Effect of Second-Sphere Coordination. 3.[1] Adduct Formation of Mononuclear and Binuclear Ruthenium−Ammine Complexes with 18-Crown-6 Ether

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Adduct formation of 18-crown-6 ether (18C6) has been investigated on $[Ru(NH_3)_5(pz)](PF_6)_2$ (pz = pyrazine), $[Ru(NH_3)_5(dmapy)](PF_6)_3$ (dmapy = 4-(dimethylamino)pyridine), and $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ by spectrophotometry, cyclic voltammetry, and ^{1}H-NMR spectroscopy. The results show that ruthenium(II)− and ruthenium(III)−ammine complexes form the adducts with 18C6 interacting at different ammine sites, that is, at the *trans*-ammine for the ruthenium(II) complex and at the *cis*-ammines for the ruthenium(III) complex. The binuclear mixed-valence complex forms the adduct stepwise with 18C6 having 1:2, 1:3, and 1:4 stoichiometries. The formation of an asymmetric 1:3 adduct offers the possibility of partial valence trapping of the delocalized valence over the binuclear complex.

Introduction

Many adducts of metal complexes with crown ethers have been obtained via second-sphere coordination.[1−9] Such interaction in the second sphere of metal complexes not only causes a microenvironmental change around the metal complexes[4] but also perturbs the electronic state of the metal center. Accordingly, the adduct formation with crown ether significantly affects electron-transfer processes involving metal complexes.[6−8] Thus, these phenomena are closely related to the function of metal complexes in biological systems, especially to the processes involving electron transfer.

Our interests lie in the perturbation of the electronic properties of the metal complexes caused by the second-sphere coordination of organic substrates to the metal complexes.[9] In our previous papers,[1,2] it was reported that ruthenium−ammine complexes formed an adduct with 18-crown-6 ether (18C6) through hydrogen bonding between the ammines coordinating to the metal and the ether oxygen of 18C6. Such adduct formations brought about a negative shift in the redox potential of the ruthenium complexes. Their stoichiometries were determined to be different depending on the valence of the metal center. This fact brought forward the interest with respect to interacting sites. It is not specified yet whether 18C6 interacts with the ammines at the *cis*- or *trans*-position or both positions, although 18C6 forms adducts with ruthenium−ammine complexes interacting with the ammine moieties. In order to determine the interaction site, in the present study, adduct formations with 18C6 were investigated with representative ruthenium(II) and ruthenium(III) complexes, $[Ru(NH_3)_5(pz)](PF_6)_2$ (pz = pyrazine) and $[Ru(NH_3)_5(dmapy)](PF_6)_3$ (dmapy = 4-(dimethylamino)pyridine).

Mixed-valence complexes are important species as intermediates in the electron transfer between metal complexes.[10,11] Our interests are also focused on the second-sphere coordination to a binuclear complex having metal centers of different valence. The adduct formation of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ with 18C6 was also investigated.

Experimental Section

Materials. Mononuclear and binuclear ruthenium complexes were prepared by the usual method[12,13] and were isolated as the hexafluorophosphate. $[Ru(NH_3)_5(pz)](PF_6)_2$, $[Ru(NH_3)_5(dmapy)](PF_6)_3$, and $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ were synthesized from $[Ru(NH_3)_5(Cl)]Cl_2$ and characterized spectrophotometrically. Commercially available 18-crown-6 ether often contains an oxidative impurity. This impurity oxidizes the ruthenium(II)−ammine complexes and $[Fe(bpy)_3](PF_6)_2$ (bpy = 2,2′-bipyridine). Accordingly, 18C6 was purified as mentioned previously.[1] The absence of an oxidative impurity was then judged on the basis of no change in absorbance of λ_{max} of $[Fe(bpy)_3](PF_6)_2$ on adding purified 18C6 to the solution of $[Fe(bpy)_3](PF_6)_2$. The solvent for NMR measurements was deuterated acetone purchased from Aldrich Chemical. Other chemicals were reagent grade and used without further purification.

Measurements. Electronic spectra were measured by means of an Hitachi 228 and a Shimadzu MPS-5000 spectrophotometer for an intervalence transfer band. ^{1}H-NMR spectra were measured at 400 MHz using a JEOL JNM GSX-400 NMR spectrometer. The chemical shifts were observed using tetramethylsilane as an internal standard. Electrochemical measurements were performed by means of a Nikko Keisoku NPGS-301 potentiogalvanostat combined with an NF Circuit Design Block FGN-121B function generator. Cyclic voltammograms were obtained with 0.10 mol dm^{-3} tetrabutylammonium hexafluorophosphate (TBAH) in acetonitrile, using a three-electrode assembly, an Ag/AgNO$_3$ reference electrode, a glassy carbon working electrode, and a platinum coil auxiliary electrode. In the case of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$, the measurements were performed within 15 min after preparing the sample solution because the complex underwent slow

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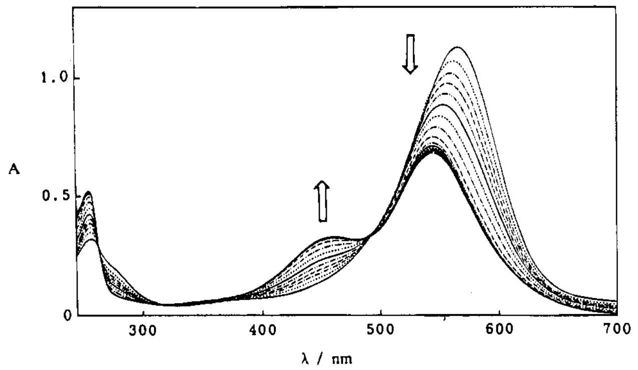

Figure 1. Spectral change for the decomposition of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ in acetonitrile at 1 h intervals. [complex] = 5.00×10^{-5} mol dm^{-3}.

decomposition in acetonitrile. A half-wave potential ($E_{1/2}$) was obtained as the average of cathodic and anodic peak potentials. All measurements were carried out at 25 °C.

Results and Discussion

The mononuclear complex $[Ru(NH_3)_5(pz)](PF_6)_2$ exhibited the metal-to-ligand charge transfer (MLCT) band (transition from the t_{2g} orbital of ruthenium(II) to the LUMO of pyrazine) at 466 nm in acetone. Adding a 100-fold excess of 18C6, the MLCT band shifted to 472 nm. This shift of MLCT band toward a longer wavelength is essentially identical to that in acetonitrile.[1] Therefore, $[Ru(NH_3)_5(pz)](PF_6)_2$ should also form an adduct with 18C6 in acetone through hydrogen bonding between the ammines coordinating to the ruthenium and the ether oxygen of 18C6. For the mixed-valence binuclear complex $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$, the MLCT band and the intervalence transfer (IT) band were observed at 567 and 1585 nm in acetone, respectively. The MLCT band shifted to 571 nm, but the IT band did not shift at all on adding the 100-fold excess of 18C6 to the solution of this pyrazine-bridged binuclear complex. This spectral change of the MLCT band reveals that $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ forms an adduct with 18C6 in a manner similar to the corresponding mononuclear pyrazine complex; because of the IT band of the class III mixed-valence complex, this complex is not affected by second-sphere ligands such as solvents.[10]

As previously reported,[1] $[Ru(NH_3)_5(pz)](PF_6)_2$ forms a 1:1 adduct and $[Ru(NH_3)_5(dmapy)](PF_6)_3$ forms a 1:2 adduct with 18C6 in alkane nitriles and 2-butanone. On the analogy of the adduct formation of mononuclear complexes, the mixed-valence binuclear complexes are expected to form asymmetric 1:3 adducts, interacting with one 18C6 molecule at one pentaammineruthenium moiety and two 18C6 molecules at another moiety. In order to evaluate the stoichiometry of adduct formation of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ with 18C6, the continuous variation method was performed at the λ_{max} of the MLCT band in acetone. The result gave only the limited suggestion that $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ forms an adduct with more than two molecules of 18C6. However, other evidence was obtained to elucidate the adduct formation and its stoichiometry. Figure 1 shows the slow decomposition of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ in acetonitrile. The MLCT band at 566 nm decreased in absorbance and shifted to 544 nm with time. At the same time, a new peak appeared at about 460 nm. Since $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{4+}$ and $[Ru(NH_3)_5(pz)]^{2+}$ show MLCT bands at 544 and 457 nm, respectively,[14] this decomposition is presumably attributed to the dissociation into the monomeric complex $[Ru(NH_3)_5(pz)]^{2+}$ via the disproportionation to $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{4+}$ and $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{6+}$. When 18C6 was added to the solution of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$, the decomposition was depressed to a great extent. The shoulder around 460 nm could not be detected when 18C6 was added at more than 5 equiv amounts. This observation reveals that the mixed-valence state of the binuclear complex became more stable and the disproportionation was depressed by the addition of 18C6. Taking the stoichiometries of the adduct formation of ruthenium(II)− and ruthenium(III)−ammine complexes into consideration,[1] it is speculated that the binuclear complex at the mixed-valence state may interact with three molecules of 18C6 in acetonitrile. This speculation is supported by the results of electrochemical and ^{1}H-NMR experiments described below.

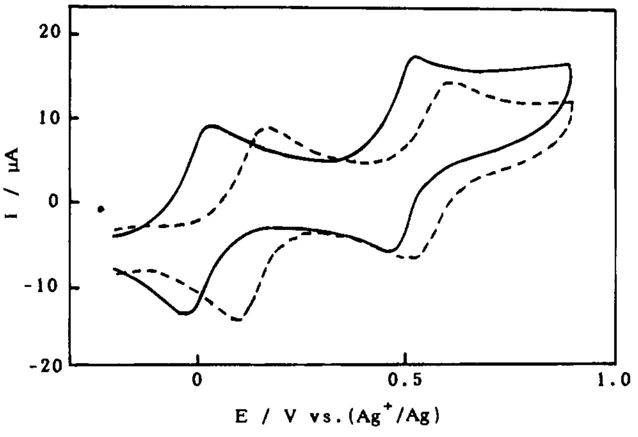

Figure 2. Cyclic voltammograms of 5.0×10^{-4} mol dm^{-3} $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ in 0.1 mol dm^{-3} TBAH acetonitrile solution in the absence (- - -) and presence (—) of 0.1 mol dm^{-3} 18C6.

Electrochemistry. As previously reported,[1] the monomeric pentaammineruthenium complexes showed a negative shift of ca. 130 mV in redox potential, $E_{1/2}$, on adduct formation with 18C6. The electrochemical behavior of the adduct of the binuclear complex which involves the metal centers at a different oxidation state is of considerable interest. The adduct formation of 18C6 was electrochemically investigated with the pyrazine-bridged binuclear complex of delocalized valence. Figure 2 shows the cyclic voltammograms of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ in acetonitrile in the absence and presence of 18C6. Without 18C6, two reversible redox couples were observed at 0.138 and 0.570 V vs $Ag/AgNO_3$ which correspond to Ru(II,III)/Ru(II,II) and Ru(III,III)/Ru(II,III) redox processes, respectively.[14] On addition of a 200-fold excess of 18C6, these two couples shifted to 0.005 and 0.493 V vs $Ag/AgNO_3$, respectively, while maintaining their reversibility. The magnitude of the shift for the second couple was much smaller, though the first couple shifted toward a negative potential with a magnitude similar to that of mononuclear systems.[1]

Thus the electrochemical behavior of the binuclear complex was examined in detail in the presence of 18C6 at various concentrations. Both redox couples shifted continuously to a more negative potential with increasing 18C6 concentration without the appearance of a new redox couple. Such dependence of the redox potentials on 18C6 concentration indicates that the electrode reactions accompany the transfer of 18C6 molecules. Therefore, the above redox reactions on the electrode are represented by the following, because these redox processes are one-electron-transfer steps.

$$\mathrm{Ru(II,II)}{-}\mathrm{C}_n + m\mathrm{C} \rightleftharpoons \mathrm{Ru(II,III)}{-}\mathrm{C}_{n+m} + \mathrm{e}^-$$

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$$\mathrm{Ru(II,III)}-\mathrm{C}_n + m\mathrm{C} \rightleftharpoons \mathrm{Ru(III,III)}-\mathrm{C}_{n+m} + \mathrm{e}^-$$

Here Ru(II,II), Ru(II,III), and Ru(III,III) and C denote the binuclear complexes at their respective oxidation states and 18C6, respectively. At an adequate high concentration range of 18C6, the Nernst equation is given as follows:

$$E = E' - 0.059m \log [\mathrm{C}]$$

Figure 3 shows the plots of $E_{1/2}$ for both redox couples against the logarithms of 18C6 concentration. The linear dependence of $E_{1/2}$ in the range of higher 18C6 concentration gave slopes of −60 and −30 mV for the Ru(II,III)/Ru(II,II) and Ru(III,III)/Ru(II,III) processes, respectively. A slope of −60 mV indicates that the electrode reaction of the first process involves the transfer of one molecule of 18C6. As previously reported,[1] the monomeric ruthenium(II)−ammine complex forms a 1:1 adduct with 18C6 in solution. The binuclear complex in this study, which involves two ruthenium(II) centers, should interact with two molecules of 18C6 at a higher concentration of 18C6. Therefore, the first redox process on the electrode can be expressed as follows:

$$[(\mathrm{NH_3})_5\mathrm{Ru(pz)Ru}(\mathrm{NH_3})_5(18\mathrm{C6})_2]^{4+} + 18\mathrm{C6} \rightleftharpoons [(\mathrm{NH_3})_5\mathrm{Ru(pz)Ru}(\mathrm{NH_3})_5(18\mathrm{C6})_3]^{5+} + \mathrm{e}^-$$

Such an electrode reaction is consistent with the stoichiometry of adduct formation reported for the monomeric complexes:[1] a $(\mathrm{NH_3})_5\mathrm{Ru^{II}}$ moiety interacts with one molecule of 18C6 and a $(\mathrm{NH_3})_5\mathrm{Ru^{III}}$ moiety interacts with two molecules of 18C6.

On the other hand, a slope of −30 mV is rather complicated to explain. The species $[(\mathrm{NH_3})_5\mathrm{Ru(pz)Ru}(\mathrm{NH_3})_5]^{6+}$, which involves two ruthenium(III) centers, can probably form a 1:4 adduct in the ratio of complex to 18C6 in a range of higher 18C6 concentration because of the stronger acidity of the ammine groups on the ruthenium(III) center. However, the stability of the 1:4 adduct may be reduced due to the steric hindrance between 18C6 molecules in the second sphere. Thus, the following two electrode reactions presumably proceed almost in parallel, resulting in a slope of ca. −30 mV.

$$[(\mathrm{NH_3})_5\mathrm{Ru(pz)Ru}(\mathrm{NH_3})_5(18\mathrm{C6})_3]^{5+} + 18\mathrm{C6} \rightleftharpoons [(\mathrm{NH_3})_5\mathrm{Ru(pz)Ru}(\mathrm{NH_3})_5(18\mathrm{C6})_4]^{6+} + \mathrm{e}^-$$

$$[(\mathrm{NH_3})_5\mathrm{Ru(pz)Ru}(\mathrm{NH_3})_5(18\mathrm{C6})_3]^{5+} \rightleftharpoons [(\mathrm{NH_3})_5\mathrm{Ru(pz)Ru}(\mathrm{NH_3})_5(18\mathrm{C6})_3]^{6+} + \mathrm{e}^-$$

^{1}H-NMR Spectroscopy. All of the ruthenium−ammine complexes form an adduct with 18C6 through the hydrogen bonding between the ammines coordinating to ruthenium and the ether oxygen of 18C6, but the stoichiometry in the adducts is different between the adduct formations of ruthenium(II) and ruthenium(III) complexes.[1] However, it is not evident yet whether 18C6 molecules interact with *cis-* or *trans*-ammines or both ammines of ruthenium−ammine complexes. Therefore, in order to decide the position of interaction sites, the adduct formation of ruthenium complexes with 18C6 was investigated by ^{1}H-NMR spectroscopy.

The ^{1}H-NMR spectrum of $[\mathrm{Ru(NH_3)_5(pz)}](\mathrm{PF_6})_2$ was obtained in deuterated acetone by the accumulation of 500 scans. Signals were observed at 2.65, 3.48, 8.22, and 8.96 ppm and are attributed to the protons of *cis-* and *trans*-ammines coordinating to ruthenium(II) and the 2,6- and 3,5-protons of the coordinated pyrazine, respectively.[15,16] These signals shifted toward a lower or higher magnetic field on addition of 18C6. The chemical shifts of their signals were examined at various 18C6 concentrations; the results are shown in Figure 4. The chemical shift of the *trans*-ammine proton changed toward a lower magnetic field with increasing 18C6 concentration and reached 3.60 ppm at a 18C6 concentration of 2.0 × 10^{-2} mol dm^{-3}. This downfield

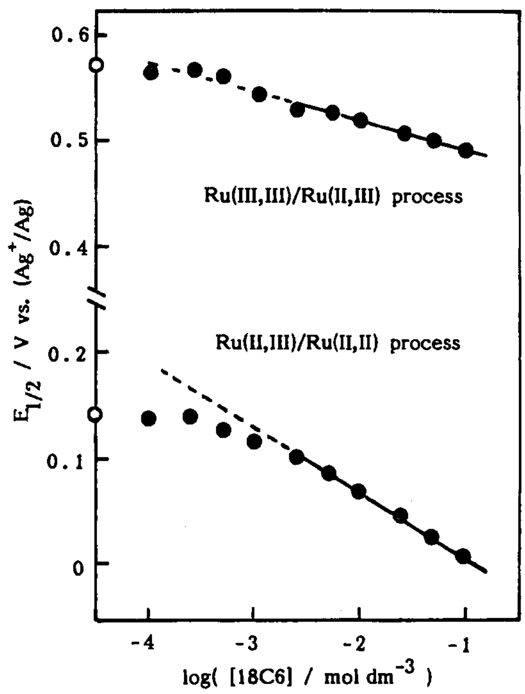

Figure 3. Dependence of $E_{1/2}$ for the redox processes, Ru(III,III)/Ru(II,III) and Ru(II,III)/Ru(II,II), of $[(\mathrm{NH_3})_5\mathrm{Ru(pz)Ru}(\mathrm{NH_3})_5](\mathrm{PF_6})_5$ on 18C6 concentration. Open symbols represent the data in the absence of 18C6.

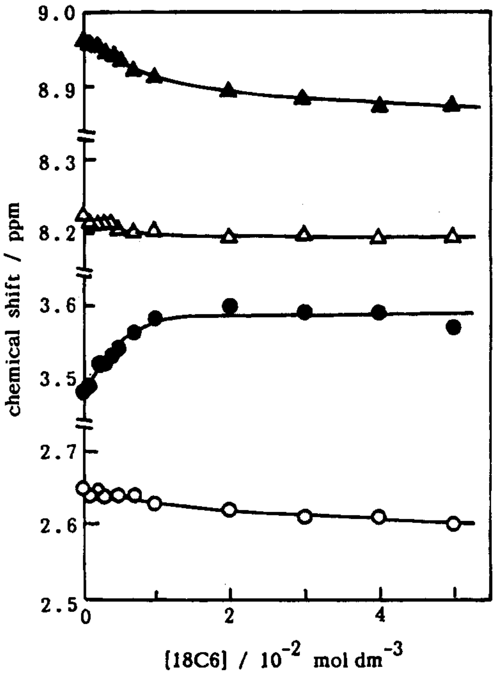

Figure 4. Dependence of the chemical shifts of the 2,6- (△) and 3,5-protons (▲) of pyrazine and the *cis-* (○) and *trans*-ammine protons (●) of $[\mathrm{Ru(NH_3)_5(pz)}](\mathrm{PF_6})_2$ on 18C6 concentration. [complex] = 1.0 × 10^{-2} mol dm^{-3}.

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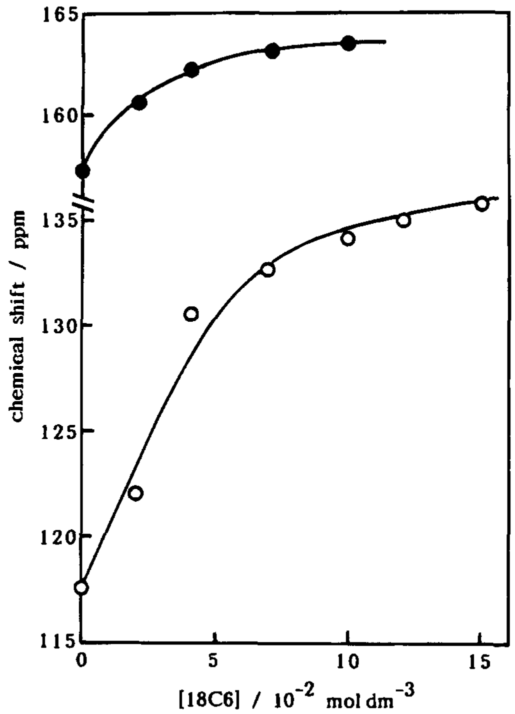

Figure 5. Dependence of the chemical shifts of the *cis*- (○) and *trans*-ammine protons (●) of $[Ru(NH_3)_5(dmapy)](PF_6)_3$ on 18C6 concentration. [complex] = 1.0 × 10^{-2} mol dm^{-3}.

shift of the *trans*-ammine proton signal indicates that the adduct should be formed through hydrogen bonding between the *trans*-ammine proton of $[Ru(NH_3)_5(pz)](PF_6)_2$ and the ether oxygen of 18C6. On the other hand, the signal of the *cis*-ammine proton gradually shifted by ca. 0.05 ppm to a higher magnetic field with increasing 18C6 concentration. This small upfield shift is due to the partial desolvation around the *cis*-ammine proton caused by the formation of a hydrogen bond between the *trans*-ammine and 18C6. For the coordinating pyrazine, the chemical shift of the proton signal at the 2,6-position was not affected at all by the addition of 18C6, but the signal of the 3,5-protons shifted by ca. 0.1 ppm to a higher magnetic field with increasing 18C6 concentration. This upfield shift corresponds to the downfield shift of the *trans*-ammine proton signal. The hydrogen-bond formation of coordinating ammines causes the increase in electron density on ruthenium(II), as $E_{1/2}$ of the complex shifted toward a negative potential on adduct formation with 18C6.[1,2] Consequently, the upfield shift of the 2,6-proton signal of the pyrazine ring reflects the perturbation in π-electron density of the pyrazine ring, because the increase in electron density on ruthenium affects the degree of π-back-donation of ruthenium(II) to pyrazine. These findings coincide with the stoichiometry of the adduct formation reported previously[1] and strongly indicate that the ruthenium(II)–ammine complexes form a 1:1 adduct with 18C6 through hydrogen bonding between the *trans*-ammine of the complex and the ether oxygen of 18C6.

For the ruthenium(III) complex, the ^{1}H-NMR spectrum of $[Ru(NH_3)_5(dmapy)](PF_6)_3$ was obtained in deuterated acetone by the accumulation of 6000 scans. The signals of the ammine protons were observed at an extremely low magnetic field and were broad and weak due to the paramagnetic effect of the ruthenium(III) center. The signals at 117 and 157 ppm are attributed to the *cis*- and *trans*-ammine protons, respectively, by their integral ratio. Both signals shifted toward a lower magnetic field on adding 18C6 as shown in Figure 5. The downfield shift of the *cis*-ammine signal is much greater than that of the *trans* signal. This indicates that 18C6 forms stronger hydrogen bonds with the *cis*-ammines and simultaneously weaker ones with the *trans*-ammine of the complex. Therefore, taking the stoichiometry of adduct formation for the ruthenium(III) complex into consideration,[1] we conclude that the 1:2 adduct is formed primarily through hydrogen bondings between the *cis*-ammine of $[Ru(NH_3)_5(dmapy)](PF_6)_3$ and two molecules of 18C6 and additionally through hydrogen bondings between the *trans*-ammine and the 18C6 bonded with *cis*-ammines.

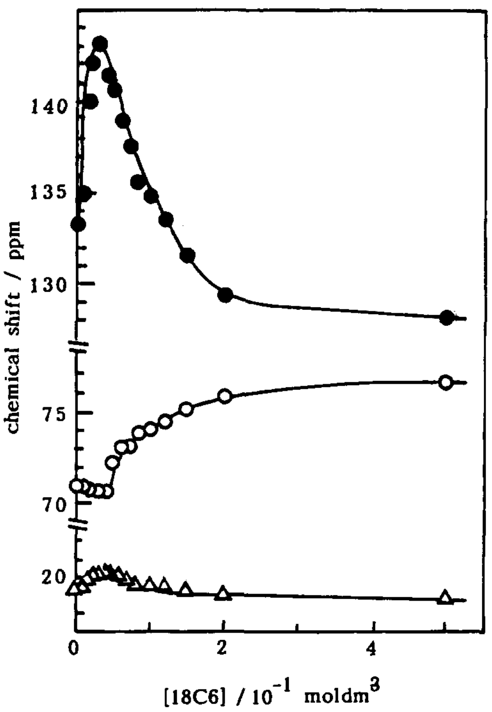

Figure 6. Dependence of the chemical shifts of the pyrazine protons (△) and the *cis*- (○) and *trans*-ammine protons (●) of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ on 18C6 concentration. [complex] = 1.0 × 10^{-2} mol dm^{-3}.

The ^{1}H-NMR spectrum of $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF6)_5$ was obtained in deuterated acetone by the accumulation of 6000 scans. Broad signals were observed at 19, 71, and 133 ppm and were assigned to the ring protons of coordinated pyrazine and the *cis*- and *trans*-ammine protons, respectively, according to the literature.[17,18] The chemical shifts of those signals were examined at various 18C6 concentrations. Figure 6 shows the dependence of the chemical shifts on 18C6 concentration. The signal of the *trans*-ammine protons shifted toward a lower magnetic field with increasing 18C6 concentration, and then the chemical shift reached a maximum value of 143 ppm at a 18C6 concentration of 3 × 10^{-2} mol dm^{-3}. This downfield shift is indicative of the hydrogen bonding of the *trans*-ammines with 18C6, which yields the adduct in a 1:2 ratio of the complex to 18C6. In this concentration range of 18C6, therefore, the amount of the 1:2 adduct increases with increasing 18C6 concentration. At an 18C6 concentration of more than 3 × 10^{-2} mol dm^{-3}, the signal of the *trans*-ammine proton shifted backward to a higher magnetic field accompanying the downfield shift of the *cis*-ammine proton signal. These shifts imply that the hydrogen bonding at *cis*-ammines replaces that at *trans*-ammines in this 18C6 concentration range. Namely, the amount of the 1:2 adduct decreases with increasing 18C6 concentration, while the asymmetric 1:3 adduct, interacting at the *cis*-ammines of one ruthenium center and at the *trans*-ammine of the other

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center, becomes one of the ingredient species. Furthermore, at 18C6 concentrations of more than 1.5×10^{-1} mol dm^{-3}, the signal of the *cis*-ammine proton shifted more and more to a lower magnetic field with increasing 18C6 concentration, and the signal of the *trans*-ammine protons shifted to a higher magnetic field than its chemical shift in the absence of 18C6. Such changes in the chemical shifts mean that the mixed-valence binuclear complex begins to form the 1:4 adduct with 18C6 at a much higher concentration of 18C6, interacting only with the *cis*-ammines of both ruthenium centers, and simultaneously desolvation around the *trans*-ammine occurs owing to steric crowding. That is, it is clear that $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ forms stepwise the adducts having 1:2, 1:3, and 1:4 stoichiometries with an increasing 18C6 concentration. On the other hand, the signal of bridging pyrazine protons showed a behavior similar to that of the *trans*-ammine proton. Hupp et al. have observed a similar behavior of the IT band for $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ on addition of crown ether.[19] On the basis of these results, they have derived a conclusion about valence trapping. Thus the formation of the asymmetric 1:3 adduct in this study is particularly interesting for the reason that the adduct formation perturbs the coupling between the two metal centers and offers the possibility of partial trapping of a delocalized valence. The stoichiometries of the adducts are strongly supported by isolation of the adducts of $[Ru(NH_3)_5(pz)](PF_6)_2$, $[Ru(NH_3)_5(dmapy)](PF_6)_3$, and $[(NH_3)_5Ru(pz)Ru(NH_3)_5](PF_6)_5$ with 18C6.[20] These adducts were characterized by reflectance electronic spectra, IR spectra, and elemental and ruthenium analyses. The stoichiometries were 1:1, 1:2, and 1:3 in the ratio of the complex to 18C6 for ruthenium(II), ruthenium(III), and the mixed-valence binuclear complex, respectively.

In conclusion it is demonstrated that 18C6 interacts with ruthenium–ammine complexes at different sites depending on the valence of the metal center: at the *trans*-ammine for the ruthenium(II) complex and at the *cis*-ammines for the ruthenium(III) complex. The mixed-valence complex, in which the valences are delocalized, forms an asymmetric adduct with 18C6, as if the complex had both ruthenium(II) and ruthenium(III) metal centers. The formation of an asymmetric adduct implies the possibility of a valence-trapping and a tuning of the trapping–untrapping of the delocalized valence by adjusting the concentrations of 18C6.

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