})]^{2+}$ that can be considered as the resting state formed prior to the rate determining step during the electrocatalytic water oxidation cycle.^{33, 36, 55, 56} An additional vibration that

exhibits an isotopic shift of 28 cm⁻¹ (790 cm⁻¹ in H₂O¹⁶; 762 cm⁻¹ in H₂O¹⁸) appears in the spectra, but its assignment has not been elucidated yet.

The redox behavior of **1**²⁺ in an aqueous pH 1 (0.1 M TA in TFE (2:1)) solution is presented in Fig. 7 (left) and ESI Fig. S27. A nearly reversible wave associated with the III/II couple appears at 1.35 V. However, at lower potential a new cathodic wave emerges (*E*_{pc} = 1.00 V) that manifests the presence of a new species associated with a chemical reaction following the generation of the Ru(III) complex. CPE of **1**²⁺ at 1.65 V results in a complex mixture of species (ESI Fig. S31). Among them, the monomeric Ru(II) complex, **4**(CF₃SO₃)₂ is formed that comes out of the solution as dark red crystals (Fig. 1). In addition, a UV-vis of the solution after the CPE (ESI Fig. S17) shows a band at 810 nm that is typical for oxo-bridge dimers and thus suggests that at this pH the dimer and monomer coexist in equilibrium. Finally, a manometric analysis using 2 mL of a 100 mM CAN (0.2 mmols; CAN = (NH₄)₂[Ce(NO₃)₆]) solution in TA at pH 1, over 2 mL of 1 mM of **1**²⁺ (2 μmols) in a mixture of 0.1 M TA in TFE (2:1 mixture), generates 20 TONs of O₂, assuming that all the pressure is entirely due to the formation of dioxygen (Fig. 7, right). At the beginning of the reaction, an induction period of about 150 s is observed that suggests the initial transformation of **1**²⁺ into the corresponding catalytically active species. The latter is probably a high-valent Ru species that could be generated in a slightly higher concentration under acidic conditions, where dimer formation (though still occurring) is somewhat less prominent, allowing further oxidations of the Ru(III) species. Attempts to identify the nature of the active species have not been conclusive.

Summary and Conclusions

The synthesis of mononuclear complex with a new N4 tetradenate equatorial ligand [Ru^{II}(bpn)(pic)₂]²⁺, **1**²⁺, is reported. One electron oxidation of **1**²⁺ at pH 7 triggers a set of reactions that yield the quantitative formation of the oxo-bridge complex {[Ru^{III}(bpn)(pic)]₂(μ-O)}⁴⁺, **3**⁴⁺. Reduction of this dimer quantitatively yields the formation of the mononuclear Ru-aquo complex [Ru^{II}(bpn)(pic)(OH₂)]²⁺, **4**²⁺. All these complexes have been thoroughly characterized by means of spectroscopic and electrochemical techniques and the crystal structures were determined for **1**²⁺ and **4**²⁺. The sequence of reactions that occur after one electron oxidation of **1**²⁺, has been kinetically characterized and is summarized in Scheme 2. It involves the substitution of one of the axial picoline ligands and the formation of the oxo-bridge dimer, in sharp contrast to their [Ru^{II}(N4)(pic)₂]²⁺ analogues with the pbp and qpy ligands. In the latter case, the main reaction occurring involves ligand oxidation to form the corresponding N-oxides, which is not observed with **1**²⁺ at pH 7.

Generally, $[\text{Ru}^{\text{III}}(\text{N}_6)]^{3+}$ polypyridyl complexes, such as $[\text{Ru}(\text{bpy})_3]^{3+}$,⁵⁷ are stable at least within the CV timescale showing chemically reversible and electrochemically reversible or quasireversible behavior of their III/II couples. However, the redox potentials of the III/II couples⁵⁸ are very high within the range of 1.1-1.3 V. Therefore, the Ru(III) oxidation state for these complexes is a highly oxidizing species that has been used in many instances as a sacrificial agent in combination with water oxidation catalysts for the generation of dioxygen.^{59,60} In the absence of a catalyst or substrate, the highly oxidizing Ru(III) species are not stable under long periods of time reacting with the solvent via one electron process and returning to their initial Ru(II) oxidation state. This is the main pathway observed for $[\text{Ru}(\text{bpy})_3]^{3+}$ in aqueous solutions, where at pH > 5 the $\text{OH}^\cdot$ radicals are generated that can attack the coordinated bpy ligands.⁶¹ Other pathways can involve O-atom insertion into the Ru-N bond and formation of N-oxide ligands, as recently proposed.^{62,63} In addition, when the transformation involves the formation of a Ru-OH₂ or Ru-OH species it can lead to other ligand based reactions, such as O-atom insertion into a C-H bond, in a bimolecular or unimolecular manner.⁶⁴

Based on this and our previous work, we can conclude that in the case of the $[\text{Ru}^{\text{II}}(\text{N4})(\text{pic})_2]^{2+}$ complexes with N4 = pbp, qpy and bpn there are two main reactivity modes that are induced by oxidation depending on the ligands, as depicted in Scheme 3. One involves Ru-N O-atom insertion, as for pbp and qpy, and another involves axial ligand substitution, as in the case of bpn. This radically different reactivity can be mainly associated with the low energy barrier for the C-C bond rotation of the external pyridyl groups of tetradentate ligands pbp and qpy (see arrows in Chart I). This low C-C energy rotation barrier is indispensable for the formation of the N-oxide bond as represented in Scheme 3. Further, the corresponding N-oxide $[\text{Ru}(\text{N4-O2})(\text{pic})_2]^{2+}$ complexes present a highly distorted octahedral geometry, due to the formation of nearly flat 6-member rings (Ru-N-C-C-N-O) containing 4 atoms with sp² hybridization, that would be highly unfavorable for the bpn analogue. For the bpn complex **1**²⁺, the restricted rotation imposed by the bpn ligand also prevents the interaction of a potential aquo/hydroxido ligand with the Ru metal center in the equatorial zone, due to the steric constraints associated with the presence of the N-alpha C-H bonds schematically shown in Scheme 3. This steric obstruction would also be unfavorable for a potential seven-coordination geometry at higher oxidation states, such as Ru(IV) and Ru(V). These steric impediments are avoided in the case of qpy and pbp *via* the easy rotation of the external pyridyl rings.

Another interesting, yet a bit deceiving property from a catalytic perspective, is the square mechanism that operates between the Ru(II) monomer **4**²⁺ and the Ru(III) dimer **3**⁴⁺, representing a sort of EC

mechanism. As represented in Scheme 2, once the monomer is oxidized by one electron to Ru(III) it immediately dimerizes *via* oxo-bridge formation. In turn, when the dimer is reduced it returns back to the initial Ru(II) monomer. This is an interesting reactivity property representing a sort of EC mechanism. However, the fact that the monomer dimerizes upon applying high positive potential significantly precludes the formation of monomeric high-valent species, such as Ru(IV) and Ru(V), because their formation is in competition with the dimerization reaction. The redox properties of 1^{2+} were also investigated in acidic pH using similar strategies. At low pH the complete monomer-dimer interconversion as a function of oxidation state does not appear, but a coexistence of monomer and dimer in an equilibrium rather occurs. In addition, CV monitoring of this reaction shows a very complex mixture of species, suggesting that besides axial ligand substitution and Ru-OH₂ formation, other reactions might also be operative under acidic conditions.

Since the high oxidation states are responsible for the O-O bond formation, the dimerization acts as a gate that significantly blocks the access to the catalytic cycle for water oxidation. Nevertheless, although the concentration of active species is low, especially at pH 7, it is sufficient to observe the Ru(IV)=O species by rR spectroscopy. Under acidic conditions, where dimerization triggered by oxidation is less favorable and the monomeric Ru(III) form (in an equilibrium with dimer) is more accessible, we could even observed dioxygen production. These new mechanistic insights provide some guidance to be consider in tuning ligand geometry and reaction conditions for efficient water oxidation.

Conflicts of interest

There are not conflicts of interest to declare.

Acknowledgments

A.G. thanks MINECO for a FPI grant (BES-2015-073069). Support from MINECO and FEDER (CTQ2016-80058-R, CTQ2015-73028-EXP, SEV 2013-0319, ENE2016-82025-REDT, CTQ2016-81923-REDC) and AGAUR (2017-SGR-1631) are gratefully acknowledged. A.F. and I.I.-B. acknowledge the support of the Deutsche Forschungsgemeinschaft, DFG, (within project IV 80/13-1 titled "High-Valent Metal-Oxo-Coordination Complexes for the Homogenous Water Oxidation").

Chart I. N4 tetradentate equatorial ligands discussed in this work. The arrows show C-C bond rotational axis.

Scheme 1 Reaction sequence used for the synthesis of complexes **1-4** and the overall square scheme presentation of a sort of EC mechanism. Orange and fuchsia colors indicate oxidation states II and III for Ru, respectively. In brackets are indicated putative transient species.

$$K_e = 1.70 \times 10^6 \quad (k_{\text{dimer}} = 5.4\text{-}12.2 \text{ M}^{-1}\text{s}^{-1}; k_b = (3.2\text{-}7.2) \times 10^{-6} \text{ M}^{-1}\text{s}^{-1})$$

Scheme 2 Summary of kinetic and thermodynamic parameters for the reaction steps involved in the sequence of reactions that occur upon oxidation of 1^{2+} at 25 °C and pH 7.2.

Scheme 3 Competing reaction pathways for Ru(III)N₆ complexes with N₄ equatorial ligands. Blue N represent axial picoline ligands. The arrows show low energy C-C rotation axis.

Fig. 1 ORTEP plots (ellipsoid drawn at 50% probability) of the X-ray structures of the cationic part of **1**Cl₂ (right) and **4**(CF₃SO₃)₂ (left). Color code: cyan, Ru; red, O; purple, N; and black, C. Hydrogen atoms are omitted for clarity purposes.

Fig. 2 A) NMR aromatic region in ^1H -NMR spectra of 1^{2+} , 4^{2+} , 3^{4+} at pH 7 in phbf solutions. * indicates the presence of free pyridine ligand. B) DOSY for 1^{2+} and 3^{4+} at pH 7 phbf solution.

Fig. 3 UV-vis spectra of 1^{2+} , 4^{2+} , 3^{4+} (50 μ M) in aqueous solution at pH 7 phbf solution

Fig. 4 A) Spectral changes of a solution of 1^{2+} before (red) and 5 minutes after (blue) adding 2 eq NaIO₄ at 25 °C. B) Spectral changes of a solution of 1^{2+} in 5 minutes (blue) and 82 minutes (green) after adding 2 eq NaIO₄ at 5 °C. The gray spectra in A and B show the spectral changes every 26 seconds. C) Kinetic traces recorded at 370 nm at various concentrations of oxidant ($(\text{NaIO}_4: 7\text{--}20 \text{ eq})$, $([\text{NaIO}_4] = (8.75 - 25) \times 10^{-5} \text{ M})$) and a constant concentration of 1^{2+} ($0.125 \times 10^{-4} \text{ M}$) at pH 7.2 in phbf solution and at 25 °C. The experimental data were fitted to 2-exponential function, fittings are represented as red traces. D) Kinetic traces recorded at 720 nm during 82 min after adding 2 eq NaIO₄ at pH 7.2 in phbf solution and at 5 °C.

Fig. 5 CV of complex 1^{2+} (1.34 mM, red trace) and 3^{4+} (0.67 mM, blue trace) in an aqueous pH 7 phbf solution. The transformation from darker to brighter orange highlight indicates the zone of the transformation from the dimer 3^{4+} to the monomer 4^{2+} (in the cathodic direction), whereas that from the brighter to darker yellow indicates the zone of the transformation from the monomer 4^{2+} to the dimer 3^{4+} (in the anodic direction). Conditions: $\nu = 100$ mV/s, WE: glassy carbon electrode; CE: platinum electrode; RE: Hg/Hg₂SO₄. Horizontal arrows show the starting point of the scan.

Fig. 6 rRaman spectra (enlargement of the 700-900 cm^{-1} region) of an aqueous solution of $\mathbf{3}^{4+}$ prepared *in situ* from $\mathbf{1}^{2+}$ after a CPE electrolysis at $E_{\text{app}} = 1.45$ V at pH 7 phbf solution in H_2O^{16} (blue) and H_2O^{18} (red).

Fig. 7 Left, CV of $\mathbf{1}^{2+}$ (black line) dissolved in a TA:TFE (2:1) mixture (TA = aqueous 0.1 M solution) and blank (orange trace) at a scan rate of 100 mV/s, WE: glassy carbon electrode; CE: platinum electrode; RE: Hg/Hg₂SO₄. Right, manometric profile over time observed upon the addition of 2 mL of a 100 mM CAN (0.2 mmols) solution at pH 1 (0.1 M TA) to 2 mL of 1 mM of $\mathbf{1}^{2+}$ (2 μmol) (0.1 M TA in TFE; a 2:1 mixture).

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