



Effect of second-sphere coordination 13. Consideration of factors affecting adduct formation of ruthenium–ammine complexes with crown ethers based on the stability constants



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ABSTRACT

Adduct formation was systematically investigated for ruthenium–ammine complex and crown ether systems. This study involved crown ether systems with different flexibility, the complex system with different numbers of ammine ligands, and the pentaammine complexes systems with aromatic ligands with different π -electron acceptability. Stability constants of the crown-ether adduct of the complexes were determined for the above systems by ^1H NMR spectroscopy. The factors affecting adduct formation were discussed on basis of the stability constant.

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1. Introduction

Weak interaction, especially hydrogen bonding, may play an important role in a wide variety of areas. A variety of transition metal complexes with a protic ligand form hydrogen bonds with organic substrates at the second sphere of a complex [1]. Such second-sphere coordination brings about a perturbation in the electronic state of a complex and hence modifies the properties of the complex. Thus, the interaction may become interesting phenomena to design new function of a complex.

Crown ether is an excellent second-sphere ligand for forming adducts with transition metal complexes carrying protic ligands in their first coordination sphere. We have been investigating the second sphere coordination of crown ethers to ruthenium–ammine complexes [2]. The second sphere coordination brings about prominent changes in the redox potential of the complex. The magnitude of change in the redox potential was affected by some factors. However, the relationship between this change in the redox potential and the stability of the crown-ether adduct is not yet clear.

Hupp and co-workers have investigated the second sphere coordination of large aromatic crown ether to ruthenium complexes [3]. They have evaluated the stability constants of the crown ether adduct from the spectral changes of MMCT or MLCT band on

adduct formation. It is difficult to evaluate the stability constant of crown ether adduct with ruthenium–ammine complexes for systems of crown ether with small ring-size from the spectral change owing to their small change. We found that ^1H NMR spectral measurement were required to effectively evaluate the stability constant of the crown-ether adduct [4].

In this study, adduct formation was systematically investigated by ^1H NMR spectroscopy for systems with small ring-size crown ethers with and ruthenium–ammine complexes.

2. Experimental

2.1. Materials

Ruthenium–ammine complexes were prepared according to literature methods or the analogous methods and characterized by spectrophotometry, comparing of λ_{max} and ϵ_{max} values [5]. The aromatic ligands used were 2,2',2''-terpyridine (trpy), 2,2'-bipyridine (bpy), *N*-methyl-4,4'-bipyridinium (Me-4,4'-bpy), pyridine (py), 2-cyanopyridine (2-cpy), *N*-methyl-2-cyanopyridinium (Me-2-cpy), 3-cyanopyridine (3-cpy), *N*-methyl-3-cyanopyridinium (Me-3-cpy), *N*-methyl-4-cyanopyridinium (Me-4-cpy), pyrazine (pz), *N*-methylpyrazinium (Mepz), isonicotinamide (isn), benzonitrile (bn), and 4-dimethylaminobenzonitrile (dmabn).

18-Crown-6 ether (18C6), 18-thiacrown-6 ether (18S6), dibenzo-18-crown-6 ether (DB18C6), dibenzo-24-crown-8 ether (DB24C8), and dibenzo-30-crown-10 ether (DB30C10) were puri-

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fied by the literature methods [6]. 12-Crown-4 ether (12C4) and 15-crown-5 ether (15C5) were dehydrated using deuterium molecular sieves 3A (Euriso-top). The absence of oxidative impurities was confirmed for all crown ethers, as previously mentioned [7].

2.2. Measurements

Absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-near-infrared spectrophotometer. Measurements of ^1H NMR spectra were performed at 400 MHz using a Varian Unity Inova 400WB NMR spectrometer and the chemical shifts were obtained using a signal of non-deuterated nitromethane as a standard.

Electrochemical measurements were performed by means of a BAS 100B/W electrochemical workstation using a three-electrode assembly, with an Ag/AgNO₃ reference electrode, a glassy carbon working electrode, and a platinum auxiliary electrode. Redox potentials were obtained from cyclic voltammograms in 0.10 mol dm⁻³ tetrabutylammonium hexafluorophosphate acetonitrile solution. The π -electron acceptability of an aromatic ligand, P_L , was calculated from the redox potentials of the complexes using the equation below [8]

$$P_L = E_{1/2}\{\text{[Ru(NH}_3)_5\text{L]}\text{(PF}_6)_2\} - E_{1/2}\{\text{[Ru(NH}_3)_5\text{(CH}_3\text{CN)]}\text{(PF}_6)_2\} \quad (1)$$

The change in redox potential of the complex caused by adduct formation, $|\Delta E_{1/2}(\text{lim})|$, was determined from the dependence of $E_{1/2}$ on crown ether concentrations as previously reported [8].

2.3. Evaluation of stability constants of crown ether adduct [4]

The stability constant was evaluated as follows. The chemical shift of the ammine proton of ruthenium–ammine complexes was obtained in the presence of crown ether with various concentrations in deuterated nitromethane. When a rapid equilibrium of adduct-formation is holding between a ruthenium–ammine complex and crown ether, the apparent chemical shift of the ammine proton, δ_{app} , can be expressed using the stability constant of the adduct, K , as follows

$$\delta_{\text{app}} = \frac{\delta_{\text{ML}} - \delta_{\text{add}}}{K[\text{C}] + 1} + \delta_{\text{add}} \quad (2)$$

where δ_{ML} , δ_{add} , and C represent the chemical shifts of the ruthenium–ammine complex and the adduct, and the concentration of crown ether, respectively. Stability constants of the adduct were obtained from the dependence of δ_{app} on the concentration of crown ether by the least square analysis of the above equation.

3. Results and discussion

^1H NMR spectra of $[\text{Ru}(\text{NH}_3)_5\text{py}](\text{PF}_6)_2$ were measured in deuterated nitromethane in both the absence and presence of 18C6. Signals were observed in the absence of 18C6 at 2.19, 2.62, 7.38, 7.81, and 8.51 ppm, which were attributed to *cis*-ammine protons, *trans*-ammine protons, and aromatic protons of the 2,4-,3-, and 1,5-position of pyridine, respectively [4]. The signals of *cis*- and *trans*-ammine protons were shifted toward lower fields by the addition of 18C6. The down-field shifts were determined in detail at various 18C6 concentrations and the results are shown in Fig. 1. It can be seen that the shift of the signal of the *trans*-ammine protons is greater than that of the *cis*-ammine protons. This implies that the complex forms adducts with 18C6 through hydrogen bonding mainly at *trans*-ammine and additionally at *cis*-ammine. Thus, the stability constant of the adduct was obtained from the dependencies of δ_{app} of both *trans*- and *cis*-ammine protons on the 18C6 concentration by the least squares analysis of

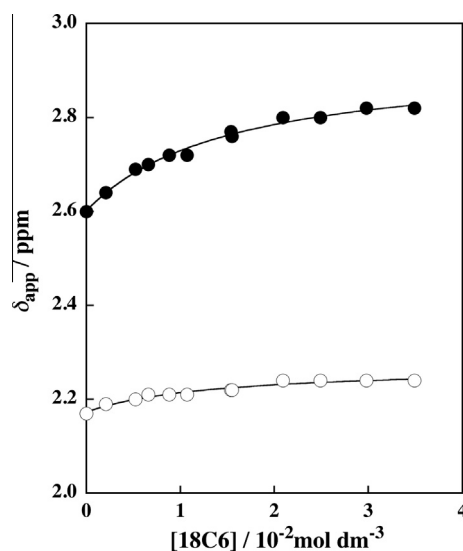


Fig. 1. Dependences of chemical shift of *trans*-ammine protons (solid circles) and *cis*-ammine protons (open circles) for $[\text{Ru}(\text{NH}_3)_5\text{py}](\text{PF}_6)_2$ on 18C6 concentration in CD_3NO_2 . Solid lines represent the regression lines of the equation in Section 2. $[\text{complex}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$.

Eq. (2) in Section 2. Table 1 summarizes the stability constants and other parameters. The obtained stability constants determined from the *trans*- and *cis*-ammine data agreed within experimental uncertainty. Thus, the stability constants were determined from the dependences of δ_{app} of more acidic ammine protons (the signal at lower field).

Adduct formation was investigated for $[\text{Ru}(\text{NH}_3)_5\text{py}](\text{PF}_6)_2$ and crown ethers with various ring sizes. The stability constants are summarized together with the change in redox potential caused by adduct formation, $|\Delta E_{1/2}(\text{lim})|$ in Table 2.

For a homologous series of crown ethers, the stability of the adduct increased with increasing ring size of the crown ether; 12C4 < 18C6, DC18C6 \approx DC24C8, DB18C6 < DB24C8 < DB30C10. The stability constant of the DB30C10 adduct agreed with that presented by Hupp and co-workers [3b]. Furthermore, for crown ethers with the same ring size, the stability of the adduct was depressed by the introduction of phenyl groups; 18C6 \approx DC18C6 > B18C6 > DB18C6. This trend corresponds to the effect on $|\Delta E_{1/2}(\text{lim})|$ and indicates that the flexibility of crown ether ring influences the stability of their adduct [8]. Thiocrown ether could not form an adduct with the ammine-complex due to the large electronegativity of the sulfur atom, in spite of its flexibility. Fig. 2 shows the approximate linear relations of $\ln K$ and $|\Delta E_{1/2}(\text{lim})|$ to $\Delta\delta$. The $\Delta\delta$ value represents the strength of hydrogen bonding between ether oxygen and the coordinating ammine. The strength of hydrogen bonding influences the stability of the adduct and the change in redox potential, although there is a poor correlation between the stability and the change in redox potential.

Table 1

Stability constants of the 18C6 adduct and other parameters for $[\text{Ru}(\text{NH}_3)_5\text{py}](\text{PF}_6)_2$ obtained from the dependencies of the chemical shift of *trans*-ammine and *cis*-ammine protons on the 18C6 concentration in CD_3NO_2 .

	<i>trans</i> -Ammine	<i>cis</i> -Ammine
$K (\text{mol}^{-1} \text{dm}^3)$	$(6.58 \pm 1.03) \times 10$	$(7.58 \pm 2.34) \times 10$
$\delta_{\text{ML}} (\text{ppm})$	2.60 ± 0.01	2.17 ± 0.00
$\delta_{\text{add}} (\text{ppm})$	2.93 ± 0.02	2.27 ± 0.01
$\Delta\delta (\text{ppm})$	0.33	0.10

$\Delta\delta = \delta_{\text{add}} - \delta_{\text{ML}}$. Error limits are the standard deviation.

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