

Effect of Second-Sphere Coordination. 4.¹ Factors Influencing the Electrochemical Behavior of Ruthenium–Ammine Complexes Caused by Second-Sphere Coordination of Crown Ethers

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Second-sphere coordination was investigated spectrophotometrically and electrochemically with various ruthenium–ammine complexes with crown ethers in acetonitrile solution. Spectrophotometric results revealed that the acidity of the ammine ligands of the complex, which depends on the valence of the metal center, predominantly affects the second-sphere coordination of the crown ether to the ruthenium–ammine complexes. This fact explains the difference in the stoichiometry between the adducts of ruthenium(II) and ruthenium(III) complexes with 18-crown-6 ether. It was found that the number of ammine ligands, the π -electron acceptability of ancillary ligands of the complex, and the flexibility of the crown ether ring affected the change in the redox potential of the complexes caused by second-sphere coordination of crown ethers.

Introduction

A variety of transition-metal complexes form adducts with organic substrates via weak interaction, e.g., hydrogen bonding, hydrophobic interaction, electrostatic interaction, or van der Waals forces.² These weak interactions may play an important role in biological systems. Such second-sphere coordination corresponds to the microenvironmental changes around the metal complex in biological systems and brings about a perturbation of the electronic state of the metal complexes. This modifies the properties of the metal complexes. We have been investigating the second-sphere coordination focusing on the modification of the properties of metal complexes, especially redox properties.

Crown ethers are capable of functioning as second-sphere ligands for metal–ammine complexes.^{1–8} Being inert and having a variety of redox potentials, ruthenium complexes are very suitable for detailed studies of the redox properties of the complex caused by second-sphere coordination. The adduct formation has been investigated for ruthenium–ammine complexes with 18-crown-6 ether (18C6 abbr.).^{1,3,4} Ruthenium–ammine complexes form an adduct with 18C6 through hydrogen bonding between the amines coordinating to the metal and the ether oxygens of 18C6. The adduct formation offers a novel negative shift of the redox potential of the complex. However, it is not clear which factor influences the change in the redox potential on the adduct formation, though the stoichiometry and

the interaction sites involved in the adduct formation were evaluated.^{1,4} Such factors are very important in designing the supramolecular species. In order to examine factors influencing the magnitude of the change in redox potential of complexes caused by adduct formation, the adduct formation was investigated for various ruthenium–ammine complexes with different kinds of crown ethers in this study.

Experimental Section

Materials. Ruthenium–ammine complexes were prepared by literature methods^{9–18} or analogous methods and isolated as the hexafluorophosphate. The complexes were characterized spectrophotometrically by comparison of the λ_{\max} and ϵ_{\max} values with literature values.^{4,12–24} If those values were not known, the complexes were identified by atomic absorption analysis of the ruthenium content and elemental analysis of the carbon, hydrogen, and nitrogen contents. The atomic absorption analysis of ruthenium was carried out according to Rowston's method²⁵ by means of a Jarrell-Ash AA-855 spectrophotometer. 18-Crown-6 ether was purified from acetonitrile and stored under nitrogen before use as mentioned previously.⁴ 12-Crown-4 ether (12C4), 15-crown-6 ether (15C5), benzo-18-crown-6 ether (B18C6), dicyclohexano-18-crown-6 ether (DC18C6), and dibenzo-30-crown-

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Table 1. Abbreviations for the Ligands Used in This Study

ligand	abbreviation
pyridine	py
4-aminopyridine	ampy
4-(dimethylamino)pyridine	dmapy
isonicotinamido	isn
2,2'-bipyridine	bpy
4,4'-bipyridine	4,4'-bpy
4,4'-dimethyl-2,2'-bipyridine	Me ₂ -bpy
5-nitro-1,10-phenanthroline	NO ₂ -phen
2,2',2''-terpyridine	trpy
4-(dimethylamino)benzotrile	dmabn
pyrazine	pz
N-methylpyrazinium	Mepz
N-methylimidazole	Melm
dinitrogen	N ₂

10 ether (DB30C10) were purchased from the Aldrich Chemical Co. and dicyclohexano-24-crown-8 ether (DC24C8) was purchased from the Nippon Soda Co. Dibenzo-18-crown-6 ether (DB18C6) and dibenzo-24-crown-8 ether (DB24C8) were purchased from the Aldrich Chemical Co. and the Nippon Soda Co., respectively, and were recrystallized twice from toluene and from ethanol, respectively. The absence of oxidative impurities in all crown ethers was confirmed as mentioned previously.¹ Other chemicals were reagent grade and were used without further purification.

Measurements. Electronic spectra were measured by means of an Hitachi 228 spectrophotometer. Electrochemical measurements were carried out with a Nikko Keisoku NPGS-301 potentiogalvanostat combined with an NF Circuit Design Block FGN-121B function generator. Cyclic voltammograms were measured in acetonitrile solution containing 0.10 mol dm⁻³ tetrabutylammonium hexafluorophosphate, using a three-electrode assembly: an Ag/AgNO₃ reference electrode, a glassy carbon working electrode, and a platinum coil auxiliary electrode. All measurements were performed at 25 °C in the dark.

Results and Discussion

Table 1 shows abbreviations of the ligands of ruthenium complexes used in this study. The analytical data and spectral characteristics of the prepared ruthenium complexes are summarized in Tables 2 and 3. For ruthenium(II)- and ruthenium(III)-ammine complexes shown in Table 4, adduct formations with 18C6 were examined spectrophotometrically in acetonitrile solution. These complexes show the MLCT [transition from the t_{2g} orbital of ruthenium(II) to the ligand LUMO] or LMCT [transition from the ligand HOMO to the unfilled t_{2g} orbital of ruthenium(III)] band in the visible region. When 18C6 was added to the solution of the complex, the MLCT band of the ruthenium(II) complexes shifted toward a longer wavelength and the LMCT band of the ruthenium(III) complexes shifted toward a shorter wavelength with increasing 18C6 concentration for each complex. This suggests that the ruthenium(II)- and ruthenium(III)-ammine complexes in Table 4 form an adduct with 18C6 through hydrogen bonding between the amines coordinating to ruthenium and the ether oxygen of 18C6, as well as the ruthenium-ammine complexes reported previously.³ The shifts of the CT bands offer information about the equilibria of adduct formation with 18C6.⁷ Unfortunately, the equilibrium

constants could not be evaluated owing to the small magnitude of their shifts. However, the magnitude of the shift of their CT bands can be considered as a tentative measure of the stability of their adduct. Table 4 summarizes the magnitude of the shift of their CT bands, Δν_{max}, in cm⁻¹ units on adding a 100-fold excess of 18C6. The values of Δν_{max} appear to be significantly different among the complexes. Any trends in Δν_{max} are not clear for individual ruthenium complexes because of their small values. However, it is clear that the |Δν_{max}| caused by the adduct formation is larger for ruthenium(III) complexes than for ruthenium(II) complexes in the tetraammine and pentaammine complexes. Namely, a ruthenium(III) complex interacts more strongly with 18C6 than a ruthenium(II) complex does. This implication is understandable in terms of the stronger acidity of ammine ligands coordinating to the ruthenium(III) metal center and is consistent with the stoichiometry of the adduct formation reported previously.⁴

As previously mentioned,^{3,4} such adduct formation causes a change in the redox potentials of the ruthenium complexes. Various factors, which originate from the natures of both the ruthenium complexes and/or the crown ethers, may influence the redox potentials. Thus, changes in the redox potentials of the ruthenium complexes were examined with respect to adduct formation for a series of various ruthenium-ammine complexes and a series of several crown ethers.

Adduct formation with a representative crown ether 18C6 was electrochemically investigated for those complexes in Table 4 in acetonitrile. The cyclic voltammograms of those complexes exhibited a couple of redox peaks in the range of -0.2 to +1.0 V vs (Ag⁺/Ag). The redox couple is symmetrical and shows a peak separation of about 60 mV for all complexes in this study, which corresponds to the Ru(III)/Ru(II) redox process. When 18C6 was added to the solution of the complex, the redox couple shifted continuously toward a more negative potential with increasing 18C6 concentration, while maintaining its reversibility. The dependence of E_{1/2} on the 18C6 concentration was determined in detail for the ruthenium complexes in Table 4. Figure 1 shows typical examples of the dependence of the change in redox potential, ΔE_{1/2}, on 18C6 concentration. The limiting change in the redox potential, ΔE_{1/2}(lim), was evaluated from the dependence of ΔE_{1/2} by curve fitting of the data to an exponential function and extrapolation to infinite 18C6 concentration. The obtained ΔE_{1/2}(lim) values are summarized in Table 5.

The correlation between ΔE_{1/2}(lim) and the formation constants, K, of the 18C6 adduct was examined for the ruthenium(II)-ammine complexes which involve ancillary ligands with mere pyridine moieties. The formation constants of the adduct²⁶ were obtained by Miyajima's method^{27,28} using HPLC. Figure 2 shows the plot of ΔE_{1/2}(lim) against log K for [Ru(NH₃)₅(py)](PF₆)₂, [Ru(NH₃)₄(bpy)](PF₆)₂, [Ru(NH₃)₃(trpy)](PF₆)₂, [Ru(NH₃)₂(bpy)₂](PF₆)₂, and [Ru(NH₃)(trpy)(bpy)](PF₆)₂. The plot shows a good linear correlation and implies that ΔE_{1/2}(lim) parallels the stability of the adduct regarding the ruthenium complexes which involve ancillary ligands with a similar π

Table 2. Analytical Data for Prepared Complexes

complex	found % (calcd %)			
	C	H	N	Ru
<i>trans</i> -[Ru(NH ₃) ₄ (dmapy) ₂](PF ₆) ₃	19.37 (19.82)	3.81 (3.80)	12.88 (13.21)	11.95 (11.91)
<i>trans</i> -[Ru(NH ₃) ₄ (ampy) ₂](PF ₆) ₃ ·2H ₂ O	14.10 (14.50)	2.91 (3.41)	13.34 (13.53)	12.48 (12.20)
<i>trans</i> -[Ru(NH ₃) ₄ (isn) ₂](PF ₆) ₂	20.55 (20.49)	3.43 (3.44)	15.86 (15.93)	14.34 (14.37)
<i>cis</i> -[Ru(NH ₃) ₄ (dmapy) ₂](PF ₆) ₃	19.98 (19.82)	3.76 (3.80)	13.26 (13.21)	12.67 (11.91)
<i>cis</i> -[Ru(NH ₃) ₄ (ampy) ₂](PF ₆) ₃ ·3H ₂ O	13.35 (14.19)	3.10 (3.57)	13.62 (14.19)	12.21 (11.94)
<i>cis</i> -[Ru(NH ₃) ₄ (Me ₂ -bpy)](PF ₆) ₂ ·2H ₂ O	20.03 (21.79)	3.66 (3.96)	13.03 (12.71)	16.18 (15.28)
<i>mer</i> -[Ru(NH ₃) ₃ (trpy)](PF ₆) ₂	26.77 (26.68)	3.06 (2.98)	12.45 (12.44)	15.82 (14.96)
[Ru(NH ₃)(trpy)(Me ₂ -bpy)](PF ₆) ₂	39.43 (39.28)	3.04 (3.17)	9.22 (10.18)	12.10 (12.25)

Table 3. Spectral Characteristics of Prepared Complexes in Aqueous Solution

complex	λ_{\max}/nm ($\epsilon_{\max}/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	
<i>trans</i> -[Ru(NH ₃) ₄ (dmapy) ₂](PF ₆) ₃	627 (1.79 × 10 ⁴)	364 (2.12 × 10 ⁴)
	267 (3.04 × 10 ⁴)	
<i>trans</i> -[Ru(NH ₃) ₄ (ampy) ₂](PF ₆) ₃ ·2H ₂ O	538 (1.01 × 10 ⁴)	350 (sh)
	339 (1.28 × 10 ⁴)	248 (2.08 × 10 ⁴)
<i>trans</i> -[Ru(NH ₃) ₄ (isn) ₂](PF ₆) ₂	494 (2.17 × 10 ⁴)	258 (7.07 × 10 ³)
<i>cis</i> -[Ru(NH ₃) ₄ (dmapy) ₂](PF ₆) ₃	621 (5.31 × 10 ³)	338 (7.81 × 10 ³)
	274 (2.34 × 10 ⁴)	
<i>cis</i> -[Ru(NH ₃) ₄ (ampy) ₂](PF ₆) ₃ ·3H ₂ O	534 (3.78 × 10 ³)	323 (6.69 × 10 ³)
	257 (1.83 × 10 ⁴)	
<i>cis</i> -[Ru(NH ₃) ₄ (Me ₂ -bpy)](PF ₆) ₂ ·2H ₂ O ^a	524 (4.51 × 10 ³)	363 (7.78 × 10 ³)
	294 (3.83 × 10 ⁴)	249 (1.22 × 10 ⁴)
<i>mer</i> -[Ru(NH ₃) ₃ (trpy)](PF ₆) ₂ ^a	620 (sh)	542 (4.10 × 10 ³)
	492 (4.05 × 10 ³)	374 (4.69 × 10 ³)
	318 (3.56 × 10 ⁴)	275 (2.37 × 10 ⁴)
	232 (2.17 × 10 ⁴)	
[Ru(NH ₃) ₃ (trpy)(Me ₂ -bpy)](PF ₆) ₂	502 (sh)	480 (9.27 × 10 ³)
	313 (3.63 × 10 ⁴)	280 (3.93 × 10 ⁴)
	230 (sh)	

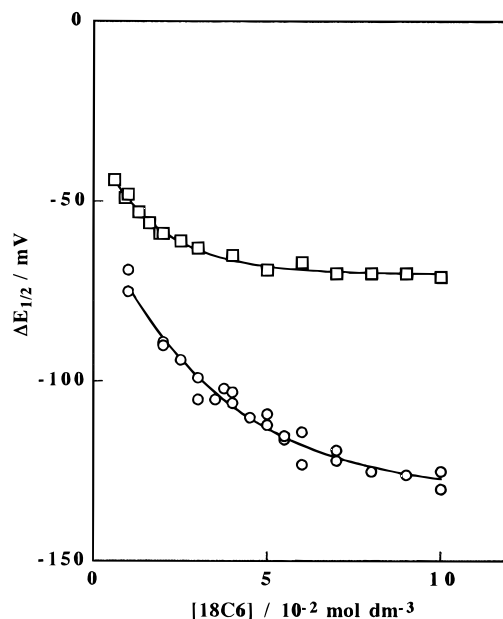
^a In acetonitrile.**Table 4.** Values of λ_{\max} of MLCT or LMCT Bands for Ruthenium–Ammine Complexes and $\Delta\nu_{\max}$ on Addition of a 100-fold Excess of 18C6 in Acetonitrile

complex	L, L'	λ_{\max}/nm ^a	$\Delta\nu_{\max}/\text{cm}^{-1} \times 10^3$
[Ru(NH ₃) ₅ (L)](PF ₆) ₃	dmapy	595 (16.81)	0.76 ^b
	ampy	514 (19.46)	0.62 ^b
	Mepz	540 (18.52)	0
[Ru(NH ₃) ₅ (L)](PF ₆) ₂	py	408 (24.51)	-0.18
	4,4'-bpy	474 (21.10)	-0.14
	isn	468 (21.37)	-0.18 ^b
	pz	458 (21.83)	-0.09 ^b
<i>cis</i> -[Ru(NH ₃) ₄ (L)](PF ₆) ₂	Me ₂ -bpy	524 (19.08)	-0.33
	bpy	524 (19.08)	-0.32
<i>cis</i> -[Ru(NH ₃) ₄ (L) ₂](PF ₆) ₃	NO ₂ -phen	515 (19.42)	-0.41
	dmapy	620 (16.13)	0.56
<i>cis</i> -[Ru(NH ₃) ₄ (L) ₂](PF ₆) ₂	ampy	534 (18.73)	0.69
	py	409 (24.45)	-0.18
<i>trans</i> -[Ru(NH ₃) ₄ (L) ₂](PF ₆) ₃	isn	469 (21.32)	-0.09
	dmapy	636 (15.72)	0.20
<i>trans</i> -[Ru(NH ₃) ₄ (L) ₂](PF ₆) ₂	ampy	538 (18.59)	0.10
	py	423 (23.64)	-0.06
<i>mer</i> -[Ru(NH ₃) ₃ (L)](PF ₆) ₂	isn	482 (20.75)	-0.09
	trpy	541 (18.48)	-0.43
<i>cis</i> -[Ru(NH ₃) ₂ (L) ₂](PF ₆) ₂	bpy	491 (20.37)	-0.13
	trpy, Me ₂ -bpy	462 (21.65)	0
[Ru(NH ₃)(L)(L')](PF ₆) ₂	trpy, bpy	458 (21.83)	-0.04
	bpy	452 (22.12)	0

^a The values in parentheses are ν_{\max} in $\text{cm}^{-1} \times 10^3$ units. ^b In ref 4.

acidity. Accordingly, the factors influencing the change in redox potential were discussed based on $\Delta E_{1/2}(\text{lim})$.

Returning to Table 5, the value of $\Delta E_{1/2}(\text{lim})$ varies from -169 mV for the hexaammine complex to -32 mV for the monoammine complexes; $\Delta E_{1/2}(\text{lim})$ seems to be primarily dependent on the number of ammine ligands. Figure 3 shows the plot of $\Delta E_{1/2}(\text{lim})$ against the number of ammine ligands. In a roughly linear manner, $\Delta E_{1/2}(\text{lim})$ decreases with the number of ammine ligands; the relationship is especially linear for the complexes with ligands including only pyridine moieties in addition to the ammines. This tendency is rationalized as follows. $\Delta E_{1/2}(\text{lim})$ is proportional to the difference between the stabilities of the ruthenium(II) and ruthenium(III) complexes due to adduct formation with 18C6. The negative value of

**Figure 1.** Dependence of $\Delta E_{1/2}$ on 18C6 concentration for [Ru(NH₃)₅-(pz)](PF₆)₂ (○) and [Ru(NH₃)₃(trpy)](PF₆)₂ (□). Solid lines are the exponential regression lines of the data.**Table 5.** Limiting Values of Change in Redox Potential, $\Delta E_{1/2}(\text{lim})$, for Ru(III)/Ru(II) Redox Couples of Ruthenium–Ammine Complexes Caused by Addition of 18C6 in Acetonitrile^a

complex	L	$E_{1/2}/\text{V vs (Ag}^+/\text{Ag)}$	$\Delta E_{1/2}(\text{lim})/\text{mV}$
[Ru(NH ₃) ₆](PF ₆) ₃		-0.186(3)	-169(2)
[Ru(NH ₃) ₅ (L)](PF ₆) ₃	Cl ⁻	-0.518(2)	-162(3)
	dmapy	-0.142(3)	-121(2)
	MeIm	-0.141(2)	-128(3)
[Ru(NH ₃) ₅ (L)](PF ₆) ₂	ampy	-0.127(4)	-131(2)
	bpy	0.060(4)	-129(2)
	4,4'-bpy	0.096(5)	-129(3)
	isn	0.118(5)	-133(2)
<i>cis</i> -[Ru(NH ₃) ₄ (L)](PF ₆) ₂	dmabn	0.146(2)	-173(2)
	pz	0.237(3)	-131(3)
	Mepz	0.661(6)	-105(2)
	Me ₂ -bpy	0.174(4)	-124(2)
	bpy	0.260(3)	-122(1)
<i>cis</i> -[Ru(NH ₃) ₄ (L) ₂](PF ₆) ₃	NO ₂ -phen	0.361(4)	-111(2)
	dmapy	-0.124(2)	-96(5)
	ampy	-0.077(2)	-116(4)
<i>cis</i> -[Ru(NH ₃) ₄ (L) ₂](PF ₆) ₂	py	0.280(3)	-99(7)
	isn	0.386(5)	-120(3)
<i>trans</i> -[Ru(NH ₃) ₄ (L) ₂](PF ₆) ₃	dmapy	-0.139(4)	-68(3)
	ampy	-0.112(3)	-97(12)
<i>trans</i> -[Ru(NH ₃) ₄ (L) ₂](PF ₆) ₂	py	0.253(4)	-91(6)
	isn	0.353(2)	-124(5)
	trpy	0.486(3)	-70(1)
<i>cis</i> -[Ru(NH ₃) ₂ (L) ₂](PF ₆) ₂	bpy	0.616(4)	-57(1)
	trpy, Me ₂ -bpy	0.730(4)	-32(9)
[Ru(NH ₃)(L)(L')](PF ₆) ₂	trpy, bpy	0.786(6)	-32(1)
	bpy	0.990	0

^a The values in parentheses are the standard deviation in mV units. [complex] = 5.0 × 10⁻⁴ mol dm⁻³.

$\Delta E_{1/2}(\text{lim})$ indicates that the stabilization by adduct formation is greater for the ruthenium(III) complex than for the ruthenium(II) complex. It is reasonable because the greater acidity of ammine ligands coordinating to ruthenium(III) makes the hydrogen bond stronger than that in the ruthenium(II) complex. In addition, the ruthenium(III) complex forms hydrogen bonds at the *cis*-ammines and at the *trans*-ammine in the 18C6 adduct, whereas the ruthenium(II) complex forms a hydrogen bond only at the *trans*-ammine in its adduct.¹ Therefore, the greater the number of ammine ligands, the greater will be the stabilization of ruthenium(III) complexes by adduct formation. Namely,

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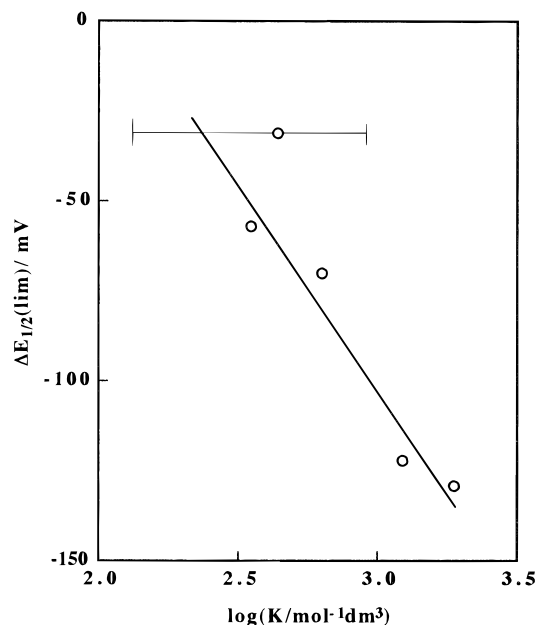


Figure 2. Relation between $\Delta E_{1/2}(\text{lim})$ and $\log K$ for $[\text{Ru}(\text{NH}_3)_n(\text{L})(\text{L}')](\text{PF}_6)_2$ $\{n = 1 \text{ to } 5; \text{L}, \text{L}' = \text{py}, \text{bpy}, \text{ and/or trpy}\}$.

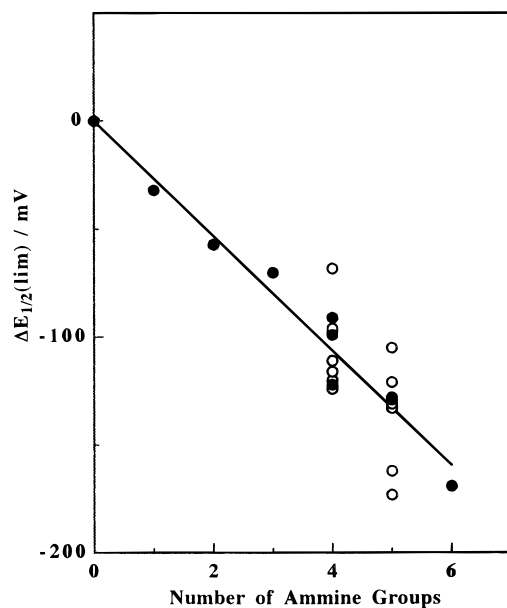


Figure 3. Plot of the limiting change in redox potential caused by adduct formation, $\Delta E_{1/2}(\text{lim})$, against the number of coordinated ammines. Solid circles denote the point for the complexes with ligands including only the pyridine moiety in addition to the ammine ligands.

$\Delta E_{1/2}(\text{lim})$ becomes more negative depending on the number of ammine ligands.

On the other hand, ligands other than ammines in the complex also contribute to $\Delta E_{1/2}(\text{lim})$. Because ligands such as pyridine behave as electron-accepting π -acids, the contribution of those ligands to $\Delta E_{1/2}(\text{lim})$ is opposite to that of the ammine; thus, $\Delta E_{1/2}(\text{lim})$ becomes more positive with increasing pyridine moieties. A detailed comparison between the individual complexes involving various ligands is discussed below.

The plot in Figure 3 shows that $\Delta E_{1/2}(\text{lim})$ is different among the complexes with the same number of ammine ligands: $\Delta E_{1/2}(\text{lim})$ varies from -105 to -173 mV and from -68 to -124 mV for pentaammine complexes and tetraammine complexes, respectively. Namely, $\Delta E_{1/2}(\text{lim})$ is also dependent to a certain extent on the ancillary ligand, L. The existence of MLCT or LMCT bands in the ruthenium complexes implies that the $d\pi$ -electron of the ruthenium-coordination center is

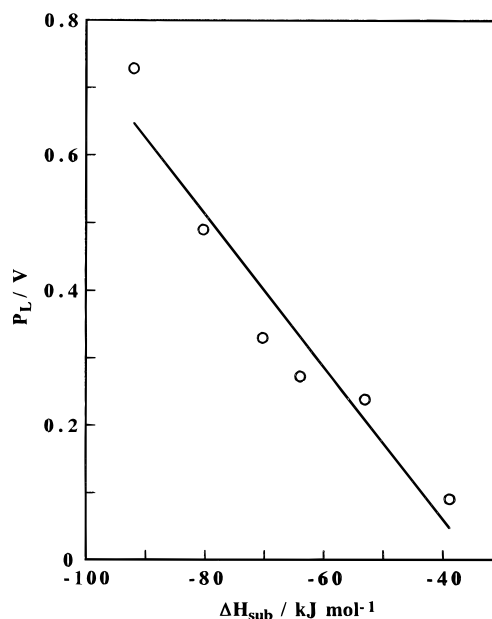
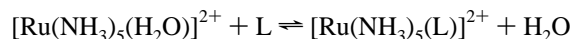


Figure 4. Plot of P_L against ΔH_{sub} for $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{2+}$ ($\text{L} = \text{N}_2, \text{DMSO}, \text{pz}, \text{isn}, \text{py}, \text{ and imidazol}$).

distributed over the whole complex to some extent. By formation of a hydrogen bond of the coordinating ammine with 18C6, the electron density of the coordination center increases. However, a net increase in their electron density may be affected by the acceptability of the π -electron of L. Accordingly, $\Delta E_{1/2}(\text{lim})$ should be closely related to the π -electron acceptability of L acting as a π -acid. In order to investigate the relation of $\Delta E_{1/2}$ to the π -electron acceptability of L, it is necessary to prepare a measure of the π -electron acceptability of L available for the complexes in this study.

The enthalpy change, ΔH_{sub} , for the substitution reaction in aqueous solution



is known to correspond to the stabilization with π -back-donation estimated directly from spectroscopic investigation.²⁹ Thus ΔH_{sub} is useful as a measure of π -electron acceptability of L, but these values are poor for the complexes in this study. Pickett and Pletcher defined the ligand constant, P_L , which stands for the contribution of L to the redox potential of the complexes, as³⁰

$$P_L = E_{1/2}\{\text{[Cr(CO)}_5(\text{L})]\} - E_{1/2}\{\text{[Cr(CO)}_6]\}$$

If its use on behalf of ΔH_{sub} is possible, P_L is a more favorable measure for the π -electron acceptability of L, because it is readily determined under the same conditions as those in this study. Figure 4 shows the plot of P_L against ΔH_{sub} for pentaammineruthenium(II) complexes. The values of P_L were calculated, using $E_{1/2}$ for $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ as a standard, from $E_{1/2}$ for pentaammine complexes which was estimated from ligand parameters, E_L , proposed by Lever.³¹ The plot in Figure 4 shows a linear relationship between P_L and ΔH_{sub} and reveals that P_L can be utilized as a measure of the π -electron acceptability of L; a ligand with a large P_L value has a large acceptability for π -electrons.

In order to investigate the effect of the π -electron acceptability of L upon $\Delta E_{1/2}(\text{lim})$ caused by adduct formation with 18C6,

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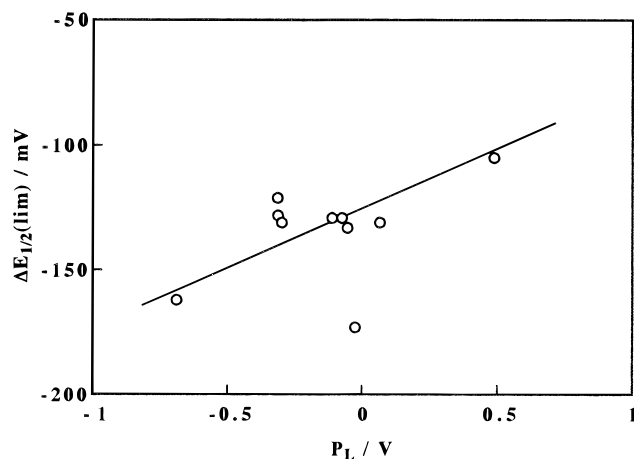


Figure 5. Plot of $\Delta E_{1/2}(\text{lim})$ against P_L for pentaammineruthenium complexes.

$\Delta E_{1/2}(\text{lim})$ was plotted against P_L . The values of P_L were calculated using $E_{1/2}$ for the complexes in Table 5. $[\text{Ru}(\text{NH}_3)_5(\text{CH}_3\text{CN})](\text{PF}_6)_2$ ($E_{1/2} = 0.173$ V vs (Ag^+/Ag)) was used as a standard complex in the calculation of P_L instead of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$, because the aqua ligand in $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ is gradually substituted by acetonitrile as the solvent. The plot of $\Delta E_{1/2}(\text{lim})$ against P_L for pentaammine-ruthenium complexes is shown in Figure 5. The plot shows that $\Delta E_{1/2}(\text{lim})$ increases with increasing P_L in a linear manner; that is, the change in redox potential caused by the adduct formation is smaller for the complex involving L with greater π -electron acceptability. Such a tendency is also found for tetraammine-ruthenium complexes with a bidentate ligand and monoammine-ruthenium complexes. Hydrogen bonding between the coordinating amines and the ether oxygen of 18C6 causes an increase in the electron density on the ruthenium center; $\Delta E_{1/2}(\text{lim})$ becomes negative. This can be interpreted in terms of Gutmann's idea of a donor-acceptor interaction.³² However, a net increase in electron density on the ruthenium center is affected by the π -electron acceptability of L, because the electron around the ruthenium center is redistributed through $d\pi-p\pi$ back-donation over the whole complex. Therefore, $\Delta E_{1/2}(\text{lim})$ is influenced by the π -electron acceptability of L.

This tendency of $\Delta E_{1/2}(\text{lim})$ is also interpreted energetically. Both ruthenium(II) and ruthenium(III) complexes are stabilized by the adduct formation with 18C6. The stabilization of the ruthenium(III) complex is greater than that of the ruthenium(II) complex because of the stronger acidity of amines coordinating to ruthenium(III). Accordingly, $\Delta E_{1/2}(\text{lim})$ becomes a negative value. In addition, the $d\pi-p\pi$ back-donation contributes to stabilizing the whole system in the ruthenium(II) complex. Therefore, $\Delta E_{1/2}(\text{lim})$ depends on the degree of the π -electron acceptability of L. In this study, the adduct formation was not discussed with respect to equilibrium constants, because $\Delta E_{1/2}(\text{lim})$ reflects the net change in electron density at the ruthenium center but not the true stabilization of the adducts discussed above.

On the other hand, in order to examine the factor originating from crown ether itself, adduct formation for several crown ethers was investigated using the representative ruthenium-ammine complex $[\text{Ru}(\text{NH}_3)_5(\text{py})](\text{PF}_6)_2$. This complex shows an MLCT band at 408 nm in acetonitrile solution (in Table 4). On addition of every crown ether used in this study, the MLCT band of the pyridine complex shifted toward a longer wavelength with increasing concentration of the crown ether. It is apparent

Table 6. Values of $\Delta E_{1/2}$ for the Ru(III)/Ru(II) Redox Couple of $[\text{Ru}(\text{NH}_3)_5(\text{py})](\text{PF}_6)_2$ on Adding a 200-fold Excess of Crown Ether^a

crown ether	$\Delta E_{1/2}/\text{mV}$	
12C4	-27(2) ^b	
15C5	-123(5) ^b	
18C6	-130(5) ^b	
B18C6	-89(2) ^b	
DC18C6	-92(5) ^b	
DC24C8	-109(4) ^b	
DB18C6	-15 ^d	-6(2) ^c
DB24C8	-29(2) ^b	-12(2) ^c
DB30C10	-143 ^d	-59(3) ^c

^a The values in parentheses are the standard deviations. ^b [complex] = 5.0×10^{-4} mol dm⁻³. ^c [complex] = 1.0×10^{-4} mol dm⁻³. ^d These values are normalized by use of the ratio of both $\Delta E_{1/2}$ values for the DB24C8 system under the conditions of *b* and *c*.

that those crown ethers also coordinate to $[\text{Ru}(\text{NH}_3)_5(\text{py})](\text{PF}_6)_2$ in the second sphere to form an adduct. The electrochemical behavior of $[\text{Ru}(\text{NH}_3)_5(\text{py})](\text{PF}_6)_2$ was examined in the absence and presence of various crown ethers by cyclic voltammetry. In the absence of the crown ether, a reversible redox couple was observed at 0.060 V vs (Ag^+/Ag) which corresponds to the Ru(III)/Ru(II) redox process. This couple shifted toward a negative potential by addition of each crown ether, while maintaining its reversibility. The redox potential shifted continuously to a more negative potential with increasing concentration of the crown ether. Table 6 summarizes the change in redox potential, $\Delta E_{1/2}$, of $[\text{Ru}(\text{NH}_3)_5(\text{py})](\text{PF}_6)_2$ on adding a 200-fold excess of crown ether. The values of $\Delta E_{1/2}(\text{lim})$ were also evaluated from the dependence of $\Delta E_{1/2}$ on the crown ether concentration. Their values were -130 ± 4 , -92 ± 2 , -87 ± 2 , and -115 ± 3 mV for 15C5, B18C6, DC18C6, and DC24C8 systems, respectively, and differ slightly from their $\Delta E_{1/2}$ values in Table 6. Because the $\Delta E_{1/2}(\text{lim})$ values for 12C4 and dibenzocrown ether systems could not be evaluated due to their small values and/or the small solubility of the crown ethers, the crown ether effect was discussed based on $\Delta E_{1/2}$ values on adding a 200-fold excess of crown ether. The absolute values of $\Delta E_{1/2}$ increase with the size of the crown ring in each series of crown ethers: 12C4 to 18C6, DC18C6 to DC24C8, and DB18C6 to DB30C10. For a series of crown ethers having the same ring size, $|\Delta E_{1/2}|$ decreases in the order 18C6 > DC18C6 > B18C6 > DB18C6 and DC24C8 > DB24C8. When a cyclohexano and a phenyl ring are introduced into the crown ether, the values of $|\Delta E_{1/2}|$ decrease. A large decrease in $|\Delta E_{1/2}|$ was brought about by the introduction of the more rigid phenyl ring. The ring size and the introduction of a cyclohexano and a phenyl ring affect the flexibility of crown ethers and hence causes the variation in $|\Delta E_{1/2}|$. A more flexible crown ether gives a greater $|\Delta E_{1/2}|$ on forming adducts, presumably because more flexible crown ethers are able to adopt a more favorable configuration for hydrogen bonding with the amines coordinating to the ruthenium.

In conclusion, the adduct formation of ruthenium complexes with 18C6 is governed by the valence at the metal center. The change in the redox potential of the ruthenium complexes caused by adduct formation is affected by the following factors: (i) the number of ammine ligands coordinating to ruthenium, (ii) the π -electron acceptability of a ligand not interacting with 18C6, and (iii) the flexibility of the crown ether ring. Combinations of those factors make it possible to design a supramolecular species with a range of redox potentials.

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