### Inorganica Chimica Acta 390 (2012) 47-52

Contents lists available at SciVerse ScienceDirect

## Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

## Oxidation states and redox behavior of ruthenium ammine complexes with redox-active dioxolene ligands

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### ARTICLE INFO

Article history: Received 18 July 2011 Received in revised form 22 March 2012 Accepted 1 April 2012 Available online 7 April 2012

Keywords: Redox-active ligands Oxidation states Ruthenium Valence tautomerism

### ABSTRACT

Synthesis of ruthenium-dioxolene complexes with ammines  $[Ru(NH_3)_4(diox-R)]^{n+}$ , where diox-R is a dioxolene with substituent R = 3,5-di-*tert*-butyl, H, tetrachloro, and 4-nitro, was carried out. These complexes were characterized by spectroscopy, magnetic susceptibility measurements, and cyclic voltammetry. The oxidation states of ruthenium and the redox-active dioxolene ligand in the complexes varied depending on the nature of the dioxolene substituents.  $[Ru(NH_3)_4(diox-R)]^{n+}$  (R = 3,5-di-*tert*-butyl and H) has a divalent ruthenium and dioxolene in the quinone oxidation state with a minor amount of the complex in Ru(III)-semiquinonato oxidation state. The complexes exhibited valence tautomerism depending on the donor number of solvents. However,  $[Ru(NH_3)_4(diox-R)]^{n+}$  (R = tetrachloro and 4-nitro) has a trivalent ruthenium and dioxolene in the catecholate oxidation state. Electrochemical and spectro-electrochemical investigation of these complexes revealed that their electrochemical behavior depended on not only the oxidation state of the prepared complex but also the nature of the dioxolene substituent in the complex. Their redox reaction was found to proceed by the EC mechanism involving valence tautomerism.

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### 1. Introduction

Transition metal complexes with redox-active ligands often exhibit unique photochemical and electrochemical behavior. Metal complexes with dioxolene ligands have been intensively studied, because dioxolene takes three oxidation states; quinone (bq), semiquinonate (sq), and catecholate (cat) [1]. The complexes may take various oxidation states with different combinations of possible metal and ligand oxidation states. Thus, the resulting electrochemical properties make these complexes considerably complicated. Various metal-dioxolene complexes, particularly ruthenium complexes, were prepared by Pierpont and co-workers [2] and Lever et al. [3]. In ruthenium-dioxolene complexes, the energy level of the 4*d* orbital of ruthenium is close to that of  $\pi^*$  orbital of dioxolene, resulting in delocalization between the two orbitals. When considerable delocalization occurs between a redox-active metal center and coordinated dioxolene, the assignment of oxidation states to the metal or dioxolene may be ambiguous, particularly for ruthenium-dioxolene complexes with polypyridines [4].

Ruthenium-dioxolene complexes with polypyridine showed the redox reaction associated with dioxolene center. In contrast, ruthenium-dioxolene complexes with ammines as an ancillary ligand may show the redox reaction associated with metal center as well

\* Corresponding author. *E-mail address:* isaoando@fukuoka-u.ac.jp (I. Ando). as that with the dioxolene center, because the ammine ligand is considerably poor  $\pi$ -acid than the polypyridine ligand. Valence tautomerism has been observed for transition metal complexes with dioxolenes [1]; furthermore, ruthenium ammine complexes show remarkable solvatochromism [5]. Therefore, the oxidation state of ruthenium-dioxolene complexes with ammines should be significantly affected by external stimuli including chemical as well as physical stimuli. We have reported that ruthenium ammine complexes produced a prominent change in redox potential by second-sphere coordination with crown ether [6]. Although ruthenium-ammine complexes are well known, rutheniumdioxolene complexes with an ammine ligand have become attractive complexes for the exploration for the diversity of oxidation states and redox behavior of the complexes with redox-active ligands. However, only a few ruthenium-dioxolene complexes with ammines as an ancillary ligand have been reported to dater [7]. Electron-donating and electron-withdrawing substituents have opposite influences on the coordination ability and redox ability of dioxolenes. The oxidation state and electrochemical behavior of the dioxolene complex may be affected by these dioxolene derivatives depending on the nature of the dioxolene substituent. However, such an effect has not been observed.

To examine the effect of the nature of the dioxolene substituents on the oxidation state of the complex and the possibility of valence tautomerism, ruthenium-dioxolene complexes with ammines were newly prepared using dioxolenes with different





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substituents in this study. The oxidation states of the prepared complexes were characterized and their redox behavior was examined.

### 2. Experimental

### 2.1. Materials and measurements

Tetrachlorocatechol (TClcatH<sub>2</sub>), 4-nitrocatechol (NO<sub>2</sub>catH<sub>2</sub>), 3,5-di-*tert*-butylcatechol (DBcatH<sub>2</sub>), and catechol (HcatH<sub>2</sub>) were obtained from Aldrich, Tokyo Kasei or Wako and used as received. The precursor complexes,  $[Ru(NH_3)_5Cl]Cl_2$  and *cis*- $[Ru(NH_3)_4Cl_2]Cl$ , were prepared according to the reported procedures [8,9]. Acetonitrile *d*-3 (containing 0.03% tetramethylsilane, Aldrich) was used for <sup>1</sup>H NMR spectra measurements. Other chemicals and solvents were of reagent grade and used as received.

Absorption spectra were recorded on a Hitachi 228A spectrophotometer. <sup>1</sup>H NMR spectra were measured at 400 MHz using a JEOL JNM/GSX-400 NMR spectrometer and chemical shifts were obtained using tetramethylsilane as an internal standard. Cyclic voltammetry was performed by means of a BAS 100W/B electrochemical workstation. Voltammograms were observed in acetonitrile solution of 0.1 mol dm<sup>-3</sup> tetrabutylammonium hexafluorophosphate using a three-electrode assembly, an Ag/AgNO<sub>3</sub> reference electrode, a glassy carbon working electrode, and a platinum coil auxiliary electrode. Spectroelectrochemical measurements were performed in an optically transparent thin-layer electrolytic (OTTLE) cell [10], using a Hitachi 228A spectrophotometer combined with a BAS 100W/B electrochemical workstation. The OTTLE cell uses a gold minigrid (500 mesh) as a working electrode, the platinum mesh as an auxiliary electrode, and the gold foil as a pseudo reference electrode. Electron spin resonance (ESR) measurements were carried out with a JES-REIX ESR spectrometer (X-band). Magnetic susceptibilities were recorded between 2 and 300 K with a Quantum Design MPM-5XL SQUID susceptometer. Analytical data for elements C, H, and N were obtained from the Microanalytical Laboratory of Kyushu University. Atomic absorption analysis of the ruthenium content of the prepared complexes was conducted according to Rowston's method [11] by using a Seiko SAS 7500A spectrophotometer.

### 2.2. Synthesis of complexes

### 2.2.1. $cis-[Ru(NH_3)_4(TClcat)](PF_6) \cdot H_2O(1)$

A suspended solution of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl (0.29 g, 1 mmol) in 5 cm<sup>3</sup> of a 3:2 H<sub>2</sub>O–EtOH mixture was reduced with Zn-amalgam under a nitrogen atmosphere until the complex was completely dissolved. A solution of TClcatH<sub>2</sub> (0.265 g, 1 mmol) in 5 cm<sup>3</sup> of a 3:2 H<sub>2</sub>O–EtOH mixture was added to the filtrate after the Zn-amalgam was removed. Then concentrated aqueous ammonia (2 mmol) was slowly added to the resulting solution and the mixture was heated at 55 °C under a nitrogen atmosphere for 1 h with stirring. After cooling to room temperature, excess of NH<sub>4</sub>PF<sub>6</sub> (1.63 g, 10 mmol) was added to the solution. The precipitated product was collected and dried over P2O5 under reduced pressure. The precipitate was washed three times with CHCl<sub>3</sub> and dissolved with a small amount of CH<sub>3</sub>CN to remove insoluble impurities. The filtrate was evaporated to dryness under reduced pressure, and the solid mass was purified by column chromatography using neutral alumina. The desired blue band was eluted with EtOH. After removal of the solvent under reduced pressure, a saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> was added to the aqueous solution of the solid mass. The precipitated blue complex was collected and dried over P<sub>2</sub>O<sub>5</sub> under vacuum. Anal. Calc. for C<sub>6</sub>H<sub>14</sub>N<sub>4</sub>Cl<sub>4</sub>F<sub>6</sub>O<sub>3</sub>-

PRu: C, 12.47; H, 2.44; N, 9.69; Ru, 17.5. Found: C, 11.83; H, 2.35; N, 9.64; Ru, 18.3%.

### 2.2.2. $cis-[Ru(NH_3)_4(NO_2cat)](PF_6) \cdot H_2O(2)$

The complex was prepared using a procedure similar to that used for *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(TClcat)](PF<sub>6</sub>) except that NO<sub>2</sub>catH<sub>2</sub> was used instead of TClcatH<sub>2</sub>. The pure complex was obtained as blue-green solid by collecting the blue-green band separated by column chromatography. *Anal.* Calc. for C<sub>6</sub>H<sub>17</sub>N<sub>5</sub>F<sub>6</sub>O<sub>5</sub>PRu: C, 14.85; H, 3.53; N, 14.43; Ru, 20.88. Found: C, 14.56; H, 3.18; N, 14.45; Ru, 22.3%.

# 2.2.3. cis-[ $Ru(NH_3)_4(DBbq)$ ]( $PF_6$ )<sub>2</sub>· $H_2O(3)$ (DBbq = 3,5-di-tert-butyl-1,2-benzoquinone)

The complex was prepared in aerobic condition by a procedure similar to that used for *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(TClcat)](PF<sub>6</sub>) except that DBcatH<sub>2</sub> was used instead of TClcatH<sub>2</sub>. The pure complex was obtained as a reddish purple solid by collecting the reddish-purple band separated by column chromatography. *Anal.* Calc. for C<sub>14</sub>H<sub>34</sub>N<sub>4</sub>F<sub>12</sub>O<sub>3</sub>P<sub>2</sub>Ru: C, 24.11; H, 4.62; N, 8.03; Ru, 14.5. Found: C, 24.17; H, 4.74; N, 8.27; Ru, 14.5%.

### 2.2.4. $cis-[Ru(NH_3)_4(Hbq)](BPh_4)_2 \cdot H_2O(4)$ (Hbq = 1,2-benzoquinone)

The complex formation reaction was conducted using a procedure similar to that used for *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(TClcat)](PF<sub>6</sub>) except that HcatH<sub>2</sub> was used instead of TClcatH<sub>2</sub>. However, the crude complex was isolated as the chloride salt by adding 200 cm<sup>3</sup> acetone to the reaction mixture. The chloride salt was purified by alumina column chromatography. The desired blue band was eluted with H<sub>2</sub>O and the solvent was removed by evaporation to dryness. Sodium tetraphenylborate (NaBPh<sub>4</sub>) was added to the aqueous solution of the chloride salt of the complex. The resulting mixture was allowed to stand overnight in contact with air. The precipitated purple complex was collected and was freely washed with H<sub>2</sub>O. *Anal.* Calc. for C<sub>54</sub>H<sub>58</sub>N<sub>4</sub>B<sub>2</sub>O<sub>3</sub>Ru: C, 69.46; H, 6.04; N, 6.00; Ru, 10.8. Found: C, 69.82; H, 6.12; N, 5.84; Ru, 9.7%.

### 3. Results and discussion

Because redox active dioxolene exists in oxidation states such as cat, sq, and bq, the tetraammineruthenium complexes containing a dioxolene can exist in several oxidation states as shown in Scheme 1. Syntheses of tetraammineruthenium-dioxolene complexes were attempted by reactions of *cis*-tetraammine precursor-complexes in Ru(II) and Ru(III) oxidation states with dioxolenes of cat and bq forms. However, the complexes were obtained only by the reaction of the precursor complex in the Ru(II) oxidation state with dioxolene in the cat form, as described in Section 2. The analytical data in Section 2 revealed that complexes **1** and **2** were obtained in either the Ru(II)-cat or Ru(II)-sq oxidation state, and complexes **3** and **4** were obtained in either the Ru(II)-bq



**Scheme 1.** Schematic diagram of redox pathways for ruthenium-dioxolene complex. Ru(II) and Ru(III) represent a tetraammineruthenium moiety in the bivalent and trivalent oxidation states, respectively. Cat, sq, and bq represent dioxolene in catecholate, semiquinonate, and benzoquinone oxidation states, respectively. VT denotes valence tautomerism.

or Ru(III)-sq oxidation state despite similar preparation procedures. The oxidation state of the obtained complexes differs extremely depending on the dioxolene substituent. Thus, the nature of these substituents significantly affects the stable oxidation state of the dioxolene complex.

### 3.1. <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR spectra of the prepared complexes were measured in deuterated acetonitrile. For complex 3, resonance signals were observed in ordinary region (0–12 ppm); the signals at 1.54 and 1.66 ppm were assigned to methyl protons of *tert*-butyl group, those at 5.25 ppm to ammine protons in the *cis*-position toward dioxolene, those at 6.44 and 8.21 ppm to aromatic protons, and those at 11.02 and 11.20 ppm to ammine protons in the transposition toward dioxolene according to the sharpness and integral ratios of the signals (Fig. S1). For complex 4, the signals of aromatic protons in dioxolene and tetraphenyl borate were observed at 6-8 ppm but those of ammine protons were not observed because of overlap with the signal of the solvent itself (Fig. S2). For complexes 1 and 2, on the other hand, broad signals were observed in the extremely low field region: 135 and 151 ppm for complex 1 and 84, 148, and 184 ppm for complex 2 (Figs. S3 and S4, respectively). For complex 1, the signals at 135 and 151 ppm were assigned to ammine protons; for complex **2**, the signals at 84 ppm was assigned to aromatic protons, and those at 148 and 184 ppm were assigned to ammine protons, respectively, according to the integral ratios [12]. Although the resonance signals were observed in the ordinary region (0-12 ppm) for complexes 3 and 4, broad signals were observed for complexes 1 and 2 in the extremely low field region. These results revealed that ammine ligands bind to the diamagnetic ruthenium center in complexes 3 and 4 but to the paramagnetic ruthenium center in complexes 1 and 2.

### 3.2. Magnetic properties

Magnetic susceptibility of the prepared complexes was also measured at 2–300 K. Fig. 1 shows the temperature dependence of the magnetic moments of the complexes. Most complexes exhibited simple paramagnetic behavior. The estimated values of the effective magnetic moments at 300 K were 2.01 and 1.97 BM for complexes **1** and **2**, respectively, which were close to the theoretical value of 1.73 BM for S = 1/2. On the other hand, the estimated values of the effective magnetic moments at 300 K were 0.94 and 0.07 BM for complexes **3** and **4**, respectively, which were



**Fig. 1.** Temperature dependence of effective magnetic moment of complexes **1**. (blue circles), **2** (green circles), **3** (red circles), and **4** (orange circles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

considerably smaller than the theoretical value for S = 1/2. This result suggests that complexes **1** and **2** were isolated in the Ru(III)-cat oxidation state, whereas complexes **3** and **4** were isolated in the Ru(II)-bq oxidation state containing a small amount of the Ru(III)-sq oxidation states.

Electron spin resonance (ESR) spectra of complexes **1–4** were measured in the solid state and in acetonitrile solution to confirm the existence of Ru(III) species and or semiquinonate species in the complex and are shown in Fig. S5. Complexes **1** and **2** exhibited a broad ESR signal at g = 2.525 and 2.819, respectively, in the solid state at 77 K indicating the existence of a Ru(III) center [13]. On the other hand, complex **3** showed only a sharp signal at g = 2.054 in the solid state at 77 K, implying the existence of radical species. Complex **4** showed a broad signal at g = 2.490 in addition to a sharp signal at g = 2.063 in the solid state at 77 K, implying the existence of Ru(III) center and radical species. At room temperature, in solid state, only a sharp signal at g = 2.005 and 2.003 was observed for complexes **3** and **4**, respectively. In acetonitrile solution at 77 K, complex **1** exhibited a broad signal at g = 2.069.

The ESR spectra supported the results of magnetic susceptibility mentioned above. Thus, rutheniumtetraammine-dioxolene complexes were isolated in the Ru(III)-cat, Ru(III)-sq, and Ru(II)-bq oxidation states depending on the dioxolene substituent, unlike tetrakis(pyridine) ruthenium complexes [14].

### 3.3. Absorption spectra

The dioxolene-tetraammineruthenium complexes were obtained at different oxidation states depending on the dioxolene substituent. Complexes **3** and **4** were isolated at both oxidation states simultaneously. This suggests the possibility of valence tautomerism between the Ru(II)-bq and Ru(III)-sq oxidation states.

Absorption spectra of the prepared complexes were measured in solution. The spectral characteristics are listed in Table 1. The complexes exhibited bands ascribed to metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) in the visible region and the dioxolene center in the ultraviolet region. The assignment of the charge transfer (CT) bands in the visible region was determined using solvent dependence as follows.

For rutheniumammine complexes, an MLCT or a LMCT band shows remarkable solvatochromism; the energies of an MLCT band decrease linearly with the donor number (DN) of the solvent, whereas those of an LMCT band increase linearly with the DN of the solvent [5]. Thus, the energy of the CT band was examined in solution using solvents with various DN. For complex **2**, solvato-

Table 1				
Spectral ch	aracteristics of	the	prepared	complexes

Complexes	$\lambda_{\rm max}$ , nm ( $\varepsilon_{\rm max}$ , mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> )	
1	$\begin{array}{l} 300 \; (6.36 \times 10^3) \\ 345 \; sh \\ 658 \; (2.40 \times 10^3) \end{array}$	in water
2	220 $(8.68 \times 10^3)$ 258 $(6.55 \times 10^3)$ 330 sh 402 $(6.47 \times 10^3)$ 650 $(1.81 \times 10^3)$	in water
3	273 $(6.36 \times 10^3)$ 352 $(1.77 \times 10^3)$ 370 sh 450 sh 523 $(7.82 \times 10^3)$	in water
4	246 $(1.82 \times 10^4)$ 440 sh 470 sh 516 $(7.49 \times 10^3)$	in acetonitrile



**Fig. 2.** Solvent dependence of the CT band energy for complexes  $1 (\Box)$ ,  $3 (\bullet)$ , and  $4 (\bigcirc)$ .

chromism of the CT band was not successfully observed because of the overlap of the CT band with absorption by NO<sub>2</sub>catH<sub>2</sub> itself. As Fig. 2 shows, the CT band of complex 1 showed solvatochromic behavior typical of LMCT band, although the CT bands of complexes **3** and **4** exhibited rather complicated behavior, *i.e.*, similar CT bands with a shoulder at shorter wavelength as listed in Table 1. The CT bands of complex **3** in several solvents are shown in inset of Fig. 3. The CT band varied with the DN of the solvent; the shoulder developed gradually with increasing solvent DN. This fact indicates that the CT band may be composed of two components attributable to species in different oxidation states. Thus, the CT band was deconvoluted into two bands and the energies of the two deconvoluted bands were plotted against the DN of the solvents in Fig. 3. Two components exhibited opposite behavior; one has a negative slope and the other has a positive slope. This indicates the coexistence of tetraammineruthenium(II)- and tetraammineruthenium(III)-species. Considering the aforementioned data, complex 3 exists in both the Ru(II)-bq and Ru(III)-sq oxidation states in solution. The inset in Fig. 3 shows that the species in Ru(III)-sq oxidation state are predominant in solvents with a smaller DN, but the species in Ru(II)-bq oxidation state become predominant with increasing DN for complex 3 in solution. To the best of our knowledge, this is the first report on ruthenium complexes demonstrating valence tautomerism induced by solvents.

### 3.4. Electrochemistry

As shown in Scheme 1, the redox reaction of ruthenium-dioxolene complexes may proceed through versatile pathways including



**Fig. 3.** Solvent dependence of the deconvoluted CT band energy in the visible region for complex **3.** Inset shows the CT band in nitromethane, methanol, and hexamethyphosphoramide.

valence tautomerism. The oxidation state of the complexes in this study is significantly affected by the dioxolene substituent on and other factors. Thus, the effect of dioxolene substituents on the electrochemical behavior of the dioxolene complexes is very interesting. To clarify their redox behavior, electrochemical and spectroelectrochemical investigation of the tetraammineruthenium-dioxolene complexes were conducted; the results are shown in Figs. 4 and 5.

The assignment of the observed redox couple is in difficult because the redox process is either metal centered or dioxolene centered, as shown in Scheme 1. Ruthenium ammine complexes reportedly exhibited a change in redox potential toward negative potential by adduct formation with crown ether [6,15]. The magnitude of the change is large for the redox process associated with the metal center (larger than ca. 100 mV) but small for that associated with the aromatic ligand center (less than ca. 50 mV). The redox couple was judged to involve either the metalcentered or dioxolene-centered redox process according to the magnitude of the change in the redox potential on addition of a 100-fold excess of crown ether to the complex. The spectroelectrochemical experiments also confirmed whether the redox processes might involve isomeric equilibrium between valence tautomers.

Complex **1** showed two reversible redox couples at -1.039 and 0.290 V versus (Ag<sup>+</sup>/Ag), as shown in Fig. 4a. These redox couples are ascribed to the redox process of Eq. (1) or (2) and of Eq. (3) or (4) considering the oxidation state at a rest potential of ca. 0 V versus (Ag<sup>+</sup>/Ag) (the oxidation state of the isolated complex, Ru(III)-cat).

(3)

(4)



**Fig. 4.** (a) Cyclic voltammograms of complex **1** in the absence (black line) and presence (red line) of 18-crown-6 ether in acetonitrile. Scan rate was  $50 \text{ mV s}^{-1}$ . [complex] =  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [18-crown-6ether] = 0 or 0.1 mol dm}^{-3}. (b) Spectral changes during electrochemical oxidation of complex **1** at (1) 0, (2) 0.30, (3) 0.32, (4) 0.34, (5) 0.36, and (6) 0.40 V vs. pseudo Au. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

 $Ru(III)-cat + e^{-} \rightleftharpoons Ru(II)-cat$ (1)

$$Ru(III)\text{-}cat \rightleftharpoons Ru(II)\text{-}sq$$
(2)

Ru(II)-sq + e<sup>-</sup>  $\Rightarrow$  Ru(II)-cat

$$Ru(III)$$
-sq + e<sup>-</sup>  $\Rightarrow$   $Ru(III)$ -cat

$$Ru(II)$$
-bq  $\Rightarrow$   $Ru(III)$ -sq

$$\mathrm{Ru}(\mathrm{II})\operatorname{-}\mathrm{Dq} + \mathrm{e}^{-} \rightleftharpoons \mathrm{Ru}(\mathrm{II})\operatorname{-}\mathrm{sq} \tag{4}$$

$$Ru(II)$$
-sq  $\Rightarrow$   $Ru(III)$ -cat

As shown in Fig. 4a, both couples were shifted toward negative potentials by the addition of a 100-fold excess of 18-crown-6 ether. The shift in the redox couple at -1.039 V versus (Ag<sup>+</sup>/Ag) (-186 mV) was considerably larger, whereas that in the redox couple at 0.290 V versus (Ag<sup>+</sup>/Ag) (-53 mV) is smaller. These voltammetric results indicate that the couples in the cathodic and anodic regions correspond to the metal-centered and dioxolene-centered processes, respectively. Thus, the redox couple at -1.039 and the redox couple at 0.290 V versus (Ag<sup>+</sup>/Ag) were assigned to the processes of Eqs. (1) and (3), respectively.

To confirm that the redox process at 0.290 V versus  $(Ag^+/Ag)$  involves the valence tautomeric equilibrium, the change in the absorption spectra was measured when complex **1** was



**Fig. 5.** (a) Cyclic voltammograms of complex **3** in the absence (black line) and presence (red line) of 18-crown-6 ether in acetonitrile. Scan rate was 50 mV s<sup>-1</sup>. [complex] =  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [18-crown-6 ether] = 0 or 0.1 mol dm<sup>-3</sup>. (b) Spectral changes during electrochemical reduction of complex **3** at (1) 0, (2) -0.25, (3) -0.28, (4) -0.31, and (5) -0.34 V vs. pseudo Au. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

electrochemically oxidized in an OTTLE cell [10] at 0–0.4 V versus pseudo Au. The band at ca. 650 nm disappeared as oxidation progressed, whereas the band at ca. 500 nm developed, as shown in Fig. 4b. This spectral change indicates the oxidation of the Ru(III)-cat oxidation state to the Ru(II)-bq oxidation state, referring to the spectral characteristics of the complexes in Table 1. Therefore, in the redox process at 0.290 V versus (Ag<sup>+</sup>/Ag), complex **1** was oxidized from the species in the Ru(III)-cat oxidation state to those in the Ru(III)-sq oxidation state, and the species in the Ru(III)-sq oxidation state. Similar results were obtained for complex **2** (Fig. S6).

Fig. 5 shows the results of similar measurements for complex **3**. Complex **3** showed three major redox waves; an irreversible redox couple at -1.205 V versus (Ag<sup>+</sup>/Ag), a reversible redox couple at -0.329 V versus (Ag<sup>+</sup>/Ag), and an oxidation peak at 0.861 V versus (Ag<sup>+</sup>/Ag). Furthermore, two minor redox waves were observed in the region of 0–0.6 V versus (Ag<sup>+</sup>/Ag); reduction peak at 0.124 V versus (Ag<sup>+</sup>/Ag) and a reversible redox couple at 0.468 V versus (Ag<sup>+</sup>/Ag). These waves were unobservable at a scan rate of 5 mV s<sup>-1</sup> but developed with increasing scan rate.

The major redox waves at -1.205, -0.329, and 0.861 V versus (Ag<sup>+</sup>/Ag) were shifted by -232, -73, and +131 mV, respectively, by the addition of a 100-fold excess of 18-crown-6 ether (see Fig. 5a) and were assigned as shown below. Because the valence tautomeric equilibrium, Eq. (5), holds at the rest potential of ca. 0 V versus (Ag<sup>+</sup>/Ag), as mentioned in Section 3.3, the oxidation wave at

$Ru(III)$ - $sq \rightleftharpoons Ru(II)$ - $bq$	(5)
$Ru(III)\text{-}bq + e^{-} \gets Ru(II)\text{-}bq$	(6)
$Ru(III)\text{-}bq + e^{-} \leftarrow Ru((III)\text{-}sq$	(7)
$Ru(II)$ -bq + e <sup>-</sup> $\rightleftharpoons$ $Ru(II)$ -sq	(8)
$Ru(III)$ - $sq + e^{-} \rightleftharpoons Ru(II)$ - $sq$	(9)
$Ru(III)$ -sq + e <sup>-</sup> $\Rightarrow$ $Ru(III)$ -cat	(10)
$Ru(II)$ -sq + e <sup>-</sup> $\rightleftharpoons$ $Ru(II)$ -cat	(11)
$Ru(III)$ -cat + e <sup>-</sup> $\rightleftharpoons$ $Ru(II)$ -cat	(12)
$Ru(II)$ -sq $\Rightarrow$ $Ru(III)$ -cat	(13)

0.861 V versus (Ag<sup>+</sup>/Ag) was ascribed to the oxidation process of Eq. (6) or (7). As the potential shift in positive direction on the addition of 18-crown-6 ether does not imply the metal-centered process, the oxidation wave was assigned to the oxidation process of Eq. (7). The redox couples in the cathodic region were similarly assigned. The redox couple at -0.329 V versus (Ag<sup>+</sup>/Ag) was ascribed to the redox process of Eq. (8)–(10) and the redox couple at -1.205 V versus  $(Ag^{+}/Ag)$  is ascribed to that of Eq. (11) or (12). Because the large negative shift in the potential of both couples on the addition of 18-crown-6 ether is associated with the metal-centered process, the redox couples at -0.329 and -1.205 V versus (Ag<sup>+</sup>/Ag) were assigned to the redox processes of Eq. (9) and (12), respectively. The spectral change during electrochemical reduction at ca -0.3 V in Fig. 5b indicates the reduction of the Ru(II)-bq oxidation state to the Ru(III)-cat oxidation state, as can be seen by comparing the spectral characteristics of the complexes in Table 1. Therefore, complex **3** was reduced from the species in the Ru(III)-sq oxidation state equilibrated with the Ru(II)-bq oxidation state to the species in the Ru(II)-sq oxidation state at -0.329 V versus (Ag<sup>+</sup>/Ag). Furthermore, the species in the Ru(II)-sq oxidation state equilibrated with those in the Ru(III)-cat oxidation state of the valence tautomer formed by intramolecular electron transfer. Thus, the Ru(III)-sq/Ru(III)-cat process proceeds through an EC mechanism; the species in the Ru(III)-sq oxidation state is reduce to the species in the Ru(III)-cat oxidation state via the species in the Ru(II)-sq oxidation state.

The minor redox waves in the region of 0–0.6 V versus  $(Ag^+/Ag)$  may be tentatively assigned to redox associated with the species of Ru(II)-bq equilibrated with the species in the Ru(III)-sq oxidation state; the reduction wave at 0.124 V versus  $(Ag^+/Ag)$  may be assigned to the reduction of Ru(II)-bq to Ru(II)-sq, and the redox couple at 0.468 V versus  $(Ag^+/Ag)$  may be assigned to the Ru(III)-bq/Ru(II)-bq redox couple. The latter assignment is consistent with the shift magnitude of the redox potential on addition of crown ether (-140 mV). Similar results were obtained for complex **4** although the oxidation wave ascribed to the oxidation of Ru(III)-sq to Ru(III)-bq was not observed owing to the oxidation of tetraphenylborate as a counter ion. (Fig. S7).

Thus, we speculate that the redox processes involve valence tautomerism for the tetraammineruthenium-dioxolene complexes in this study.

### 4. Conclusions

In this study, dioxolene complexes of ruthenium were synthesized using ammines as an ancillary ligand. The oxidation state of the prepared complexes varied depending on the dioxolene substituent. For complex 3, both valence tautomers exist in the Ru(III)sq and Ru(II)-bq oxidation state in the solid state. In the solution, the ratio of the tautomers varied with the DN of the solvents. The reduction and oxidation of the complexes can proceed through several pathways, as shown in Scheme 1. Complexes 1 and 2 undergo reduction-oxidation via the EC mechanism involving a valence tautomeric equilibrium, whereas complexes 3 and 4 undergo reduction-oxidation via rather complicated pathways involving two valence tautomeric equilibria. The redox pathway of a dioxolene complex is significantly affected by the properties of the dioxolene substituents, and valence tautomerism may play an important role in changing the redox pathway of dioxolene complexes of ruthenium. Unfortunately, the effect of temperature on the valence tautomerism was not observed in this study, and the investigations of the other factors are in progress.

### Acknowledgments

The authors thank Dr. H. Tanaka of Fukuoka University for ESR measurements. This work was partly supported by the "Nanotechnology Support Project" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.04.002.

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