

# Synthesis, and redox behavior of tetraammineruthenium complexes with *N*, *O*-donor quinonoid for a search of semiquinone oxidation-state

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## Abstract

*cis*-Tetraammine-ruthenium complexes were synthesized using redox active ligands with N and O donor atoms. Aminophenol derivatives were chosen as a redox-active ligand involved electron-withdrawing or electron-donating substituent on phenyl ring or/and amino group of aminophenol. Oxidation states of central ruthenium and aminophenol in the complexes were characterized by analysis of Ru, C, H, N content, <sup>1</sup>H-NMR and absorption spectroscopies, and cyclic voltammetry. Pourbaix diagram analysis of the complexes was performed to explore the semiquinone oxidation-state of the complexes.

**Keywords:** Ruthenium-ammine complex, *N*, *O*-coordination, Semiquinone oxidation-state, Pourbaix diagram

## 1. Introduction

Quinonoid takes relatively stable oxidation states; catecholate (**cat**), semiquinone (**sq**), and quinone (**q**), and their transition metal complexes are possible to exist at several oxidation states. Quinonoid complexes of transition metals were reported by many groups. [1, 2] Pierpont et al. developed the chemistry of the **sq** oxidation-state of their complexes. [2] In their complexes, the oxidation states may be changed by external stimuli. Valence tautomerism was observed in the iron, manganese, and cobalt complexes of dioxolenes by applying the external stimuli such as heat, light and electric field. [3]

Focusing on **sq** oxidation state, many ruthenium complexes of dioxolenes were reported using polypyridines as an ancillary ligand. [2, 4] For ruthenium-dioxolene complexes with polypyridines, the assignment of oxidation states to ruthenium or dioxolene may be ambiguous because the energy level of the *4d* orbital of ruthenium is close to that of  $\pi^*$  orbital of dioxolene resulting in delocalization between the two orbitals. In contrast, ruthenium-dioxolene complexes with amines as an ancillary ligand may show the redox reaction associated with metal center as well as that with the dioxolene center, because the ammine ligand is considerably poor  $\pi$ -acid than the polypyridine ligand. We have investigated ruthenium-ammine complexes with

dioxolenes. [5-7]

*cis*-Tetraammineruthenium complexes with dioxolenes were isolated at the different oxidation states of ruthenium and the dioxolene depending on the nature of the dioxolene substituents. [7] Furthermore, *cis*-tetraammineruthenium complexes with 3,5-di-*tert*-butyl-1,2-benzoquinone exhibited valence tautomerism by organic solvents and the pH of aqueous solution of the complex. [5,7] The oxidation state of the dioxolene complex involving amines as an ancillary ligand is significantly affected by the substituent on dioxolene and the environment around the complex. The electronic state of ruthenium-ammine complexes is also affected by the second sphere ligand.[8] Tetraammineruthenium complexes of *N*, *N*-donor quinonoid showed different redox process from *O*, *O*-donor quinonoid complex though isolating at the same oxidation state.[6] Thus, it is interested in *cis*-tetraammineruthenium complex of *N*, *O*-donor quinonoid.

In this study, *cis*-tetraammineruthenium complexes of *o*-aminophenol derivatives were prepared and Pourbaix analysis was performed in order to investigate the factors affecting the oxidation state of their complexes.

## 2. Experimental

### 2.1 Materials and measurements

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*o*-Aminophenol, 2-amino-4-chlorophenol, and 2-amino-4-*tert*-butylphenol were obtained from Kanto and Wako, and used as received. *N*-phenyl-2-aminophenol was prepared from *o*-aminophenol and iodobenzene. [9] *N*-(4-methoxyphenyl)-3,5-di-*tert*-butyl-2-aminophenol was prepared from 3,5-di-*tert*-butylcatechol and *p*-methoxyaniline purchase from Tokyo Kasei.[10] The precursor complex,  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , was prepared according to the literature.[11] Acetone *d*-6 (Cambridge Isotope Laboratories) was used for measurements of  $^1\text{H}$  NMR spectra. Other chemicals and solvents were of reagent grade and used without further purification.

Absorption spectra were recorded on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer.  $^1\text{H}$  NMR spectra were measured at 400 MHz using a Varian UNITY INOVA 400WB and chemical shifts were obtained using the chemical shift of nondeuterated acetone, 2.09 ppm, as a standard. Cyclic voltammetry and differential pulse voltammetry were performed by means of a BAS 100W/B electrochemical workstation. Voltammograms were observed in acetonitrile solution of  $0.1 \text{ mol dm}^{-3}$  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. For examination of Pourbaix diagrams, voltammograms were observed in aqueous solution of  $0.1 \text{ mol dm}^{-3}$  sodium sulfate using an Ag/AgCl reference electrode instead of an Ag/AgNO<sub>3</sub> reference electrode. The pH of the solution was adjusted by CH<sub>3</sub>COOH – CH<sub>3</sub>COONa, NaH<sub>2</sub>PO<sub>4</sub> – Na<sub>2</sub>HPO<sub>4</sub>, and NH<sub>4</sub>Cl – NH<sub>3</sub> buffers at the concentration of  $0.01 \text{ mol dm}^{-3}$ . 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 [12] by using a Shimadzu AA-7000 spectrophotometer.

## 2.2 Synthesis of complexes

### 2.2.1 *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{L}^1)](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ $\{\text{L}^1 = 2$ -iminobenzoquinone (*ibq*), 4-chloro-2-imino-benzoquinone (*Cl-ibq*), and 4-*tert*-butyl-2-iminobenzoquinone (*Bu-ibq*)

A suspended solution of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (0.29 g, 1 mmol) in  $15 \text{ cm}^3$  of water was reduced with Zn-amalgam under a nitrogen atmosphere until the complex was completely dissolved. To the solution of the complex, 5 mmol of 2-aminophenol or its derivatives was added and the resulting solution was stirred for 1 h under a nitrogen atmosphere. The brown reaction mixture was filtered to

remove the insoluble residue. The color of the filtrate turned from brown to blue during filtration. Saturated aqueous solution of ammonium hexafluoro-phosphate (10 mmol) was added to the filtrate. After standing overnight, the blue precipitates were corrected and dried on P<sub>2</sub>O<sub>5</sub> under reduced pressure. The precipitate was freely washed with diethyl ether and air-dried. Thereafter, the precipitate was dissolved in methanol and was heated for 1 h. at 60 °C. The resulting reddish-brown solution was filtered and the filtrate was concentrated to dryness under reduced pressure. The obtained crude complex was purified on a Sephadex LH-20 column using methanol as an eluent. *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{ibq})](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ : *Anal. Calc.* for C<sub>6</sub>H<sub>21</sub>N<sub>5</sub>F<sub>12</sub>O<sub>3</sub>P<sub>2</sub>Ru: C, 11.97; H, 3.52; N, 11.63; Ru, 16.8. *Found*: C, 11.23; H, 3.05; N, 12.53; Ru, 18.1.  $^1\text{H}$  NMR(400 MHz, acetone *d*-6):  $\delta$  16.53(1H, s), 8.13(1H, t, J = 8 Hz), 7.69(1H, d, J = 8 Hz), 7.60(1H, d, J = 8 Hz), 6.98(1H, t, J = 8 Hz), 6.63(3H, s), 4.13(3H, s), 3.83(6H, s). *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{Cl-ibq})](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ : *Anal. Calc.* for C<sub>6</sub>H<sub>20</sub>N<sub>5</sub>ClF<sub>12</sub>O<sub>3</sub>P<sub>2</sub>Ru: C, 11.32; H, 3.17; N, 11.00; Ru, 15.9. *Found*: C, 10.99; H, 2.86; N, 11.44; Ru, 16.9.  $^1\text{H}$  NMR(400 MHz, acetone *d*-6):  $\delta$  16.26(1H, s), 8.14(1H, d, J = 9 Hz), 7.81(1H, s), 7.74(1H, d, J = 9 Hz), 6.76(3H, s), 4.34(3H, s), 4.05(6H, s). *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{Bu-ibq})](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ : *Anal. Calc.* for C<sub>10</sub>H<sub>29</sub>N<sub>5</sub>F<sub>12</sub>O<sub>3</sub>P<sub>2</sub>Ru: C, 16.80; H, 4.07; N, 10.89; Ru, 15.7. *Found*: C, 16.70; H, 4.08; N, 10.47; Ru, 16.2.  $^1\text{H}$  NMR(400 MHz, acetone *d*-6):  $\delta$  16.03(1H, s), 8.39(1H, d, J = 9 Hz), 7.59(1H, s), 7.54(1H, d, J = 9 Hz), 6.45(3H, s), 4.05(3H, s), 3.73(6H, s), 1.68(9H, s).

### 2.2.2 *cis*- $[\text{Ru}(\text{NH}_3)_4(\text{L}^2)](\text{PF}_6)_2$ $\{\text{L}^2 = N$ -phenyl-2-iminobenzoquinone (*N-ph-ibq*) and *N*-(4-methoxyphenyl)-3,5-di-*tert*-butyl-2-iminobenzoquinone (*N-MeOph-DB-ibq*)

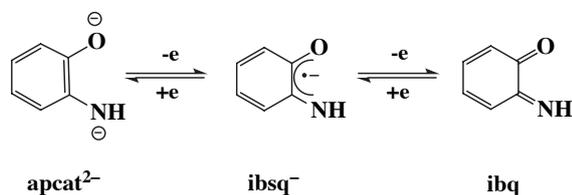
An Ag(I) solution (1.5 mmol) was added to a suspended solution of  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (0.29 g, 1 mmol) in  $8 \text{ cm}^3$  of water and the mixture was heated for 30 min. at 80 °C. After the resulting precipitate of AgCl was removed, the precursor complex was reduced by stirring for 1 hour with 2 g of Zn-amalgam. Thereafter, *N*-phenyl-2-aminophenol or *N*-(methoxyphenyl)-3,5-di-*tert*-butyl-2-aminophenol (1 mmol) in  $10 \text{ cm}^3$  acetone was added to the solution of the reduced precursor complex and the resulting suspension was stirred overnight. Saturated aqueous solution of ammonium hexafluorophosphate (10 mmol) was added to the reddish-purple reaction mixture after the insoluble residue was removed. After standing overnight, the complex was isolated as a hexafluorophate and dried on P<sub>2</sub>O<sub>5</sub> under reduced pressure. The crude complex was

purified on a Sephadex LH-20 column using methanol as an eluent.

*cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(*N*-ph-ibq)](PF<sub>6</sub>)<sub>2</sub>: *Anal. Calc.* for C<sub>12</sub>H<sub>21</sub>N<sub>5</sub>F<sub>12</sub>O<sub>2</sub>P<sub>2</sub>Ru: C, 32.16; H, 3.56; N, 11.82; Ru, 15.2. Found: C, 22.44; H, 3.30; N, 10.90; Ru, 15.7. <sup>1</sup>H NMR(400 MHz, acetone *d*-6): δ 16.03(1H, s), 8.39(1H, d, J = 9 Hz), 7.59(1H, s), 7.54(1H, d, J = 9 Hz), 6.45(3H, s), 4.05(3H, s), 3.73(6H, s), 1.68(9H, s). *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(*N*-MeOph-DB-ibq)](PF<sub>6</sub>)<sub>2</sub>: *Anal. Calc.* for C<sub>21</sub>H<sub>35</sub>N<sub>5</sub>F<sub>12</sub>O<sub>2</sub>P<sub>2</sub>Ru: C, 37.38; H, 5.16; N, 9.63; Ru, 15.2. Found: C, 32.15; H, 5.01; N, 8.93; Ru, 12.9. <sup>1</sup>H NMR(400 MHz, acetone *d*-6): δ 16.03(1H, s), 8.39(1H, d, J = 9 Hz), 7.59(1H, s), 7.54(1H, d, J = 9 Hz), 6.45(3H, s), 4.05(3H, s), 3.73(6H, s), 1.68(9H, s).

### 3. Results and Discussion

*o*-Aminophenol is an *N*, *O*-donor quinonoid and possibly exists at some oxidation states as shown in Scheme. Accordingly, their ruthenium complexes can take several redox states in combination of the oxidation state of *o*-aminophenol with that of ruthenium. *cis*-Tetraammineruthenium complexes with dioxolenes were isolated at different redox state depending on the substituents of the dioxolene. [7]



**Scheme.** Redox states of *o*-aminophenolate.

In this study, all the five *cis*-tetraammineruthenium complexes with *o*-aminophenol derivatives were isolated as reddish-brown powder. It is interested in the redox state of them. These complexes were characterized by an elemental analysis, <sup>1</sup>H NMR and absorption spectroscopies, and cyclic voltammetry. The results of the elemental analysis for the complexes agreed with the compositions of the complexes at Ru(II)-ibq and Ru(III)-ibsq<sup>-</sup> redox states. <sup>1</sup>H NMR spectra of the complexes were measured in deuterated acetone (see Experimental section). The resonance signals were observed in ordinary region (0-17 ppm); the signals at 1.25, 1.54, and 3.94 ppm were assigned to methyl protons of *tert*-butyl and methoxy groups, those at 3.8~4.7 ppm to ammine protons in *cis*-position toward iminobenzoquinone, those at 4.0~7.0 ppm to ammine protons in *trans*-position toward iminobenzoquinone, those at 6.9~8.2 ppm to

aromatic protons, and those at *ca.* 16 ppm to imine protons according to the sharpness and integral ratio of the signals. This reveals that the all complexes were isolated as Ru(II)-ibq redox state. This results is corresponding to the redox state for *cis*-tetraammineruthenium complex of dioxolene with *tert*-butyl substituents; even on *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(Cl-ibq)](PF<sub>6</sub>)<sub>2</sub>. [7]

Absorption spectra of the prepared complexes were measured in acetonitrile. The spectral characteristics are listed in Table 1. The complexes exhibited bands with comparable intensity ascribed to metal-to-ligand charge transfer band in the visible region and the ligand center in the ultraviolet region. This supported the Ru(II)-ibq redox state of the complexes. For the prepared complexes, cyclic voltammograms were measured in acetonitrile and their electrochemical parameters are listed in Table 2. A reversible couple and an irreversible redox couple were observed in cathodic region for all the complexes. These redox couples are ascribed to the redox processes on the ligand center listed in Table 2 considering the oxidation state at a rest potential of *ca.* 0 V vs. (Ag<sup>+</sup>/Ag) {Ru(II)-ibq}. [7]

**Table 1.** Spectral characteristics of the prepared complexes in acetonitrile.

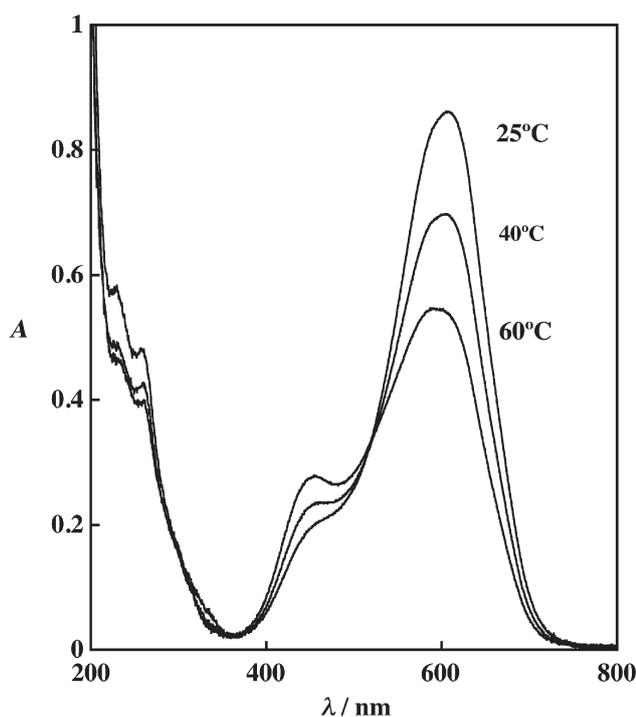
Complexes	$\lambda_{\max}$ / nm	$\epsilon_{\max}$ / mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup>
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (ibq)](PF <sub>6</sub> ) <sub>2</sub>	258	6.54×10 <sup>3</sup>
	450	6.05×10 <sup>3</sup>
	524	5.14
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (Cl-ibq)](PF <sub>6</sub> ) <sub>2</sub>	268	7.37×10 <sup>3</sup>
	499	5.29×10 <sup>3</sup>
	533	5.51×10 <sup>3</sup>
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (Bu-ibq)](PF <sub>6</sub> ) <sub>2</sub>	260	5.82×10 <sup>3</sup>
	331 sh	1.28×10 <sup>3</sup>
	456	3.80×10 <sup>3</sup>
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> ( <i>N</i> -ph-ibq)](PF <sub>6</sub> ) <sub>2</sub>	536	4.17×10 <sup>3</sup>
	256	6.88×10 <sup>3</sup>
	464	6.23×10 <sup>3</sup>
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> ( <i>N</i> -MeOph-DB-ibq)](PF <sub>6</sub> ) <sub>2</sub>	520 sh	5.22×10 <sup>3</sup>
	258	3.54×10 <sup>3</sup>
	487 sh	2.42×10 <sup>3</sup>
	539 sh	2.46×10 <sup>3</sup>

All the complexes were isolated as reddish-brown powder but the solution of the complex changed color in each step on preparation of the complex depending on the atmosphere and the temperature for the ibq, Cl-ibq and Bu-ibq complexes; brown in the presence of Zn-amalgam, blue on exposure to air, reddish-brown at 60°C in methanol. The crude blue complex was isolated in the course of the preparation of the ibq complex. The absorption spectra of

**Table 2.** Electrochemical parameters of the prepared complexes in acetonitrile.

Complexes	$E_{1/2}$ / V vs. (Ag <sup>+</sup> /Ag)	$\Delta E_p$ / mV	assignment
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (ibq)](PF <sub>6</sub> ) <sub>2</sub>	-0.706	69	R(II)-ibq / Ru(II)-ibsq <sup>-</sup>
	-1.589	275	Ru(II)-ibsq <sup>-</sup> / Ru(II)-apcat <sup>2-</sup>
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (Cl-ibq)](PF <sub>6</sub> ) <sub>2</sub>	-0.583	63	R(II)-ibq / Ru(II)-ibsq <sup>-</sup>
	-1.583	224	Ru(II)-ibsq <sup>-</sup> / Ru(II)-apcat <sup>2-</sup>
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (Bu-ibq)](PF <sub>6</sub> ) <sub>2</sub>	-0.741	80	R(II)-ibq / Ru(II)-ibsq <sup>-</sup>
	-1.525	213	Ru(II)-ibsq <sup>-</sup> / Ru(II)-apcat <sup>2-</sup>
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> ( <i>N</i> -ph-ibq)](PF <sub>6</sub> ) <sub>2</sub>	-0.671	75	R(II)-ibq / Ru(II)-ibsq <sup>-</sup>
	-1.589	98	Ru(II)-ibsq <sup>-</sup> / Ru(II)-apcat <sup>2-</sup>
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> ( <i>N</i> -MeOph-DB-ibq)](PF <sub>6</sub> ) <sub>2</sub>	-0.602	69	R(II)-ibq / Ru(II)-ibsq <sup>-</sup>
	-1.726	155	Ru(II)-ibsq <sup>-</sup> / Ru(II)-apcat <sup>2-</sup>

it were preliminary examined at different temperatures in acetonitrile and the results are shown in Fig. 1. Absorption at *ca.* 600 nm decreased and absorption at *ca.* 450 nm increased with increasing the temperature. This spectral change is resemble to those of the change in oxidation state by electric field for tetraammineruthenium complexes of dioxolenes.[13] However, the *N*-ph-ibq and *N*-MeOph-DB-ibq complexes showed no color change in the preparation steps. These observations indicate that the redox state of the complexes in this study is affected by the external stimuli and the substituents of the ligands. Furthermore, the ibq complex in aqueous solution exhibited the color change between blue and red by the addition of acid and base. Therefore, Pourbaix analysis was performed for the



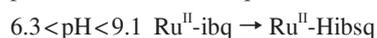
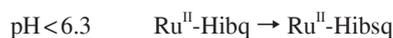
**Figure 1.** Absorption spectra of the crude blue ibq-complex in acetonitrile, maintaining for 5 minutes at different temperatures.

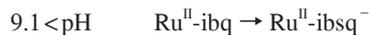
tetraammineruthenium complexes of *o*-aminophenol derivatives in this study in order to examine the influence of pH on their oxidation states.

### Pourbaix analysis

Cyclic voltammograms of the five complexes in this study were measured at various pH in buffered aqueous solutions. Two redox couples were observed in the negative potential region for all complexes in this study and are ascribed to the one-electron redox processes on the ligand center as those in acetonitrile solutions. Their couples are irreversible in acidic solution but the reversibility increases with increasing pH as shown in Fig. 2. Thus, the peak potentials of the reduction waves were plotted against pH for Pourbaix analysis. The peak potentials obtained by differential pulse voltammetry were plotted for the *N*-ph-ibq and *N*-MeOph-DB-ibq complexes, as one of the two redox couples were observed as a shoulder at a certain pH owing to the overlapping of the two redox waves as shown in Fig. 3. Figure 4 shows the obtained Pourbaix diagrams. For the all five complexes, pH dependent and independent processes were observed on both redox couples depending on pH range. As listed in Table 3, the pH dependent processes show the slope of *ca.* -60 mV/pH for each process. This implies that the processes proceed through the proton coupled electron transfer (PCET) mechanism involving the one-electron and the one-proton transfer. Therefore, the oxidation state of the complexes can be assigned in the range of potential-pH to those as shown in Fig. 4. Accordingly, *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(ibq)](PF<sub>6</sub>)<sub>2</sub> is reduced from the oxidation state Ru<sup>II</sup>-ibq as below :

on the first reduction,

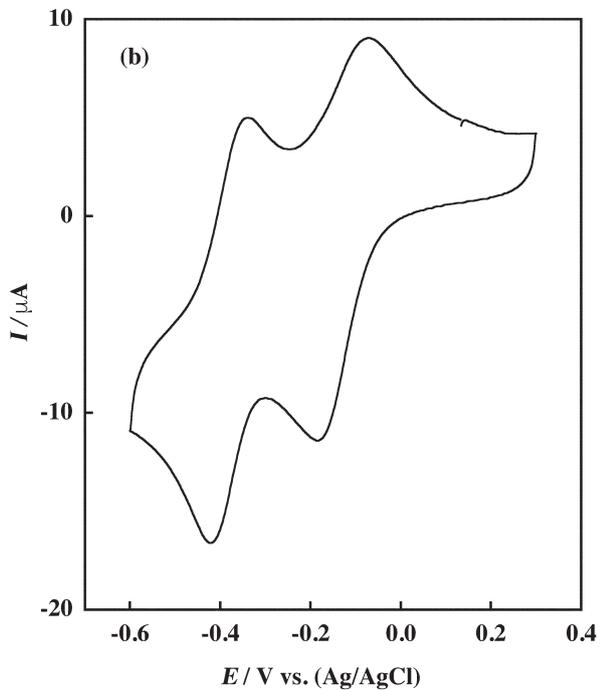
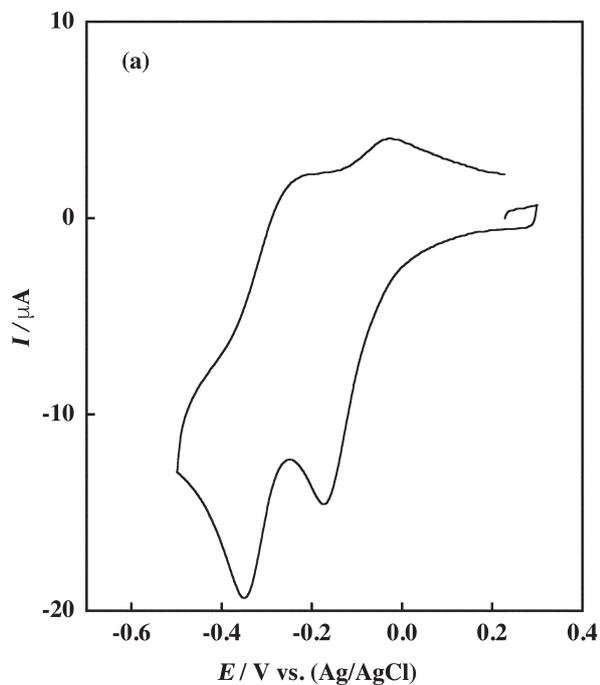




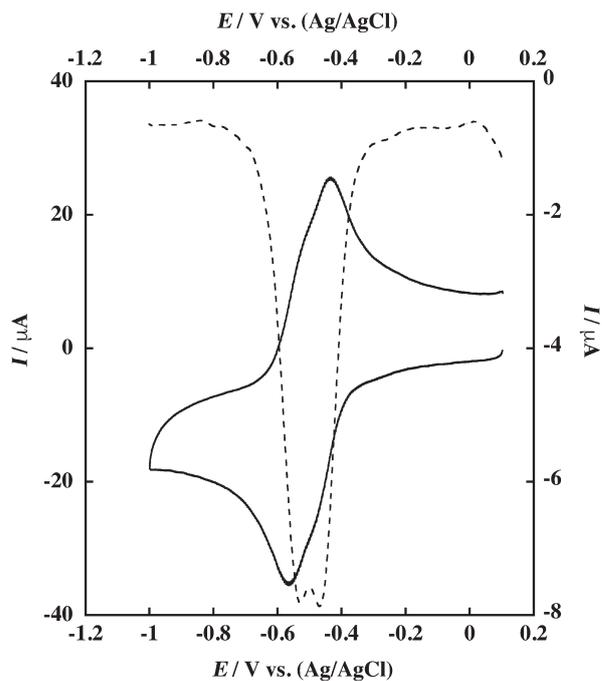
on the second reduction,



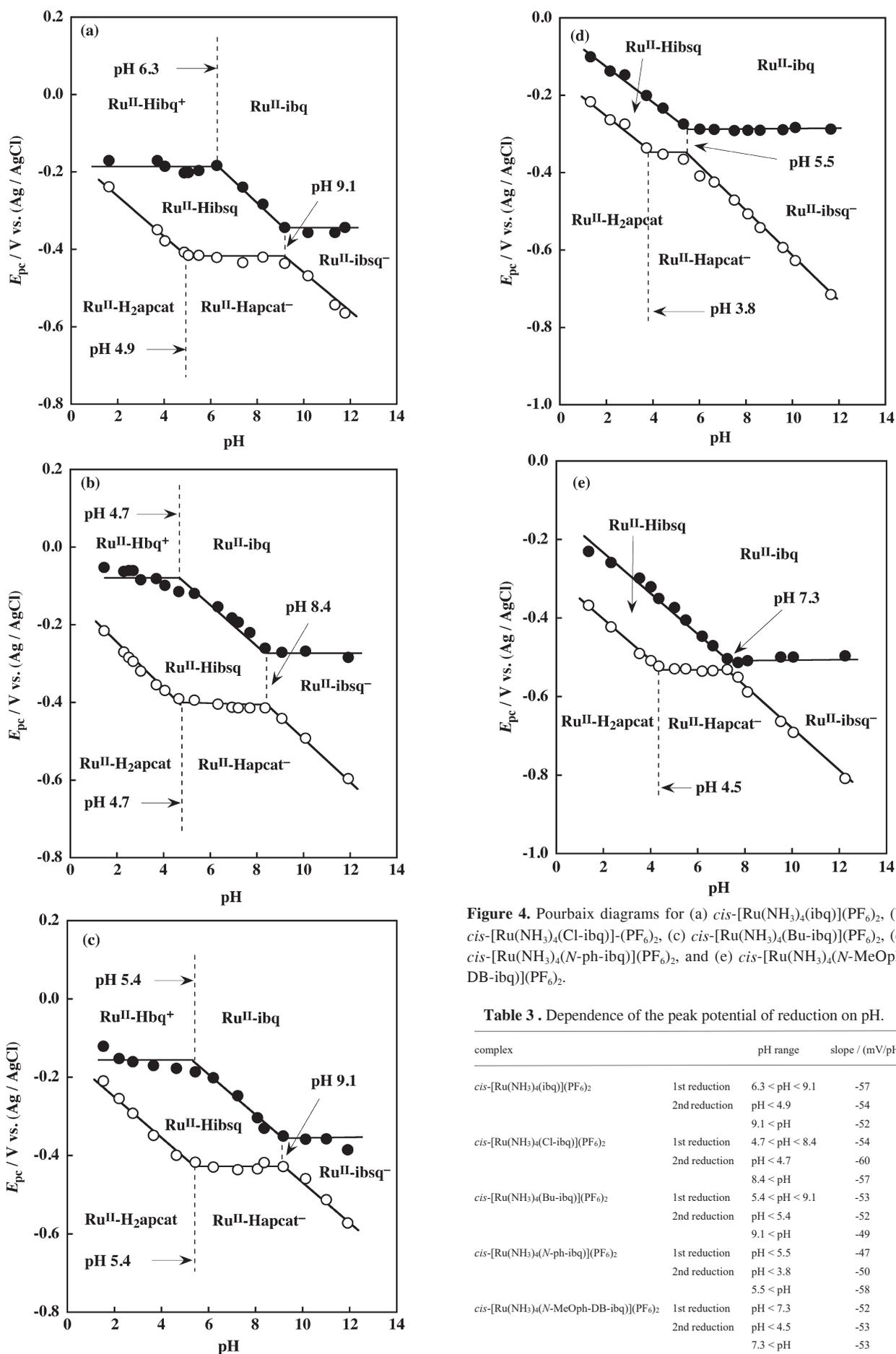
The other complexes are similarly reduced.



**Figure 2.** Cyclic voltammograms of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(ibq)](PF<sub>6</sub>)<sub>2</sub> (a) at pH 3.70 and (b) pH 6.26 in aqueous solution.



**Figure 3.** Cyclic voltammogram (solid line) and differential pulse voltammogram (dashed line) of *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(*N*-MeOph-DB-ibq)](PF<sub>6</sub>)<sub>2</sub> at pH 6.64 in aqueous solution.



**Figure 4.** Pourbaix diagrams for (a) *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(ibq)](PF<sub>6</sub>)<sub>2</sub>, (b) *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(Cl-ibq)]-(PF<sub>6</sub>)<sub>2</sub>, (c) *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(Bu-ibq)](PF<sub>6</sub>)<sub>2</sub>, (d) *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(*N*-ph-ibq)](PF<sub>6</sub>)<sub>2</sub>, and (e) *cis*-[Ru(NH<sub>3</sub>)<sub>4</sub>(*N*-MeOph-DB-ibq)](PF<sub>6</sub>)<sub>2</sub>.

**Table 3 .** Dependence of the peak potential of reduction on pH.

complex		pH range	slope / (mV/pH)
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (ibq)](PF <sub>6</sub> ) <sub>2</sub>	1st reduction	6.3 < pH < 9.1	-57
	2nd reduction	pH < 4.9	-54
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (Cl-ibq)](PF <sub>6</sub> ) <sub>2</sub>	1st reduction	9.1 < pH	-52
	2nd reduction	pH < 4.7	-60
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> (Bu-ibq)](PF <sub>6</sub> ) <sub>2</sub>	1st reduction	8.4 < pH	-57
	2nd reduction	pH < 5.4	-52
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> ( <i>N</i> -ph-ibq)](PF <sub>6</sub> ) <sub>2</sub>	1st reduction	9.1 < pH	-49
	2nd reduction	pH < 5.5	-47
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> ( <i>N</i> -MeOph-DB-ibq)](PF <sub>6</sub> ) <sub>2</sub>	1st reduction	pH < 3.8	-50
	2nd reduction	5.5 < pH	-58
<i>cis</i> -[Ru(NH <sub>3</sub> ) <sub>4</sub> ( <i>N</i> -MeOph-DB-ibq)](PF <sub>6</sub> ) <sub>2</sub>	1st reduction	pH < 7.3	-52
	2nd reduction	pH < 4.5	-53
		7.3 < pH	-53

The oxidation state of the complex may be significantly affected by the substituents of the ligand iminobenzoquinone as shown in Fig. 4. The potential of the first reduction was shifted *ca.* 100 mV toward positive potential by the electron-withdrawing substituent on *p*-position of iminobenzoquinone oxygen. The methoxyphenyl group on nitrogen of iminobenzoquinone shifted the potentials of the first and second reduction toward negative potential. Also, the substituents except *tert*-butyl group facilitate the proton dissociation of the complexes.

It is concluded that these effects affect the oxidation state of the complex and are possible to change the potential-pH region of existing the complex as **sq** oxidation-state. Considering a linear correlation between the redox potentials and the sum of the Hammett's substitution constants for polysubstitued quinonoid compounds,[14, 15] the complex can be isolated as **sq** oxidation-state and /or the oxidation state can be change by the external stimuli such as heat and pH for the complex involving iminobenzoquinone with more electron -withdrawing substituents.

## References

- [ 1 ] (a) K. S. Min, T. Weyhermuller, E. Bothe, and K. Wieghardt, *Inorg. Chem.* **43**, 2922 (2004); (b) S. Kokatam, T. Weyhermuller, E. Bothe, P. Chaudhuri, and K. Wieghardt, *Inorg. Chem.* **44**, 3709 (2005); (c) M. M. Khusniyarov, T. Weyhermuller, E. Bill, and K. Wieghardt, *J. Am. Chem. Soc.* **131**, 1208 (2009).
- [ 2 ] (a) C. G. Pierpont, C. W. Lange, *Prog. Inorg. Chem.* **41**, 331 (1994); (b) C. G. Pierpont, *Coord. Chem. Rev.* 216-217 (2001) 99; (c) C. G. Pierpont, *Coord. Chem. Rev.* **219-221**, 415 (2001).
- [ 3 ] (a) A. S. Attia and C. G. Pierpont, *Inorg. Chem.* **37**, 3051 (1998) ; (b) A. Caneschi, A. Cornia, and A. Dei, *Inorg. Chem.* **37**, 3419 (1998); (c) D. Ruiz, J. Yoo, I. A. Guzei, A. L. Rheingold, and D. N. Hendrickson, *Chem. Commun.* (1998) 2089 ; (d) A. Beni, L. Bussotti, A. Dei, P. L. Gentili, and R. Righini, *J. Phys. Conference Series*, **21**, 124 (2005) ; (e) N. G. R. Hearn, J. L. Korook, M. M. Paquette, and K. E. Preuss, *Inorg. Chem.* **45**, 8817 (2006).
- [ 4 ] (a) K. Kobayashi, H. Ohtsu, T. Wada, T. Kato, and K. Tanaka, *J. Am. Chem. Soc.*, **125**, 6729 (2003); (b) Y. Hitomi, A. Ando, H. Matsui, T. Ito, T. Tanaka, S. Ogo, and T. Funabiki, *Inorg. Chem.*, **44**, 3473 (2005); (c) D. A. Jose, A. D. Shukla, D. K. Kumar, B. Ganguly, and A. Das, *Inorg. Chem.* **44**, 3414 (2005) ; (d) H. Ozawa, T. Hino, H. Ohtsu, T. Wada, and K. Tanaka, *Inorg. Chim. Acta* **366**, 298 (2011).
- [ 5 ] I. Ando, M. Ogawa, T. Hamaguchi, and K. Ujimoto, *Fukuoka Univ. Sci. Reports* **40**, 9 (2008).
- [ 6 ] I. Umemura, I. Ando, and T. Hamaguchi, *Fukuoka Univ. Sci. Reports* **40**, 195 (2010).
- [ 7 ] I. Ando, T. Fukuishi, K. Ujimoto, and H. Kurihara, *Inorg. Chim. Acta* **390**, 47 (2012).
- [ 8 ] (a) I. Ando, *Coord. Chem. Rev.* **248**, 185 (2004); I. Ando, H. Katae, and M. Okamura, *Inorg. Chim. Acta* **411**, 56 (2014).
- [ 9 ] D. Maiti and S. L. Buchwald, *J. Am. Chem. Soc.* **131**, 17423 (2009).
- [10] P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermuller, and K. Wieghardt, *J. Am. Chem. Soc.* **123**, 2213 (2001).
- [11] A. D. Allen, F. Bottomly, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *Inorg. Synth.* **12**, 2 (1970).
- [12] W. M. Rowston and J. M. Ottaway, *Anal. Lett.* 3 (1970) 411.
- [13] T. Hamaguchi, Y. Kurashige, and I. Ando, *Inorg. Chim. Acta* **405**, 410 (2013).
- [14] P. Zuman, "Substituent Effects on Organic Polarography," Plenum, New York(1969), Chap. 8.
- [15] I. Ando, H. Miyake, K. Ujimoto, and H. Kurihara, *Bull. Chem. Soc. Jpn.* **75**, 1539 (2002).