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# Effect of second-sphere coordination 14. Adduct formation of ruthenium complexes with protic ligands of different types



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#### 1. Introduction

A variety of transition metal complexes interact with solvents and organic substrates in their second coordination-spheres through non-covalent interaction [1-11]. Such second-sphere coordination, especially hydrogen bonding, brings about a perturbation of the electronic state of the complex and modifies its properties. Thus, we have been investigating this second-sphere coordination, focusing on modification of the properties of ruthenium–ammine complexes, especially redox-tuning [12].

The second-sphere coordination of a crown ether to a ruthenium-ammine complex through hydrogen bonding leads to a prominent change in the redox potential of the complex [12]. This change in redox potential is akin to that caused by displacement of a ligand from the complex. The change in redox potential is due to several factors, which have been elucidated by determining stability constants of crown ether adducts with rutheniumammine complexes [13]. The acidity of protic ligands and the steric compatibility between a protic ligand and a crown ether may be among the most important factors for selective interaction with a certain protic ligand site of the complex.

For adduct formation of aliphatic crown ethers of different ring sizes with  $[Ru(trpy)(bpy)L](PF_6)_2$  {trpy = 2,2',2"-terpyridine, bpy = 2,2'-bipyridine, L = NH<sub>3</sub> and 4-mercaptopyridine}, we reported that the ammine ligand preferred 18-crown-6 ether to 12-crown-4 ether whereas the 4-mercaptopyridine preferred

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## ABSTRACT

Adduct formation between a ruthenium complex with protic ligands of different types,  $[Ru(NH_3)_5(qdiH)](PF_6)_3 (qdi = 1,4-quinonediimine)$ , and crown ethers with different flexibilities has been investigated by absorption and <sup>1</sup>H NMR spectroscopies and cyclic voltammetry. This adduct formation is rationalized in terms of hydrogen bonding of the crown ether to both protic-ligand sites of the complex. A greater change in redox potential was caused by hydrogen bonding to both protic-ligand sites in a complex.

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12-crown-4 ether to 18-crown-6 ether [14]. In this case, the steric compatibility predominantly affects the selectivity of adduct formation. Conversely, for adduct formation with  $[Ru(NH_3)_5(imidazole)](PF_6)_3$ , 18-crown-6 ether exhibits stepwise adduct formation through hydrogen bonding at the imidazole, *trans*-ammine, and *cis*-ammine sites in the order of the acidities of the protic ligands: *cis*-ammine < *trans*-ammine < imidazole [15–17]. In this case, the acidity of a protic ligand is significantly affected in the adduct formation of the complex.

[Ru(NH<sub>3</sub>)<sub>5</sub>(qdiH)](PF<sub>6</sub>)<sub>3</sub> {qdi = 1,4-quinonediimine} contains protic ligands of different configurations, NH<sub>3</sub> and qdiH<sup>+</sup> (shown in Scheme 1). The coordinated ammine ligand with tetrahedral geometry has less acidic protons and exhibits the best compatibility for hydrogen bonding with 18-crown-6 ether [4]. The other protic ligand, qdiH<sup>+</sup>, has more acidic protons than those of an ammine ligand [15]. Furthermore, qdiH<sup>+</sup> shows better compatibility with crown ethers, 18-crown-6 ether or 15-crown-5 ether. Thus, it was of interest to determine the change in redox potential caused by hydrogen bonding to qdiH<sup>+</sup> because of its stronger  $\pi$ -electron acceptor ability [13].

#### 2. Experimental

#### 2.1. Materials

[Ru(NH<sub>3</sub>)<sub>5</sub>(qdiH)](PF<sub>6</sub>)<sub>3</sub> was prepared by the reaction of [Ru(NH<sub>3</sub>)<sub>5</sub>Cl](Cl)<sub>2</sub> with p-phenylenediamine according to the literature method and characterized spectrophotometrically by comparison of its  $\lambda_{max}$  and  $\varepsilon_{max}$  values [18].









Scheme 1. Ruthenium complex and crown ethers used in this study.

18-Crown-6 ether (abbreviated as 18C6) was purchased from Wako Pure Chemical Industries and purified by the literature method [19]. 15-Crown-5 ether (15C6) and 12-crown-4 ether (12C4) were purchased from Tokyo Kasei Kogyo and were used for NMR measurements after dehydration with deuterium molecular sieves 3A (Euriso-top). The absence of oxidative impurities in the crown ether was confirmed as mentioned previously [20]. Deuterated nitromethane for NMR measurements obtained from Aldrich Chemical Co. and was used after dehydration with deuterium molecular sieves 3A. Other chemicals were reagent grade and were used without further purification.

#### 2.2. Measurements

Absorption spectra and absorbances were measured on a Hitachi 228 spectrophotometer. <sup>1</sup>H NMR spectra were recorded at 400 MHz on a JEOLJMM GSX-400 NMR spectrometer. The chemical shifts were determined based on those of residual non-deuterated nitromethane in the deuterated nitromethane, which was referenced to the signal of tetramethylsilane as an internal standard. A BAS 100 W/B electrochemical workstation was used to record the cyclic voltammograms. Voltammograms were acquired using a 0.10 mol dm<sup>-3</sup> solution of tetrabutylammonium hexafluorophosphate in acetonitrile solution as the supporting electrolyte and, a three-electrode assembly consisting of an Ag/AgNO<sub>3</sub> reference electrode, a glassy carbon working electrode, and a platinum coil auxiliary electrode. In aqueous solution, the supporting electrolyte was 0.10 mol dm<sup>-3</sup> sodium sulfate and an Ag/AgCl electrode served as the reference.

### 3. Results and discussion

Ruthenium complexes with protic ligands form adducts with crown ethers through hydrogen bonding, and several factors affect the adduct formation [12–15]. In the case of the complexes containing protic ligands of different configurations, the steric compatibility may preferentially or selectively affect hydrogen bonding depending on the ring size of the crown ether. [Ru(NH<sub>3</sub>)<sub>5</sub>(imidazole)](PF<sub>6</sub>)<sub>3</sub> containing protic ligands of different configurations exhibits stepwise adduct formation with crown ethers, although the adduct formation with 18C6 is somewhat different from those with 15C5 and 14C4 [15]. The qdiH<sup>+</sup> ligand has a similar configuration of protons to that of the ammine ligand but different acidity. The question arises as to how hydrogen bonding

to the qdiH<sup>+</sup> ligand with stronger  $\pi$ -electron acceptor ability affects the change in redox potential of the complex. Thus, it was deemed of interest to assess the adduct formation behavior of [Ru(NH<sub>3</sub>)<sub>5</sub>(qdiH)](PF<sub>6</sub>)<sub>3</sub> with crown ethers.

Spectral changes of  $[Ru(NH_3)_5(qdiH)](PF_6)_3$  were examined upon the addition of crown ethers in nitromethane, and the results are shown in Fig. 1.  $[Ru(NH_3)_5(qdiH)](PF_6)_3$  exhibits an intense metal-to-ligand charge-transfer (MLCT) band at 534 nm in nitromethane. The CT band initially shifted from 534 to 527 nm and then reverted to 529 nm with increasing 18C6 concentration. The spectral change exhibited two sets of isosbestic points at 537 nm in the 18C6 concentration range  $0-3.69 \times 10^{-4}$  mol dm<sup>-3</sup> and at 543 nm in the 18C6 concentration range  $1.84 \times 10^{-3}-1.84 \times 10^{-2}$ mol dm<sup>-3</sup>. This indicated two stepwise equilibria of adduct formation of  $[Ru(NH_3)_5(qdiH)](PF_6)_3$  with 18C6, as seen for the ruthenium(III)-ammine complex  $[Ru(NH_3)_5(imidazole)](PF_6)_3$ . Unfortunately, the spectral changes upon addition of 15C5 and 12C4 could not be clearly observed due to the small magnitude.

To obtain information about the hydrogen bonding sites in  $[Ru(NH_3)_5(qdiH)](PF_6)_3$ -crown ether systems, adduct formation was investigated by <sup>1</sup>H NMR spectroscopy in deuterated nitromethane.  $[Ru(NH_3)_5(qdiH)](PF_6)_3$  showed the signals of *cis*-ammine protons at  $\delta = 2.91$  ppm, *trans*-ammine protons at  $\delta = 5.72$  ppm, and imine protons of the coordinated qdiH<sup>+</sup> at  $\delta = 8.63$  and 9.05 ppm which were assigned on the basis of their integral ratios (Fig. S1). Three doublet signals were observed at  $\delta = 7.36$ , 7.76 and 8.28 ppm and were assigned to the aromatic protons of the coordinated qdiH<sup>+</sup> according to their integral ratios. Intense signals observed at  $\delta = 2.05$  and 4.31 ppm are attributed to the solvent. The chemical shifts of the ammine and qdiH<sup>+</sup> protons were measured at various concentrations of the crown ethers.



**Fig. 1.** Spectral change of  $[Ru(NH_3)_5(qdiH)](PF_6)_3$  on adding 18C6 in nitromethane. [complex] =  $3.69 \times 10^{-5}$  mol dm<sup>-3</sup>. (a) and (b) represent the spectra at concentration ratio, R = [18C6]/[complex], R = 0-10 and 50–500, respectively. Arrows indicate isosbestic points.

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