

Synthesis and Redox Behavior of Tetraammineruthenium Complexes with *S, S*- and *N, N*-Donor Quinonoid

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Abstract

cis-Tetraammineruthenium complexes were synthesized using *o*-dithiocatechol and *o*-phenylenediamine as a redox active ligand. Ru(NH₃)₄-*o*-dithiocatechate complex was characterized by X-ray photoelectron spectroscopy (XPS) because of its insolubility in any solvent. The XPS data indicate that the complex involves divalent ruthenium. Ru(NH₃)₄-*o*-phenylenediamine complex was characterized by analysis of Ru, C, H, N content, ¹H-NMR and absorption spectroscopies, and cyclic voltammetry. In the complex, it was found that the metal center exists in Ru^{II} and the quinonoid ligand does *o*-diiminobenzoquinone. The redox behavior of Ru(NH₃)₄-*o*-diiminobenzoquinone complex was also investigated and discussed in terms of comparison with that of Ru(NH₃)₄-dioxolene complex.

Introduction

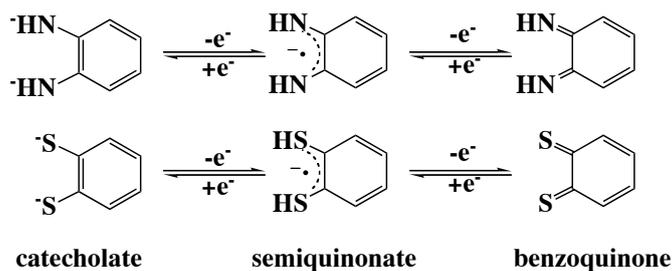
Quinonoids are widely spread in nature and play an important role in biological systems. For example, dioxolenes of a typical quinonoid play a key role in a antioxidant and electron transport system of biological systems owing to its redox active nature.^{1,2}

Dioxolenes exist in relatively stable oxidation states of catecholate (cat), semiquinonate (sq), and benzoquinone (bq), and also act as a bidentate ligand to metal ion. Quinonoids involving sulfur or nitrogen atoms as a coordination atom other than oxygen atoms may have similar nature to that of a dioxolene. (Scheme 1) Thus, metal complexes with a quinonoid are likely to be in several oxidation states, depending on combination of the oxidation states of both metal center and quinonoid center. (Scheme 2) Moreover, the charge of metal ion is easily delocalized over a quinonoid because of a small difference between

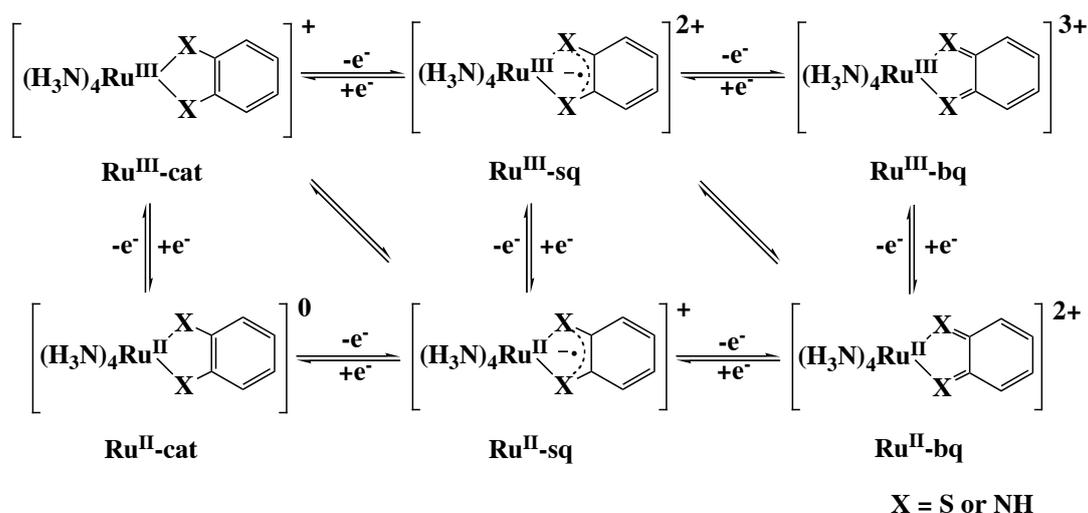
the energy levels of *d* orbital of metal center and π^* orbital of quinonoid. Accordingly, the electronic state of the complex will be significantly affected by slight physical and/or chemical external stimuli. Transition metal complexes with a quinonoid have been widely investigated in focusing on modification of the properties of the complexes caused by external stimuli.³⁻⁶ Mn-, Fe-, and Co-dioxolene complexes exhibit valence tautomerism induced by heat, pressure, and light.⁷⁻¹¹ Ru-quinonoid complexes have also been investigated for complexes involving polypyridines as an ancillary ligand.¹²⁻¹⁴ However, the valence state of both metal and quinonoid center remains obscure in their quinonoid complexes due to the delocalization of electrons mentioned above.

We have synthesized several Ru-dioxolene complexes involving ammine ligand with small π -electron acceptability as an ancillary ligand.¹⁵ Investigation for oxidation state of the complexes revealed that the oxidation state was affected by

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Scheme 1 Oxidation states of the quinonoids.



Scheme 2 Schematic representation of oxidation states and redox processes for the tetraammineruthenium complex with quinonoid. Abbreviations denote the oxidation state of the complex.

slight difference in the nature of substituents on dioxolenes. In addition, it was clarified that the oxidation state of the complex was dependent on pH.¹⁶

These facts imply that the properties of the complexes can be modified by changing the physical and chemical environments around dioxolene-tetraammineruthenium complexes. In the tetraammineruthenium complexes of quinonoid containing *S, S*- or *N, N*- donor atoms, the properties of the complexes is likely to be changed by introducing physical stimuli and changing chemical environments. This would be interesting for the creation of functionality of the complexes.

In this study, tetraammineruthenium complexes of *o*-dithiocatechol and *o*-phenylenediamine were synthesized and characterized. Redox behavior of these complexes was investigated and discussed with respect to the difference in nature of the donor

atoms.

Experimental

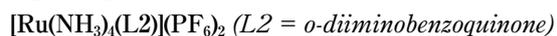
Materials. Precursor complex *cis*-[Ru(NH₃)₄Cl₂]Cl was prepared according to the literature method.¹⁷

All other chemicals were of reagent grade and used without further purification. Precursor complex *cis*-[Ru(NH₃)₄Cl₂]Cl was synthesized according to a published procedure.¹⁵

Preparation of Complexes [Ru(NH₃)₄(L)](PF₆)_n (*n* = 0 or 2). The complexes *cis*-[Ru(NH₃)₄(L)](PF₆)_n (*n* = 0 or 2) were prepared by following a general procedure.

[Ru(NH₃)₄(L1)] (*L1* = *o*-dithiocatecholate) *cis*-[Ru(NH₃)₄Cl₂]Cl (0.28 g, 1 mmol) was suspended into water (10 mL). Reduction of *cis*-[Ru(NH₃)₄Cl₂]Cl was made by adding zinc amalgam¹⁸ (4.0 g) to the

suspension and stirring until the suspension turned to a yellow clear solution. Then an ethanol solution (2 mL) of *o*-dithiocatechol (0.71 g, 5 mmol) was added to the clear solution. The purple product was immediately precipitated after addition of *o*-dithiocatechol. The precipitate was filtered off, washed thoroughly with water, ethanol, and acetone, and then air-dried. Total yield was 31%. XPS: binding energy 280.7 eV



The reaction mixture was obtained by a similar procedure to the preparation of $[\text{Ru}(\text{NH}_3)_4(\text{L}1)]$ except for using a methanol solution (5 mL) of *o*-phenylenediamine (0.71 g, 5 mmol). The reaction mixture was stirred for 3 h until the yellow solution turned to orange and then the mixture was filtered. A saturated aqueous solution (2 mL) of NH_4PF_6 (1.63 g, 10 mmol) was added to the filtrate, and the mixture was allowed to stand for overnight. The resulting precipitate was collected by filtration, and dried under vacuum over P_2O_5 . The crude product was purified by chromatography using a sephadex LH-20 gel. The orange product corresponding to $[\text{Ru}(\text{NH}_3)_4(\text{L}2)](\text{PF}_6)_2$ was eluted with methanol. Total yield was 13%. Anal. Calcd. for $\text{C}_6\text{H}_{18}\text{F}_{12}\text{N}_6\text{P}_2\text{Ru}$: C, 12.8, H, 3.22, N, 14.9, Ru, 17.9%. Found: C, 13.3, H, 3.27, N, 15.0, Ru, 16.4%. $^1\text{H-NMR}$ ($\text{CD}_3\text{NO}_2\text{-}d_3$, δ / ppm): δ 11.6 (s, 2H), 7.39 (d, 1H), 7.38 (d, 1H), 6.94 (t, 1H), 6.92 (t, 1H), 3.95 (s, 6H), 1.56 (s, 6H).

Measurements. Absorption spectra were recorded on a Shimadzu UV-3600 ultraviolet-visible-near-infrared spectrophotometer. $^1\text{H-NMR}$ measurements were carried out with a Varian Unity Inova 400WB NMR spectrometer, and the chemical shifts were obtained using a signal of non-deuterated nitromethane as a standard. XPS measurements were made on an Ulvac PHI 1800 X-ray photoelectron spectrometer with monochromatized Al $K\alpha$ radiation. Magnetic susceptibility was measured on a magnetic susceptibility balance MSB-MKI, and magnetic moments were corrected using Pascal constant. Cyclic voltammetry was performed by means of a BAS 100W/B electrochemical workstation. Voltammograms were obtained in CH_3CN solutions containing 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate using a three electrodes assembly, an Ag/AgNO₃ reference electrode, a glassy carbon working electrode, and

a platinum coil auxiliary electrode. In aqueous solution, voltammograms were observed in 0.1 mol dm^{-3} sodium sulfate aqueous solution containing 0.01 mol dm^{-3} acetate, phosphate, or ammonium buffer solution using Ag/AgCl reference electrode instead of an Ag/AgNO₃ reference electrode. Analytical data for elements C, H and N were obtained from the Microanalytical Laboratory of Kyushu University. Atomic absorption analysis of the ruthenium content was carried out according to Rowston's method¹⁰ by means of a Shimadzu AA 6800 spectrophotometer.

Results and Discussion

Ruthenium complex of quinonoids is likely to exist in several oxidation states depending on combination of both valences on a ruthenium and a quinonoid, as mentioned above. Abbreviations of oxidation state of the complex are described in Scheme 2. Moreover, compositions of the complex including a counter ion vary with protonation onto donor atoms, especially in the case of *o*-phenylenediamine ligand. Prepared ruthenium complexes were characterized and the composition and the oxidation state were determined as below.

Preparation and Characterization. Reaction of Ru^{II} precursor complex with *o*-dithiocatechol gave violet powder complex that is insoluble in water. The complex was characterized by X-ray photoelectron spectroscopy (XPS) due to its insolubility in most solvents. Table 1 lists the binding energies of $3d$ electron of ruthenium for the complex together with those of other ruthenium complexes reported. As can be seen in Table 1, the binding energy of Ru^{II} complex is below 281 eV, whereas that of Ru^{III} complex is above 281 eV. The binding energy of the prepared complex is 280.7 eV and thus suggests the Ru^{II} state. Since the complex is insoluble in water, the prepared complex probably contain *o*-dithiocatecholate dianion in the Ru^{II}-cat oxidation state.

The complex was obtained as redish-brown powder by reaction of Ru^{II} precursor complex with *o*-phenylenediamine. Table 2 shows the analytical data of the prepared complex and the calculated content of elements for the complex in possible oxidation states. The analytical data correspond to those for Ru^{II}-bq and Ru^{III}-sq among several possible

oxidation states. $^1\text{H-NMR}$ and absorption spectra, cyclic voltammogram, and magnetic moment were measured in order to examine the oxidation state of the complex and whether or not valence tautomerism exists between both isomers.

Figure 1 shows $^1\text{H-NMR}$ spectrum of the prepared complex and the chemical shifts of resonance signals are summarized in Table 3. All resonance signals were observed in an ordinary region (0-12 ppm). This indicates that both ammine and quinonoid ligands coordinate to a diamagnetic Ru^{II} center. The signals observed at 1.56, 3.95, 6.92-7.39 and 11.60 ppm are assigned to protons of *cis*- NH_3 and *trans*- NH_3 , aromatic protons of quinonoid, and NH protons of quinonoid, respectively, according to the integral ratios in Table 3. Therefore, it is concluded from the analytical data and $^1\text{H-NMR}$ results that the oxidation state of the prepared

complex is Ru^{II} -bq in Scheme 2. The magnetic moment value was nearly zero, supporting this conclusion.

Absorption spectrum of the prepared complex was measured in acetonitrile and is shown in Fig. 2. Table 4 summarizes spectral characteristics of the complex. The spectrum showed a $\pi-\pi^*$ CT band of the quinonoid and an MLCT band at 256 nm and 472 nm, respectively, and a similar intensity of both bands revealed a typical spectrum of Ru^{II} -ammine complexes. This result is also consistent with Ru^{II} -bq oxidation state of the complex identified above.

In addition, cyclic voltammogram of the prepared complex in acetonitrile is shown in Fig. 3, and the electrochemical parameters are summarized in Table 5. The voltammogram shows three redox couples. Taking the oxidation state of the prepared complex into consideration, these couples were

Table 1. Binding energies of ruthenium 3d electron for the prepared complex and other ruthenium complexes reported.

Complex	Ru 3d / eV	Reference
$[\text{Ru}^{\text{II}}(\text{NH}_3)_4(\text{L}2)]$	280.7	This work
$[\text{Ru}^{\text{II}}(\text{trpy})(\text{Bu}_2\text{SQ})(\text{OAc})]$	280.5	19
$[\text{Ru}^{\text{II}}(\text{trpy})(4\text{ClSQ})(\text{OAc})]$	280.4	19
$[\text{Ru}^{\text{III}}(\text{trpy})(\text{Bu}_2\text{SQ})(\text{OH}_2)](\text{ClO}_4)_2$	281.5	19
$[\text{Ru}^{\text{II}}(\text{trpy})(\text{Bu}_2\text{SQ})\text{O}^-]$	280.4	19
$[\text{Ru}^{\text{II}}(\text{bpy})_2\text{Cl}_2]$	280.1	20
$[\text{Ru}^{\text{II}}(3\text{Clpy})_2(\text{Bu}_2\text{SQ})_2]$	280.4	21
$[\text{Ru}^{\text{III}}(\text{bpy})_2\text{Cl}_2]\text{Cl}$	282.1	20
$[\text{Ru}^{\text{III}}(3\text{Clpy})_2(\text{Bu}_2\text{SQ})_2]\text{ClO}_4$	281.4	21
$[\text{Ru}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$	282.1	22

(Bu_2SQ = 3,5-di-*tert*-butylsemiquinonato, 4ClSQ = 4-chloro- semiquinonato)

Table 2. Analytical data for $[\text{Ru}(\text{NH}_3)_4(\text{L}2)](\text{PF}_6)_2$.

	Ru / %	C / %	H / %	N / %
Observed	16.4	13.26	3.27	15.03
Calcd. for Ru^{II} -bq	17.9	12.70	3.55	14.82
Ru^{III} -sq	17.9	12.70	3.55	14.82

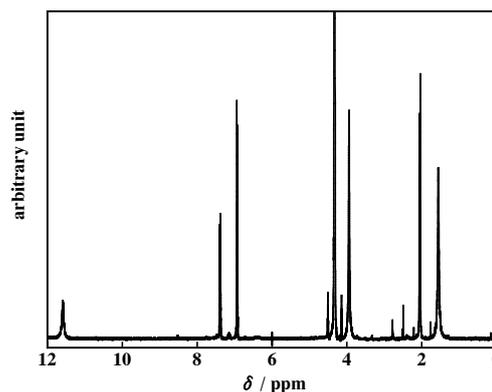


Figure 1 $^1\text{H-NMR}$ spectrum of $[\text{Ru}(\text{NH}_3)_4(\text{L}2)](\text{PF}_6)_2$ in deuterated nitromethane.

Table 3. Chemical shifts and assignments of $[\text{Ru}(\text{NH}_3)_4(\text{L}2)](\text{PF}_6)_2$.

δ / ppm	Integral ratio	Assignment
1.56	5.9	<i>cis</i> - NH_3
3.95	5.8	<i>trans</i> - NH_3
6.92	0.8	ring-H
6.94	1.1	ring-H
7.38	1.0	ring-H
7.39	1.3	ring-H
11.60	1.3	NH

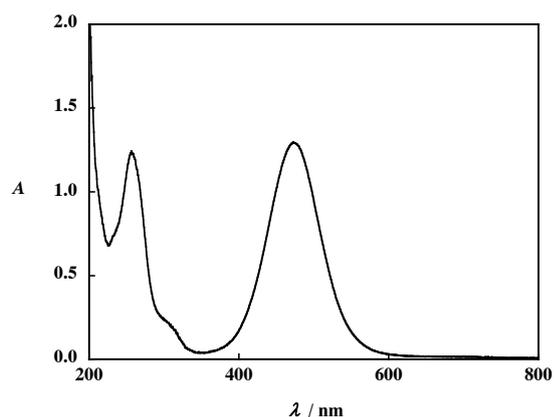


Figure 2 Absorption spectrum of $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$ in acetonitrile solution.

Table 4. Spectral characteristics of $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$.

$\lambda_{\text{max}} / \text{nm}$	$\epsilon_{\text{max}} / \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$	Assignment
256	1.16×10^4	$\pi - \pi^*$
472	1.21×10^4	MLCT

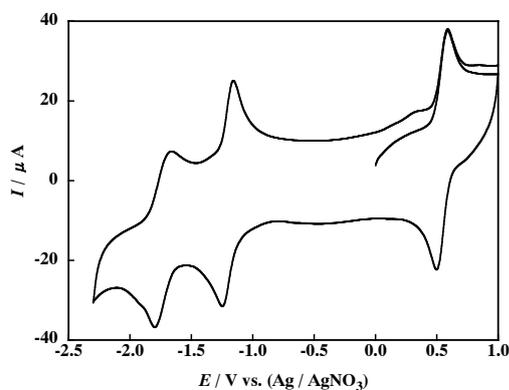


Figure 3 Cyclic voltammogram of $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$ in acetonitrile solution. Concentration of the complex is $5 \times 10^{-4} \text{mol dm}^{-3}$. Scan rate: 100 mV/s

reasonably assign as follows; that at +0.546 V vs Ag/AgNO₃ to Ru^{III}-bq/Ru^{II}-bq associated with metal center, and those at -1.202 and -1.729 V vs Ag/AgNO₃ to Ru^{II}-bq/Ru^{II}-sq and Ru^{II}-sq/Ru^{II}-cat associated with quinonoid, respectively. This result supports again the oxidation state of the isolated complex as mentioned above.

Electrochemical behavior. As mentioned above, *o*-phenylenediamine, a quinonoid with *N, N*-coordination, gave the tetraammineruthenium complex in the Ru^{II}-bq oxidation state. 3,5-di-*tert*-butylcatechol, a quinonoid with *O, O*-coordination, also gave the tetraammineruthenium complex in the same oxidation state.

In order to investigate the difference in electrochemical behavior between the quinonoids with *N, N*-coordination and *O, O*-coordination, voltammograms of $[\text{Ru}(\text{NH}_3)_4(\text{DBbq})](\text{PF}_6)_2$ (DBbq = 3,5-di-*tert*-butylbenzoquinone) and $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$ were measured in aqueous solution at various pHs. Figure 4 shows an example of cyclic voltammogram for $[\text{Ru}(\text{NH}_3)_4(\text{DBbq})](\text{PF}_6)_2$ in aqueous solution of pH 6.8. The voltammogram showed a major redox wave at ca. 0.1 V vs (Ag/AgCl) and a reduction wave at -0.8 V vs (Ag/AgCl) in the pH range in this study. Thus, the redox potentials and the reduction potentials are plotted against pH of the solution in Fig. 5. The redox potential was 0.1 V vs (Ag/AgCl) and independent of pH. This redox process may be associated with metal center. Moreover, the reduction potential decreased from pH 1.1 to 8.3 with a slope of a -60 mV/pH and became constant of -0.853 V vs (Ag/AgCl) in a pH range higher than 8.3. This reduction process may be ascribed to ligand center reduction due to possible protonation to oxygen atom of dioxolene in an acidic pH region. Taking possible valence tautomers Ru^{II}-bq and Ru^{III}-sq for $[\text{Ru}(\text{NH}_3)_4(\text{DBbq})](\text{PF}_6)_2$ into consideration¹², the

Table 5. Electrochemical parameters for $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$.

E_{pa} / V	E_{pc} / V	$\Delta E_{\text{p}} / \text{mV}$	$E_{1/2} / \text{V}$	Assignment
+0.584	+0.507	77	+0.546	Ru ^{II} -bq / Ru ^{III} -bq
-1.165	-1.239	74	-1.202	Ru ^{II} -bq / Ru ^{II} -sq
-1.669	-1.785	116	-1.727	Ru ^{II} -sq / Ru ^{II} -cat

Potential is given relative to Ag/AgNO₃.

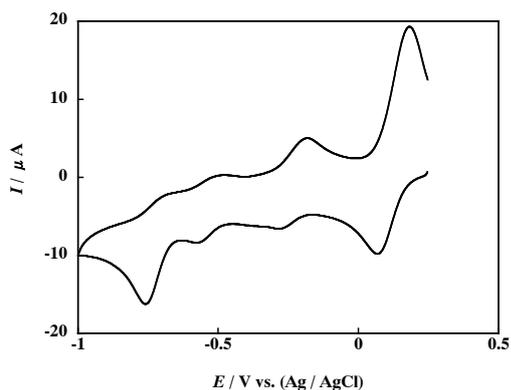


Figure 4 Cyclic voltammogram of $[\text{Ru}(\text{NH}_3)_4(\text{DBbq})](\text{PF}_6)_2$ in aqueous solution at pH 6.8.

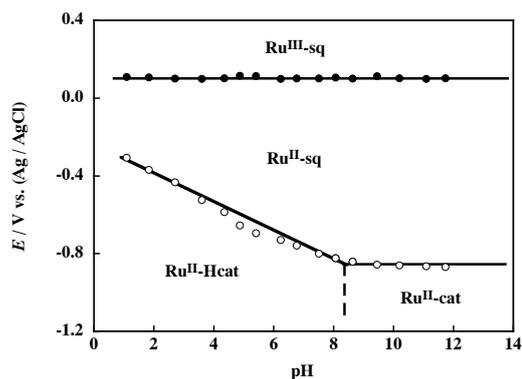


Figure 5 pH dependence of redox and reduction potentials for $[\text{Ru}(\text{NH}_3)_4(\text{DBbq})](\text{PF}_6)_2$. Solid and open circles represent redox and reduction potentials, respectively.

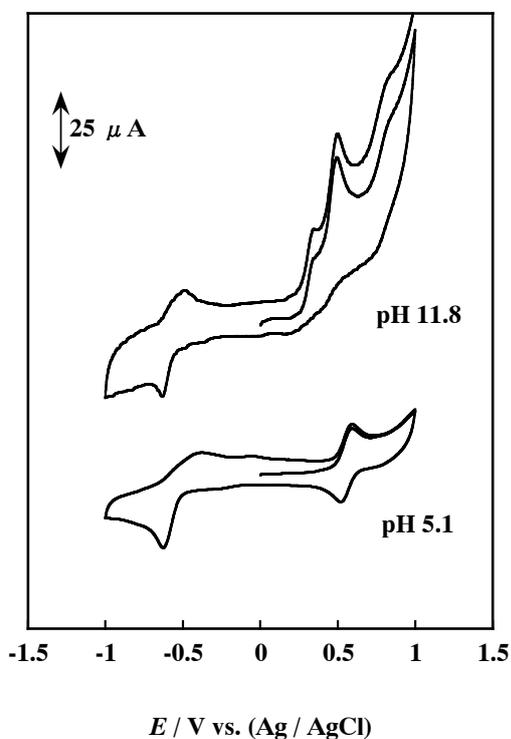


Figure 6 Cyclic voltammogram of $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$ in aqueous solution at pH 5.1 and 11.8.

redox processes of $[\text{Ru}(\text{NH}_3)_4(\text{DBbq})](\text{PF}_6)_2$ might be assigned as described in Fig. 5.

Figure 6 shows cyclic voltammograms of $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$ in acidic and basic solutions of pH 5.1 and 11.8, respectively. In the acidic solution, the voltammogram exhibited a reversible redox wave in an anodic range and irreversible redox wave in a cathodic range. However, the anodic wave became

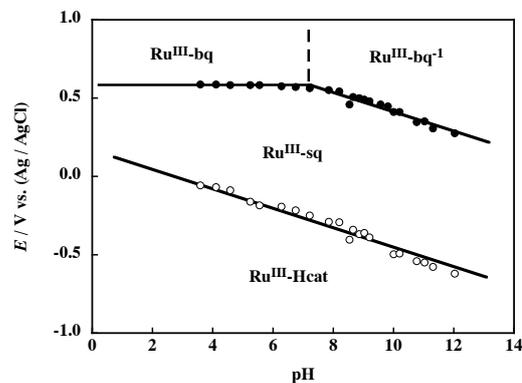


Figure 7 pH dependence of oxidation and reduction potentials for $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$. Solid and open circles represent oxidation and reduction potentials, respectively.

irreversible, whereas the cathodic wave became reversible in the basic solution. Thus, differential pulse voltammograms with an anodic scan were measured in detail in buffered aqueous solution. The obtained oxidation potentials of major peaks are plotted against pH of the solution in Fig. 7. Redox processes of $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$ in aqueous solution were tentatively assigned to the proton-coupled process as described in Fig. 7.

In this study, quinonoid complexes of ruthenium were prepared using ammine ligands as an ancillary ligand. The oxidation state of the prepared complexes was identified as $\text{Ru}^{\text{II}}\text{-cat}$ and $\text{Ru}^{\text{II}}\text{-bq}$ for using *o*-dithiocatechol and *o*-phenylenediamine

as a quinonid, respectively. It is clear that the redox processes $[\text{Ru}(\text{NH}_3)_4(\text{DBbq})](\text{PF}_6)_2$ and $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$ are significantly different from each other, although these complexes were isolated as the same oxidation state Ru^{II} -bq. While the redox reaction of $[\text{Ru}(\text{NH}_3)_4(\text{DBbq})](\text{PF}_6)_2$ may proceed through a metal-centered redox-path including valence tautomerism and a ligand-centered redox-path, the $[\text{Ru}(\text{NH}_3)_4(\text{L2})](\text{PF}_6)_2$ may proceed through two ligand-centered redox-paths including protolysis.

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