Influence of Chloro Substituent on Photoisomerization, Redox Reactions and Water Oxidation Catalysis of Mononuclear Ruthenium Complexes

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Abstract

$distal-[Ru(Cl-tpy)(pynp)Cl]^+$ ($d-2Cl$) (Cl-tpy = 4'-chloro-2,2';6',2''-terpyridine, pynp = 2-(2-pyridyl)-1,8-naphthyridine), and $distal$ - and $proximal$ - $[Ru(Cl-tpy)(pynp)OH_2]^{2+}$ (d - and $p-2H_2O$) complexes are newly synthesized and characterized to compare structures and physicochemical properties with a 2,2';6',2''-terpyridine (tpy) ligand derivatives of $distal-[Ru(tpy)(pynp)Cl]^+$ ($d-1Cl$), $distal$ - and $proximal$ - $[Ru(tpy)(pynp)OH_2]^{2+}$ (d - and $p-1H_2O$). The equilibrium turned out to be involved in the aquation reaction of $d-2Cl$ to $d-2H_2O$ in contrast to observed irreversible aquation reaction of $d-1Cl$ under the same conditions. The kinetic analysis showed that the aquation reaction of $d-2Cl$ is slightly slower than that of $d-1Cl$. The stoichiometric photoisomerization of $d-2H_2O$ to $p-2H_2O$ occurs by visible light irradiation as it is for $d-1H_2O$, and Φ (2.1%) at 520 nm for photoisomerization of $d-2H_2O$ was higher than that (1.5%) observed for $d-1H_2O$. $d-2H_2O$ undergoes the two-step reaction involving the successive one-proton-coupled one-electron reactions of the $Ru^{II}-OH_2/Ru^{III}-OH$ and $Ru^{III}-OH/Ru^{IV}=O$ redox couples, whereas $p-2H_2O$ undergoes the one-step reaction involving the two-proton-coupled two-electron reaction of the $Ru^{II}-OH_2/Ru^{IV}=O$ redox couple. These redox potentials of d - and $p-2H_2O$ are higher than those for d - and $p-1H_2O$ at pH = 7.0 by 10 ~ 50 mV due to the electron-withdrawing chloro substitution. The turnover frequency ($k_{O_2} = 6.3 \times 10^{-3} s^{-1}$) of $d-2H_2O$ for water oxidation was higher than that ($3.9 \times 10^{-4} s^{-1}$) of $p-2H_2O$ by a factor of 16. k_{O_2} for $d-2H_2O$ was also 1.6 times higher than that ($3.8 \times 10^{-3} s^{-1}$) for $d-1H_2O$, whereas k_{O_2} for $p-2H_2O$ was 1.2 times lower than that ($4.8 \times 10^{-4} s^{-1}$) for $p-1H_2O$.

Introduction

The ruthenium(II) complexes with polypyridyl ligands have been extensively studied as promising functional molecules due to the unique photochemical[1-6] and photophysical[7-9] properties related to a photoexcited triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) state as well as redox properties including electrochromism[10, 11], and the multi-electron transfer catalysis.[12-15] These properties are responsible for potential applications of the ruthenium(II) complexes to a large variety of devices including sensors[16, 17], photovoltaic cells[18-20], displays[21, 22], and photocatalysts.[7, 23] Polypyridyl ruthenium(II) aquo complexes have recently been attracting much attention as active water oxidation catalysts that are essential for artificial photosynthesis.[12-15, 24-29] Although water oxidation catalysts are expected to be applied to photochemical systems (finally to artificial photosynthesis), there are only a few reports on any photochemical reaction of the ruthenium(II) aquo complexes as water oxidation catalysts.[30-32] We recently reported that the observed catalytic activity of *distal*- $[\text{Ru}(\text{tpy})(\text{pynp})\text{OH}_2]^{2+}$ (*d*-**1H₂O**) (tpy = 2,2',6',2''-terpyridine, pynp = 2-(2-pyridyl)-1,8-naphthyridine; see Figure 1) for water oxidation significantly changes by visible light irradiation due to photoisomerization to *proximal*- $[\text{Ru}(\text{tpy})(\text{pynp})\text{OH}_2]^{2+}$ (*p*-**1H₂O**) in water because the catalytic activity of *distal*-isomer is higher than that of the *proximal*-isomer by one order of magnitude.[30, 34] This photoisomerization is an irreversible and stoichiometric reaction, being very rare with respect to polypyridyl ruthenium(II) aquo complexes, although a huge number of photochemical reactions[1-6, 30, 31, 35-38] of the ruthenium(II) complexes have been reported.

The correlation between structure and reactivity is of fundamental importance for understanding and predicting the outcome and mechanism of chemical reactions.

The investigation of substitution effects on chemical reactions is a useful method due to their simplicity and predictability in gaining insight into the dependence on electronic factors. Although molecular catalysts for water oxidation have prospered during the last decade, the catalysts which offer simple systematic tuning of the ligand environment are still relatively scarce [26, 39-41]. Likewise, there are no reports of the substitution effect on photoisomerization of polypyridyl ruthenium(II) aquo complexes. In the present paper, *distal*-[Ru(Cl-tpy)(pynp)Cl]⁺ (*d*-**2Cl**) (Cl-tpy = 4'-chloro-2,2';6',2''-terpyridine), *distal*- and *proximal*-[Ru(Cl-tpy)(pynp)OH₂]²⁺ (*d*- and *p*-**2H₂O**) complexes are newly synthesized and characterized to compare structures and physicochemical properties with **1** derivatives with a tpy ligand (*distal*-[Ru(tpy)(pynp)Cl]⁺ (*d*-**1Cl**) and *d*- and *p*-**1H₂O**) (see Figure 1). The unique reactions of the aquation reaction, photoisomerization, proton-coupled electron transfer and water oxidation catalyses of **2** derivatives are investigated to gain insight into influence of electronic factors on these reactions.

Experimental section

Materials

2-(2-pyridyl)-1,8-naphthyridine (pynp)[42] and Ru(Cl-tpy)Cl₃[43] were synthesized according to literatures. All the chemicals of analytical grade were used as received.

Synthesis of complexes

distal-[Ru(Cl-tpy)(pynp)Cl]Cl ([*d*-**2Cl**]Cl)

distal-[Ru(Cl-tpy)(pynp)Cl]Cl was prepared referring to the previous report[30], as follows. 108.8 mg (0.229 mmol) of Ru(Cl-tpy)Cl₃ and 45.8 mg (0.221

mmol) of pynp were refluxed in 20 mL of 75 (v/v)% ethanol/water containing 52 mg (1.23 mmol) of LiCl and 1.45 mL (10.4 mmol) of triethylamine as a reductant for 4 h in the dark. The reaction mixture was filtered remaining hot, and the filtrate was concentrated to 4 mL with a rotary evaporator. The solution was then chilled in a refrigerator for 24 h. The solid was collected on a frit and washed with chilled 3 M HCl, acetone, and ether, and then dried *in vacuo* at room temperature to give *distal*-[Ru(Cl-tpy)(pynp)Cl]Cl (101.8 mg, 0.157 mmol, 71% yield). It was characterized by UV-Visible absorption and NMR spectroscopic measurements and elemental analysis. UV-Visible absorption spectrum (EtOH) : λ_{max} (ϵ) = 559 nm (9,200 M⁻¹ cm⁻¹). ¹H NMR (399.937 MHz, CDCl₃) δ ppm 10.43 (dd, J = 5.50, 0.99 Hz, 1H), 9.63 (d, J = 8.68 Hz, 1H), 9.38 (d, J = 8.26 Hz, 1H), 8.49 (d, J = 8.31 Hz, 1H), 8.36 (t, J = 7.35, 7.35 Hz, 1H), 8.15 (dd, J = 8.04, 1.67 Hz, 1H), 8.08 (dd, J = 4.09, 1.61 Hz, 1H), 8.04 (d, J = 7.97 Hz, 2H), 7.84 (dd, J = 7.20, 5.99 Hz, 1H), 7.68 (t, J = 7.42, 7.42 Hz, 2H), 7.52 (d, J = 5.16 Hz, 2H), 7.26 (dd, J = 7.99, 4.14 Hz, 1H), 8.22 (s, 2H), 7.14 (t, J = 3.62 Hz, 2H). ¹³C NMR (175.993 MHz, CDCl₃) δ ppm 165.99, 160.12, 158.76, 158.57, 156.97, 153.09, 151.53, 151.21, 137.91, 137.07, 135.34, 131.79, 131.10, 129.39, 128.37, 127.14, 126.09, 125.11, 123.84, 118.75, 110.23. Anal. calcd. for C₂₈H₁₉Cl₃N₆Ru: C, 51.98; H, 2.96; N, 12.99; Found: C, 51.61; H, 2.73; N, 12.66.

***distal*-[Ru(Cl-tpy)(pynp)OH₂](NO₃)₂ ([*d*-2H₂O](NO₃)₂)**

30 mg (0.0435 mmol) of [*d*-2Cl]Cl and 14.78 mg (0.087 mmol) of AgNO₃ were refluxed in 10 mL of 75 (v/v)% acetone/water for 1 h. After cooling at room temperature, the mixture was filtered, and then concentrated to 2 mL with a rotary evaporator. To the solution was added a saturated NaNO₃ aqueous solution by drops,

and then it was chilled in a refrigerator for 24 h. The solid was collected on a frit and washed with chilled water, and then dried *in vacuo* at 50°C for 5 h to give *distal*-[Ru(Cl-tpy)(pynp)OH₂](NO₃)₂ (27.5 mg, 0.0361 mmol, 83% yield). The product was characterized by UV-Visible absorption and NMR spectroscopic measurement and elemental analysis. UV-Visible absorption spectrum (H₂O): λ_{max} (ϵ) = 524 nm (8,600 M⁻¹ cm⁻¹). ¹H-NMR (400 MHz, D₂O) : ¹H-NMR (399.937 MHz, D₂O) : δ ppm 9.70(d, J = 5.68 Hz, 1H), 8.94(d, J = 8.24 Hz, 1H), 8.67(s, 1H), 8.49(d, J = 8.64 Hz, 1H), 8.42(d, J = 8.20 Hz, 1H), 8.33(d, J = 8.16 Hz, 1H), 8.26(dd, J = 1.52 and 2.4 Hz, 1H), 8.23(d, J = 8.64 Hz, 1H), 8.12(dd, J = 1.72 and 6.52 Hz, 2H), 8.10(t, J = 6.72 Hz, 1H), 7.88(t, J = 8.04, 2H), 7.71(d, J = 5.48 Hz, 2H), 7.35(dd, J = 4.24 and 3.88 Hz, 1H), 7.24(t, J = 6.48 Hz, 2H). Anal. calcd. for C₂₈H₂₁ClN₈O₇Ru·H₂O: C, 46.84; H, 2.95; N, 15.61; Found: C, 46.58; H, 2.73; N, 15.46.

***proximal*-[Ru(Cl-tpy)(pynp)OH₂](NO₃)₂ ([*p*-2H₂O](NO₃)₂)**

p-2H₂O was formed by visible-light ($\lambda > 420$ nm) irradiation to an aqueous *d*-2H₂O solution over 30 min from a filtered halogen lamp. The *in situ* stoichiometric formation *p*-2H₂O in water was corroborated by UV-visible absorption and NMR spectroscopic measurement of the completed reaction solution. ([*p*-2H₂O](NO₃)₂) λ_{max} (ϵ) = 518 nm (9,120 M⁻¹ cm⁻¹). ¹H-NMR (699.841 MHz, D₂O) : δ ppm 9.09 (dd, J = 4.37 and 1.86 Hz, 1H), 8.86 (d, J = 8.90 Hz, 1H), 8.71(s, 2H), 8.61(d, J = 7.96 Hz, 1H), 8.41(d, J = 7.87 Hz, 2H), 8.01(dd, J = 8.33, 4.37 Hz, 1H), 7.93(dt, J = 7.96, 7.91, and 1.49 Hz, 2H), 7.80-7.72 (m, 1H), 7.66 (dd, J = 5.59 and 0.77 Hz, 2H), 7.58(dd, J = 5.87 and 0.69 Hz, 1H), 7.20 (ddd, J = 7.46, 5.62 and 1.25, 2H), 7.07(ddd, J = 7.34, 5.90 and 1.30 Hz, 1H), 8.95-8.93 (m, 1H), 8.93-8.92 (m, 1H).

Experimental details

^1H -NMR spectra were recorded with 400 and 700 MHz NMR spectrometers (Varian). ^1H NMR spectra were referenced using tetramethylsilane in organic solvents or sodium trimethylsilyl propanesulfonate in D_2O as an internal standard. X-ray diffraction data were recorded on a diffractometer (Rigaku, XtaLAB mini) using the ω scan technique to a maximum 2θ value of 55.0° with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71075 \text{ \AA}$) radiation at 25°C . Crystals for X-ray diffraction measurements were mounted on a glass fiber. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on the observed reflections ($I > 2.00 \sigma(I)$) and variable parameters and converged with unweighted and weighted agreement factor R and R_w . The cyclic voltammogram (CV) were measured in 0.5 mM Ru complex solutions ($\text{pH} = 0.5 \sim 13.0$) using a conventional single-compartment electrochemical cell equipped with a glassy carbon rod working electrode (effective area, 0.071 cm^2), a saturated calomel reference electrode (SCE) and a Pt wire counter electrode. For Pourbaix diagram, the pHs of the solutions were buffered at an ionic strength of 0.1 M by HNO_3 (pH 0-2), Na_2HPO_4 and KH_2PO_4 (pH 3-10), and NaOH (pH 11-14). At $\text{pH} = 0$ and 14, the ionic strength was 1 M (1 M HNO_3 and 1 M NaOH , respectively). All the electrochemical experiments were implemented under argon atmosphere at 25°C using an electrochemical analyzer (Hokuto Denko, HZ-3000). The potentials were expressed as the values versus SCE unless otherwise noted. The UV-visible absorption spectra were measured in a quartz cell with 1 cm of a light pass length using a photodiode array spectrophotometer

(Shimadzu, Multispec-1500). For chemical water oxidation experiments, an excess $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (0.5 mmol) as an oxidant was added quickly to 0.2 ~ 0.6 mM *d*-**2H₂O** or *p*-**2H₂O** aqueous solution (5.0 ml) in a gas-tight vessel under argon atmosphere at 25°C and pH = 1.0. The pH change during the reaction for several hours was less than 0.1. The O₂ gas in the head space of the vessel was analyzed on a gas chromatograph (Shimadzu, GC-8A) equipped with a molecular sieve 5Å column using argon carrier gas (flow rate = 40 cm³ min⁻¹) at 50°C.

Results and Discussion

Synthesis and structure of *d*-**2Cl**

A reaction of $\text{Ru}(\text{Cl-tpy})\text{Cl}_3$ and pynp in 75 (v/v)% ethanol/water containing LiCl and triethylamine gave a single product of *d*-**2Cl** being characterized by the ¹H NMR spectrum (the *proximal* isomer not formed). This is the same as the case of single formation of *d*-**1Cl** in a reaction of $\text{Ru}(\text{tpy})\text{Cl}_3$ and pynp under the similar conditions.[30, 34] *d*-**2Cl** could also be selectively formed due to repulsion between the chloro ligand and a lone pair of the nitrogen atom of the naphthyridine moiety for the *proximal*-isomer. The formation of *d*-**2Cl** was corroborated by X-ray crystallographic analysis of the product. The X-ray crystallographic data of [*d*-**2Cl**](ClO₄) are summarized in Table 1, and Oak Ridge thermal ellipsoid plot (ORTEP) drawings and the selected bond lengths and angles are shown in Figure 2 and Table 2, respectively. The bond length (1.967(3) Å) of Ru-N_{central}(2) (N_{central}(2) : a nitrogen atom at a central pyridine of tpy) is shorter than the bond lengths between ruthenium atom and other nitrogen atoms on tpy (Ru-N_{distal}(1), 2.071(2) Å and Ru-N_{distal}(3), 2.080(3) Å) (Table 2), which is similar to the bond length characters of *d*-**1Cl** [30, 34]. However, the Ru-N bond lengths on tpy for *d*-**2Cl** are longer than

those for *d*-**1Cl** by 0.004 ~ 0.011 Å due to electron-withdrawing property of chloro substitution on tpy. The bond length (2.069(6) Å) of Ru-N_{np}(5) (nitrogen atom at a naphthyridine moiety of pynp) is shorter than that (2.083(3) Å) of Ru-N_{py}(4) (nitrogen atom at a pyridine moiety of pynp) by 0.014 Å for *d*-**2Cl**, although the bond lengths of Ru-N_{np}(5) (2.075(3) Å) and Ru-N_{py}(4) (2.073(3) Å) are nearly the same for *d*-**1Cl**. Correspondingly, the angle (102.85(13)°) of N_{central}(2)-Ru-N_{np}(5) for *d*-**2Cl** is larger than that (101.3(1) °) for *d*-**1Cl**. This is ascribed to more significant repulsion between Cl-tpy and the naphthyridine moiety of pynp for *d*-**2Cl**.

Aquation of *d*-**2Cl** to *d*-**2H₂O**.

¹H-NMR spectrum of *d*-**2Cl** in CDCl₃ did not change for several days, whereas in D₂O the peak intensity at 10.2 ppm (assigned to the 7-position on naphthyridine) gradually decreased with time concurrently with an increase of the doublet signal at 9.7 ppm (Figure 3A). This change was assigned to the aquation reaction of *d*-**2Cl** to form *d*-**2H₂O** based on the similar ¹H NMR spectral change in the aquation reaction of *d*-**1Cl** (10.0 ppm) to *d*-**1H₂O** (9.5 ppm) in D₂O.[30, 34] 13% of the signal intensity at 10.2 ppm for *d*-**2Cl** still remained after 24 hours, in contrast to completion of the reaction of *d*-**1Cl** to *d*-**1H₂O** under the same conditions. This result indicates that aquation of *d*-**2Cl** involves equilibrium under the conditions employed (eq. (1)).

The kinetic profiles of aquation of *d*-**2Cl** (Figure 3B) were analyzed using a reversible reaction model. The best fitting was obtained when $(k_1)_{obs} = 5.3 \pm 0.3 \times 10^{-5}$

s^{-1} and $(k_{-1})_{\text{obs}} = 8.5 \pm 0.8 \times 10^{-6} \text{ s}^{-1}$ as observed rate constants for aquation and reverse reactions were given, respectively. The observed equilibrium constant defined as $K_{\text{obs}} = (k_1)_{\text{obs}} / (k_{-1})_{\text{obs}}$ was calculated to $K_{\text{obs}} = 6.2 \pm 0.2$. The $(k_1)_{\text{obs}}$ value is comparable but slightly lower than the rate constant ($(k_1)_{\text{obs}} = 5.7 \times 10^{-5} \text{ s}^{-1}$) for aquation of *d*-**1Cl** under the same conditions (see Table 3). The $(k_{-1})_{\text{obs}}$ value is estimated to be higher than that of the reverse reaction from *d*-**1H₂O** to *d*-**1Cl** at least by one order of magnitude when taking no observation of the reverse reaction from *d*-**1H₂O** to *d*-**1Cl** into account. This result might be explained by entropy factor, e.g., solvation, ion pair formation rather than enthalpy factor because the Ru-Cl bond length and angles around the Cl ligand for *d*-**2Cl** is very close to those for *d*-**1Cl** (Table 2).

Photoisomerization from *d*-**2H₂O** to *p*-**2H₂O**

When an aqueous solution of *d*-**2H₂O** was irradiated with visible light ($\lambda > 420 \text{ nm}$, 180 mWcm^{-2}), the signal at 9.7 ppm for *d*-**2H₂O** decreased with irradiation time, and a new signal at 9.1 ppm appeared at the same time (Figure 4A). This is similar spectral change in photoisomerization of *d*-**1H₂O** to *p*-**1H₂O** (9.5 ppm to 8.9 ppm), showing that *d*-**2H₂O** also undergoes photoisomerization to form *p*-**2H₂O** in water by visible light irradiation (Scheme 1). The photoisomerization completed after 800 s as shown by the time course of the concentration of *d*-**2H₂O** in Figure 4B. The slope of plots of $\ln([d\text{-}\mathbf{2H_2O}])$ versus time provided a rate constant ($k_{\text{pi}} = 4.9 \times 10^{-3} \text{ s}^{-1}$) [44] for photoisomerization, which is higher than that ($k_{\text{pi}} = 4.1 \times 10^{-3} \text{ s}^{-1}$) [30, 34] observed for *d*-**1H₂O** under the same conditions. The internal quantum yield (Φ) for photoisomerization was provided from the UV-visible absorption spectral change in the experiment using monochromatic light (520 nm, 26.4 mW cm^{-2}) and calculated according to the following eq. (2):

$$\Phi = \frac{hcN_A k_{pi} n_{int}}{p\lambda A(1-T)} \quad (2)$$

where k_{pi} , n_{int} , h , p , λ , c , N_A , T and A are the rate constant ($1.6 \times 10^{-2} \text{ s}^{-1}$) for photoisomerization, initial amount (0.26 mol) of *d*-**2H₂O**, Plank's constant, photon flux ($26.4 \times 10^{-3} \text{ W cm}^{-2}$), wavelength ($5.2 \times 10^{-7} \text{ m}$), the speed of light, Avogadro's number, the transmittance and the irradiated area (3.0 cm^2), respectively. The Φ value of *d*-**2H₂O** was given to be 2.1%, which is higher than that ($\Phi = 1.5\%$) of *d*-**1H₂O**. For the photoisomerization, photo-dissociation of an aquo ligand on the complexes occurs *via* the $^3\text{MLCT}$ photoexcited state, thereby forming a five-coordinate intermediate. The *proximal*-isomer is then produced by re-coordination of a water molecule to this intermediate from the opposite side relative to the *tpy* plane. The higher Φ value might be due to the relatively longer lifetime of the $^3\text{MLCT}$ photoexcited state for *d*-**2H₂O** than *d*-**1H₂O** although the lifetimes of the $^3\text{MLCT}$ state are too short to be measured from the photoluminescence decay at room temperature.

Comparison of UV-visible absorption spectra

The UV-visible absorption spectra of *d*-**2Cl**, *d*-**2H₂O** and *p*-**2H₂O** are shown in Figure 5, and absorption data are summarized in Table 3 including those of *d*-**1Cl**, *d*-**1H₂O** and *p*-**1H₂O**. The MLCT band ($\lambda_{\text{max}} = 590 \text{ nm}$) for *d*-**2Cl** is located at longer wavelength compared with that ($\lambda_{\text{max}} = 542 \text{ nm}$) of *d*-**1Cl** due to the chloro substitution on *tpy*. The π - π^* level of the *tpy* ligand could be stabilized by the electron-withdrawing chloro substitution to lead to the red shift of the MLCT band. The UV-visible absorption spectrum of *d*-**2H₂O** ($\lambda_{\text{max}} = 524 \text{ nm}$) and *p*-**2H₂O** ($\lambda_{\text{max}} = 518 \text{ nm}$) are very similar, as it is for *d*- and *p*-**1H₂O** isomers. The MLCT bands of *d*-

and *p*-**2H₂O** do not shift to red by the chloro substitution rather slightly shift to blue, compared with *d*- and *p*-**1H₂O**, respectively. This shows that the MLCT bands of *d*- and *p*-**1H₂O** are not influenced by the chloro substitution on tpy as much as *d*-**1Cl**. The d orbital level of the Ru center could be stabilized by the chloro substitution, being coincided with stabilization of the π - π^* level of the tpy ligand for *d*- and *p*-**2H₂O**, in contrast to no longer stabilization of the Ru d orbital level by the chloro substitution for *d*-**2Cl**. The stabilized Ru d orbital level for *d*- and *p*-**2H₂O** will be supported by the following electrochemical data.

The electrochemical properties of *d*-**2H₂O** and *p*-**2H₂O**

The cyclic voltammogram (CV) of *d*-**2H₂O** in an aqueous solution at pH 7.0 exhibits two redox waves at 0.47 and 0.61 V in a potential range from 0.0 to 1.2 V, whereas the CV of *p*-**2H₂O** exhibiting a redox wave at 0.56 V (Figure 6). The corresponding half-wave potentials ($E_{1/2}$) *d*- and *p*-**2H₂O** are higher than those for *d*- and *p*-**1H₂O** under the same conditions by 10 ~ 50 mV due to the electron-withdrawing chloro substitution on tpy (Table 3). As shown by the Pourbaix diagram of *d*- and *p*-**2H₂O** in Figure 7, the $E_{1/2}$ values of two redox waves for *d*-**2H₂O** were pH-dependent (slope = 55 mV/pH) over a wide pH range of 1.5 ~ 9.3, suggesting the two-step reaction involving the successive one-proton-coupled one-electron reactions of the $\text{Ru}^{\text{II}}\text{-OH}_2/\text{Ru}^{\text{III}}\text{-OH}$ and $\text{Ru}^{\text{III}}\text{-OH}/\text{Ru}^{\text{IV}}\text{=O}$ redox couples. The $E_{1/2}$ value of the single redox wave for *p*-**2H₂O** was also pH-dependent (slope = 54 mV/pH) over the similar pH range, suggesting the one-step reaction involving the two-proton-coupled two-electron reaction of the $\text{Ru}^{\text{II}}\text{-OH}_2/\text{Ru}^{\text{IV}}\text{=O}$ redox couple. The redox properties of *d*- and *p*-**2H₂O** are similar to those of *d*- and *p*-**1H₂O** reported previously.[30, 34] The Pourbaix diagram also suggests that pK_a values of *d*- and

p-**2H₂O** are 9.2 and 10.9, respectively from the pH at which the slope changes under the basic conditions. These are nearly identical to p*K*_a values (9.3 and 10.9) of *d*- and *p*-**2H₂O** calculated from UV-vis absorption spectral change in pH titration. The comparison of the p*K*_a values in Table 3 shows that the p*K*_a value for *d*-**2H₂O** is decreased by the chloro substitution on tpy, but it is increased for *proximal*-isomer.

Water oxidation catalyzed by Ce^{IV} as an oxidant

The catalytic activities of *d*- and *p*-**2H₂O** for chemical water oxidation were investigated in a homogeneous aqueous solution using a Ce^{IV} oxidant. O₂ was significantly evolved in water oxidation by *d*-**2H₂O** with Ce^{IV}, and the amount (*n*_{O₂} / mol) of O₂ evolved increased linearly with time up to 2 h to reach 76 μmol at 16 h (Figure 8). *n*_{O₂} was 1.2 times higher than that (*n*_{O₂} = 62 μmol) for *d*-**1H₂O** under the same conditions. *p*-**2H₂O** does not work as efficiently as *d*-**2H₂O**, as illustrated by lower *n*_{O₂} for *p*-**2H₂O** compared with *d*-**2H₂O** in Figure 8. This is a similar character for the *d*- and *p*-**1H₂O** isomer system[30]. The initial O₂ evolution rates (*v*_{O₂} / mol s⁻¹) was calculated from the initial slope of the time course of *n*_{O₂} and are plotted versus the amount of the complex in Figure 9. These plots gave a linear relationship for both *d*- and *p*-**2H₂O** isomers, suggesting that water oxidation is a first order with respect to the complex for both isomers (Figure 9). The turnover frequency (*k*_{O₂} / s⁻¹) was provided from the slope of linear lines; *k*_{O₂} (6.3 × 10⁻³ s⁻¹) for *d*-**2H₂O** was higher than that (3.9 × 10⁻⁴ s⁻¹) for *p*-**2H₂O** by a factor of 16. From a perspective of the effect of chloro substitution on tpy, *k*_{O₂} for *d*-**2H₂O** was also 1.6 times higher than (3.8 × 10⁻³ s⁻¹) for *d*-**1H₂O**, whereas *k*_{O₂} for *p*-**2H₂O** was 1.2 times lower than that (4.8 × 10⁻⁴ s⁻¹) for *p*-**1H₂O**. If assuming that the formation of an O-O bond by the water nucleophilic attack on the Ru^V=O intermediate is rate-determining step, *k*_{O₂} could increase by the

chloro substitution because electrophilicity of $\text{Ru}^{\text{V}}=\text{O}$ increased, as is the case for $d\text{-2H}_2\text{O}$ relative to $d\text{-1H}_2\text{O}$. However, another explanation is required for the k_{O_2} decrease for $p\text{-2H}_2\text{O}$ relative to $p\text{-1H}_2\text{O}$. The detailed investigation on the catalysis by other derivatives with a variety of substitution groups needs to be explicated to gain better understanding of substitution effect on water oxidation catalysis by mononuclear ruthenium complexes.

Conclusion

$d\text{-2Cl}$, $d\text{-}$ and $p\text{-2H}_2\text{O}$ derivatives with a Cl-tpy ligand were newly synthesized to compare structures, physicochemical properties and unique reactions of aquation photoisomerization, proton-coupled redox reactions, water oxidation catalysis with $d\text{-1Cl}$, $d\text{-}$ and $p\text{-1H}_2\text{O}$ derivatives with a tpy ligand. The influence of chloro substitution of the tpy ligand on the outcome and mechanism for the examined reactions was revealed to provide insight into the electric factor affecting the reactions. These results are undauntedly informative and useful for design and development of ruthenium-based functional molecules including active catalysts for water oxidation that is indispensable to artificial photosynthesis.

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[44] The k_{pi} value is not real rate constant, rather than apparent one, because they are dependent on the light intensity.

Table 1 Data of X-ray structure analysis for *d*-[Ru(Cl-tpy)(pynp)Cl](ClO₄)

Compound	<i>d</i> -[Ru(Cl-tpy)(pynp)Cl](ClO ₄)
empirical formula	C ₂₈ H ₁₉ Cl ₃ N ₆ O ₄ Ru
formula weight	710.92
crystal system	orthorhombic
a / Å	30.666(4)
b / Å	8.7143(8)
c / Å	20.8983(17)
α / deg	90
β / deg	90
γ / deg	90
unit cell volume / Å ³	5584.7(9)
space group	<i>Pbcn</i>
cell formula units-Z	8
<i>R</i> ₁	0.0639(5198)
<i>wR</i> ₂	0.2230(6333)
GOF	1.029

Table 2 Summary of selected bond lengths [Å] and angles [°]

<i>distal</i> -[Ru(Cl-tpy)(pynp)Cl]ClO ₄							
selected bond lengths [Å]				selected angles [°]			
Ru-N _{distal} (1)	2.071(2)	Ru-N _{py} (4)	2.083(3)	N _{central} (2)-Ru-N _{np} (5)	102.85(13)	N _{central} (2)-Ru-Cl	86.20(10)
Ru-N _{central} (2)	1.967(3)	Ru-N _{np} (5)	2.069(6)	N _{distal} (3)-Ru-N _{np} (5)	90.69(14)	N _{distal} (3)-Ru-Cl	89.37(10)
Ru-N _{distal} (3)	2.080(3)	Ru-Cl	2.428(2)	N _{distal} (1)-Ru-N _{np} (5)	92.00(14)	N _{distal} (1)-Ru-Cl	91.23(10)
				N _{py} (4)-Ru-N _{np} (5)	78.02(15)	N _{py} (4)-Ru-Cl	92.87(12)
						Cl-Ru-N _{np} (5)	170.81(10)
<i>distal</i> -[Ru(tpy)(pynp)Cl]ClO ₄ ^{a)} [30]							
selected bond lengths [Å]				selected angles [°]			
Ru-N _{distal} (1)	2.060(3)	Ru-N _{py} (4)	2.073(3)	N _{central} (2)-Ru-N _{np} (5)	101.3(1)	N _{central} (2)-Ru-Cl	87.31(8)
Ru-N _{central} (2)	1.960(3)	Ru-N _{np} (5)	2.075(3)	N _{distal} (3)-Ru-N _{np} (5)	90.9(1)	N _{distal} (3)-Ru-Cl	88.72(8)
Ru-N _{distal} (3)	2.076(3)	Ru-Cl	2.421(1)	N _{distal} (1)-Ru-N _{np} (5)	92.5(1)	N _{distal} (1)-Ru-Cl	90.99(8)
				N _{py} (4)-Ru-N _{np} (5)	78.1(1)	N _{py} (4)-Ru-Cl	93.19(9)
						Cl-Ru-N _{np} (5)	171.14(8)

a) The numbering of elements for *distal*-[Ru(tpy)(pynp)Cl]ClO₄ is the same as that for *distal* -[Ru(Cl-tpy)(pynp)Cl]ClO₄ in Figure 2.

Table 3 Summary of physicochemical properties and kinetic parameters for various reactions of **1** [30, 34] and **2** derivatives.

complex	λ_{max} / nm (ϵ / $\text{M}^{-1}\text{cm}^{-1}$)	$\text{p}K_{\text{a}}$ ^{a)}	E^0 / V vs SCE (pH = 7.0)		Aquation ^{b)}	Photoisomerization		Water oxidation
			$\text{Ru}^{\text{II}}\text{-OH}_2/\text{Ru}^{\text{III}}\text{-OH}$	$\text{Ru}^{\text{III}}\text{-OH}/\text{Ru}^{\text{IV}}\text{=O}$	$(k_1)_{\text{obs}}$ / s^{-1} $(k_{-1})_{\text{obs}}$ / s^{-1}	k_{pi} / s^{-1} ^{c)}	Φ / % ^{d)}	k_{O_2} / s^{-1} ^{e)}
<i>d</i> - 2Cl	590 (9,200) ^{f)}	-	-	-	5.3×10^{-5} (8.5×10^{-6})	-	-	-
<i>d</i> - 2H₂O	524 (8,600) ^{g)}	9.3	0.47	0.61	-	4.9×10^{-3}	2.1	6.3×10^{-3}
<i>p</i> - 2H₂O	518 (8,900) ^{g)}	10.9	0.56 ^{h)}	0.56 ^{h)}	-	-	-	3.9×10^{-4}
<i>d</i> - 1Cl	542 (8,600) ^{f)}	-	-	-	5.7×10^{-5} (not observed)	-	-	-
<i>d</i> - 1H₂O	527 (9,300) ^{g)}	9.7	0.42	0.60	-	4.1×10^{-3}	1.5	3.8×10^{-3}
<i>p</i> - 1H₂O	524 (9,300) ^{g)}	10.7	0.53 ^{g)}	0.53 ^{g)}	-	-	-	4.8×10^{-4}

a) $\text{p}K_{\text{a}}$ values are measured from UV visible absorption spectral change in pH titration.

b) $(k_1)_{\text{obs}}$ and $(k_{-1})_{\text{obs}}$ are observed rate constants for aquation and reverse reactions, respectively, and measured at 3.9 mM and 25°C from ^1H NMR spectral data.

c) k_{pi} is rate constant for photoisomerization [44], as measured at 3.9 mM and 25°C from ^1H NMR spectral data.

d) The internal quantum yield (Φ) at 520 nm for photoisomerization was measured at 88 μM , 25°C from the UV-visible absorption spectral data and calculated using eq. (2).

e) The turnover frequencies (k_{O_2}) of the complexes for water oxidation conducted under the conditions: 0.2 ~ 0.6 mM complex solution (5.0 ml), 0.5 mmol $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, 25°C and pH = 1.0.

f) and g) Measured in EtOH and H_2O , respectively

h) The redox reaction was observed as $2\text{e}^-/2\text{H}^+$ process of $\text{Ru}^{\text{II}}\text{-OH}_2/\text{Ru}^{\text{IV}}\text{=O}$

Scheme and Figure Captions

Scheme 1. Photoisomerization of *distal*-[Ru(Cl-tpy)(pynp)OH₂]²⁺ (*d*-**2H₂O**) to *proximal*-isomer (*p*-**2H₂O**).

Figure 1. Structures of *distal*- and *proximal*-isomers of **1** and **2** derivatives.

Figure 2. ORTEP view of [*d*-**2Cl**](ClO₄) (30 % probability). A counter anion and a solvent are omitted for clarity.

Figure 3. (A) ¹H-NMR spectral change of *d*-**2Cl** in D₂O at 25°C and pD = 7.4. (B) Plots of the concentrations of *d*-**2Cl** versus time. The initial concentrations of *d*-**2Cl** is 3.9 mM.

Figure 4. (A) ¹H-NMR spectral change of *d*-**2H₂O** in D₂O with visible light irradiation ($\lambda > 420$ nm, 180 mWcm⁻²) at 25°C and pD = 7.4. (B) Plots of the concentrations of *d*-**2H₂O** versus time. The initial concentration of *d*-**2H₂O** is 3.9 mM.

Figure 5. UV-visible absorption spectra of *d*-**2Cl** in EtOH (black), *d*-**2H₂O** in H₂O (red) and *p*-**2H₂O** in H₂O (blue).

Figure 6. Cyclic voltammograms of 0.5 mM *d*-**2H₂O** (red) and *p*-**2H₂O** (blue) in 0.1 M phosphate buffer (pH 7.0) at 20 mV s⁻¹ at a scan rate. The effective area of glassy carbon rod working electrode is 0.071 cm².

Figure 7. Pourbaix diagram for *d*-**2H₂O** (◻) and *p*-**2H₂O** (◊) in an aqueous solution.

Figure 8. Time courses of the amount (n_{O_2}) of O₂ evolved by *d*-**2H₂O** (■), *p*-**2H₂O** (●), *d*-**2H₂O** (◻), *p*-**2H₂O** (◊) in chemical water oxidation experiments in an aqueous solution at 25°C using a Ce^{IV} oxidant. Conditions: Ce^{IV}, 0.1 M (0.5 mmol) ; Ru complex, 1.0 μmol; liquid volume, 5.0 mL ; pH = 1.0.

Figure 9. Plots of initial rate (v_{O_2} / mol s⁻¹) of O₂ evolved vs. the amount of *d*-**2H₂O** (■), *p*-**2H₂O** (●), *d*-**2H₂O** (◻), *p*-**2H₂O** (◊). Conditions: Ce^{IV}, 0.1 M (0.5 mmol); liquid volume, 5.0 mL; pH = 1.0.

Scheme 1
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distal-isomer

proximal-isomer

1Cl : X = H, Y = Cl⁻

1H₂O : X = H, Y = H₂O

2Cl : X = Cl, Y = Cl⁻

2H₂O : X = Cl, Y = H₂O

Figure 1
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Figure 2

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Figure 3A

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Figure 3B

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Figure 4A

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Figure 4B

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Figure 5

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Figure 6

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Figure 7

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Figure 8

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Figure 9

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