# Inorganic Chemistry

Article

# Study of the Ligand Substitution Reactions of *cis,cis*-[(bpy)$_2$(L)RuORu(L′)(bpy)$_2$]$^{n+}$ (L, L′ = H$_2$O, OH$^-$, NH$_3$) Using Electrospray Ionization Mass Spectrometry and $^1$H NMR

**Ryuichi Arakawa,\* Naoko Kubota, and Tsuyoshi Fukuo**

*Department of Applied Chemistry, Kansai University, Suita, Osaka 564-8680, Japan*

**Osamu Ishitani\* and Emiko Ando†**

*Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, Ookayam 2-12-1, Meguro-ku, Tokyo 152-8551, Japan*

We have successfully applied electrospray ionization mass spectrometry (ESI-MS) and $^1$H NMR analyses to study ligand substitution reactions of $\mu$-oxo ruthenium bipyridine dimers *cis,cis*-[(bpy)$_2$(L)RuORu(L′)(bpy)$_2$]$^{n+}$ (bpy = 2,2′-bipyridine; L and L′ = NH$_3$, H$_2$O, and HO$^-$) with solvent molecules, that is, acetonitrile, methanol, and acetone. The results clearly show that the ammine ligand is very stable and was not substituted by any solvents, while the aqua ligand was rapidly substituted by all the solvents. In acetonitrile and acetone solutions, the substitution reaction of the aqua ligand(s) competed with a deprotonation reaction from the ligand. The hydroxyl ligand was not substituted by acetonitrile or acetone, but it exchanged slowly with CH$_3$O$^-$ in methanol. The substitution reaction of the aqua ligands in [(bpy)$_2$(H$_2$O)Ru$^{III}$ORu$^{III}$(H$_2$O)(bpy)$_2$]$^{4+}$ was more rapid than that of the hydroxyl ligand in [(bpy)$_2$(H$_2$O)Ru$^{III}$ORu$^{IV}$(OH)(bpy)$_2$]$^{4+}$. In methanol, slow reduction of Ru$^{III}$ to Ru$^{II}$ was observed in all the $\mu$-oxo dimers, and the Ru–O–Ru bridge was then cleaved to give mononuclear Ru(II) complexes.

## Introduction

The oxidation chemistry of $\mu$-oxo ruthenium dimers *cis,-cis*-[(bpy)$_2$(L)Ru$^{III}$ORu$^{III}$(L′)(bpy)$_2$]$^{n+}$ (bpy = 2,2′-bipyridine; L and L′ = monodentate ligands such as H$_2$O, HO$^-$, pyridine, NH$_3$) has attracted attention because of their different reactivities from the corresponding monometallic complexes.[1−11]

For example, six-electron oxidation of the bisammine complex [(bpy)$_2$(NH$_3$)RuORu(NH$_3$)(bpy)$_2$]$^{4+}$ (**1$^{4+}$**) followed by elimination of 6 protons causes the formation of dinitrogen.[1] The bisaqua complex [(bpy)$_2$(H$_2$O)RuORu(H$_2$O)(bpy)$_2$]$^{4+}$ (**2$^{4+}$**) has been closely studied as an oxidation catalyst for water to dioxygen[2−8] and for Cl$^-$ to Cl$_2$.[10]

\* To whom correspondence should be addressed. E-mail: ishitani@chem.titech.ac.jp (O.I.); arak@ipcku.kamsai-u.ac.jp (R.A.).
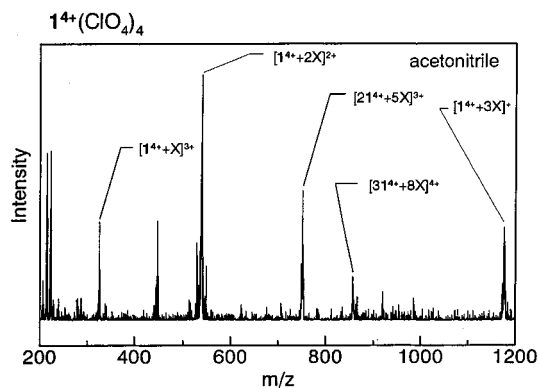† Graduate School of Science and Engineering, Saitama University.

(1) Ishitani, O.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2167.
(2) (a) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029−4030. (b) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855−3864. (c) Doppelt, R.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2027−2034. (d) Raven, S. J.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4478−4483. (e) Geselowitz, D.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 3894−3896. (f) Chronister, C. W.; Binstead, R. A.; Ni, J. F.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 3814−3815. (g) Schoonover, J. R.; Ni, J. F.; Roecker, L.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 5885−5892. (h) Bartolotti, L. J.; Pedersen, L. G.; Meyer, T. J. *Int. J. Quantum Chem.* **2001**, *83*, 143−149. (i) Binstead, R. A.; Chronister, C. W.; Ni, J.; Hartshorn, C. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 8464−8473.
(3) Petach, H. H.; Elliott, M., C. *J. Electrochem. Soc.* **1992**, *139*, 2217−2221.
(4) (a) Hurst, J. K.; Zhou, J.; Lei, Y. *Inorg. Chem.* **1992**, *31*, 1010−1017. (b) Yamada, H.; Hurst, J. K. *J. Am. Chem. Soc.* **2000**, *122*, 5303−5311. (c) Yamada, H.; Koike, T.; Hurst, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 12775−12780.
(5) Ramaraj, R.; Kira, A.; Kaneko, M. *J. Electroanal. Chem.* **1993**, *348*, 367−376.
(6) Lai, Y. K.; Wong, K. Y. *J. Electroanal. Chem.* **1995**, *380*, 193−200.
(7) (a) Rotzinger, F. P.; Munavalli, S.; Comte, P.; Hurst, J. K.; Pern, F. J.; Frank, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 6619−6626. (b) Comte, P.; Nazeeruddin, M. K.; Rotzinger, F. P.; Frank, A. J.; Grätzel, M. *J. Mol. Catal.* **1989**, *52*, 63−84.
(8) (a) Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C−228C. (b) Ruttinger, W.; Dismukes, G. C. *Chem. Rev.* **1997**, *97*, 1−24.
(9) Weaver, R. T.; Meyer, T. J.; Adeyemi, S. A.; Brown, G. M.; Eckberg, R. P.; Hatfield, E. E.; Johnson, E. C.; Murray, R. W.; Untereker, D. *J. Am. Chem. Soc.* **1975**, *97*, 3039−3048.
(10) Ellis, C. D.; Gilbert, J. A.; Murphy, J. W. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 4842−4843.
(11) Dobson, J. C.; Sullivan, B. P.; Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3863−3866.

X-ray crystallographic analyses have been used in determining the solid-phase molecular structures of several $\mu$-oxo ruthenium dimers.[1,2b,3] However, we have very limited information on their structures and structural changes in solution. Despite the paramagnetic properties of the Ru(III) complexes, relatively sharp ^{1}H NMR peaks are observed in a wide range of chemical shifts (typically 30 to −30 ppm) because of electronic coupling between the Ru(III) sites through the $\mu$-oxo bridge.[11] Although ^{1}H NMR data show how many kinds of magnetically inequivalent protons the four bpy ligands have (it shows if a 2-fold axis of symmetry through the $\mu$-oxo bridge is either present or absent), there is very limited or no information about the monodentate ligands, L and L′. Furthermore, it is difficult to label the ^{1}H NMR signals of the $\mu$-oxo dimers unambiguously, and only a few fully assigned examples have so far been reported.[11] Resonance Raman spectroscopy has been used to show the presence of the $\mu$-oxo bridge but is less useful for determining the structures of other parts of the complexes.[2g,4] Consequently, an additional method for determining the structure of the $\mu$-oxo dimers in solution has been awaited to develop this important research field.

Although ligand (L and L′) substitution of the $\mu$-oxo dimers has been presumed to play an important role in the catalytic reactions, there have been only a few reports about spectroscopic data relating to the ligand substitution reactions.[4c,11] Meyer and co-workers have reported changes of the ^{1}H NMR spectrum of $2^{4+}$ in an acetonitrile-$d_3$ solution: immediately after dissolving $(2^{4+})(ClO_4^-)_4$, 36 resonances attributed to the unsymmetrical complex $[(bpy)_2(CD_3CN)RuORu(H_2O)(bpy)_2]^{4+}$ were observed, and another set of 16 resonances attributed to symmetrical $[(bpy)_2(CD_3CN)RuORu(CD_3CN)(bpy)_2]^{4+}$ later appeared.[11] Lack of information on the ligand substitution reactivities of the $\mu$-oxo dimers has made clarification of the catalytic mechanism difficult.[2e,2i,4]

Recently, electrospray ionization mass spectroscopy (ESI-MS) has been applied to the identification of metal complexes in solution.[12,13] This is such a soft ionization method that both the molecular weights of relatively unstable metal complexes and their charges can readily be determined. In this paper, we show that ESI-MS is a powerful analytical method for determining the structures of the $\mu$-oxo ruthenium dimers in solution; the ligand substitution reactions of $[(bpy)_2(L)Ru^{III}ORu^{III}(L')(bpy)_2]^{n+}$ ($1^{4+}$, L = L′ = NH₃; $2^{4+}$, L = L′ = H₂O; $3^{3+}$, L = HO⁻, L′ = NH₃; $4^{4+}$, L = H₂O, L′ = NH₃) and $[(bpy)_2(H_2O)Ru^{III}ORu^{IV}(OH)(bpy)_2]^{4+}$ ($5^{4+}$) with various solvent molecules have been successfully investigated using both ESI-MS and ^{1}H NMR techniques.

(12) (a) Traeger, J. C. *Int. J. Mass Spectrom.* **2000**, *200*, 387−401. (b) Colton, R.; Dagostino, A.; Traeger, J. C. *Mass Spectrom. Rev.* **1995**, *14*, 79−106.
(13) (a) Hori, H.; Ishihara, J.; Koike, K.; Takeuchi, K.; Ibusuki, T.; Ishitani, O. *Anal. Sci.* **1998**, *14*, 287−292. (b) Konno, H.; Kobayashi, A.; Sakamoto, K.; Fagalde, F.; Katz, N. E.; Saitoh, H.; Ishitani, O. *Inorg. Chim. Acta* **2000**, *299*, 155−163. (c) Arakawa, R.; Tachiyashiki, S.; Matsuo, T. *Anal. Chem.* **1995**, *67*, 4133−4138. (d) Arakawa, R.; Mimura, S.; Matsubayashi, G.; Matsuo, T. *Inorg. Chem.* **1996**, *35*, 5725.
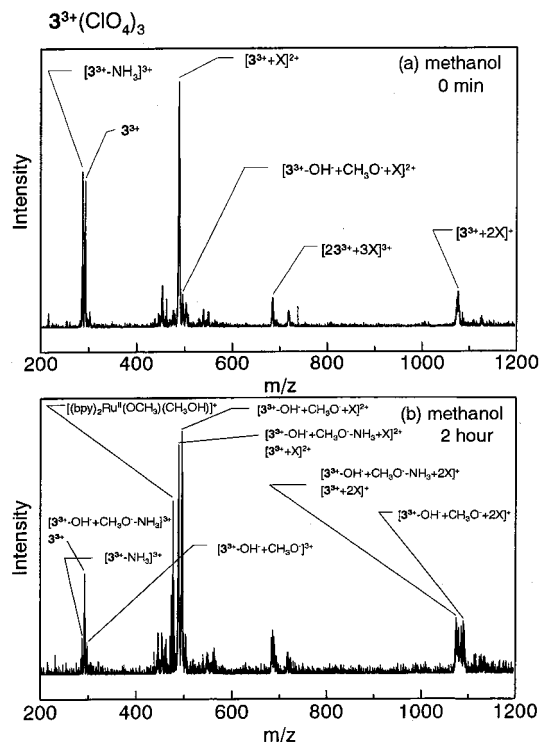
**Figure 1.** ESI-MS spectrum of $(1^{4+})(ClO_4^-)_4$ measured immediately after dissolving the complex in acetonitrile. X = ClO₄⁻.

## Experimental Section

**Materials.** HPLC-grade nondeuterated and NMR-grade deuterated solvents were purchased from Aldrich Chemical Co. and used without further purification. The perchlorate salt of $1^{4+}$ and the hexafluorophosphate salt of $5^{4+}$ were synthesized by the literature methods.[2b] *Warning: perchlorate salts are hazardous because of the possibility of explosion!* Syntheses of the perchlorate salts of $2^{4+}$ and $3^{4+}$ have been reported previously.[1] The perchlorate salt of $4^{4+}$ was obtained by adding a saturated NaClO₄ aqueous solution to a 0.1 M NaH₂PO₄ aqueous solution of $(3^{4+})(ClO_4^-)_4$. The hexafluorophosphate salt of $1^{4+}$ was obtained by adding a saturated NH₄PF₆ aqueous solution to an aqueous solution of $(1^{4+})(ClO_4^-)_4$.

**Measurements.** ESI-MS measurements were carried out with a sector-type mass spectrometer (JEOL-D300) connected to an ESI interface constructed in our laboratory of Kansai University.[13c] Mass spectra were obtained up to $m/z$ 1200 by electrospraying 0.1 mM sample solutions at a flow rate of 2 $\mu$L min⁻¹.[13c] This equipment is capable of distinguishing clearly between ions differing in $m/z$ by 1/3; it suffices for the present task because the metal complexes were observed as ion pairs with a counteranion or anions, only rarely with charge exceeding three. Low-temperature ESI-MS experiments were carried out by cooling both the sample and spray needle portion with a dry ice and acetone mixture adjusted to −20 °C. The $m/z$ values of the complexes were calculated from ¹⁰²Ru.

Proton NMR spectra were recorded on Bruker AC200P (200 MHz) and 300P (300 MHz) spectrometers at 25 °C. Saturated solutions of the complexes were used, and integration was 240 times for all ^{1}H NMR measurements. Preparation of a solution and adjustment of the ^{1}H NMR equipment required at least 10 min. The proton NMR spectra of $(2^{4+})(ClO_4^-)_4$ in methanol-$d_4$ and of $(3^{4+})(ClO_4^-)_4$ in acetone-$d_6$ and in methanol-$d_4$ could not be measured because of their low solubilities.

## Results and Discussion

**$[(bpy)_2(NH_3)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{4+}$ ($1^{4+}$).** The mass spectrum of $(1^{4+})(ClO_4^-)_4$ measured immediately after dissolving the complex in acetonitrile (Figure 1) showed three parent peaks $[1^{4+} + (4 − n)X]^{n+}$ ($n = 1−3$) where X represents the counteranion ClO₄⁻. The oligomeric ions $[21^{4+} + 5X]^{3+}$ and $[31^{4+} + 8X]^{4+}$ were also observed. The mass spectrum measured after the solution was allowed to stand for 3 h showed no change, so that substitution reaction of

the $NH_3$ ligand by acetonitrile molecule does not occur. The mass spectrum obtained in acetone was similar to that obtained in acetonitrile. Proton NMR spectra of $(1^{4+})(PF_6)_4$ measured in both $CD_3CN$ and acetone-$d_6$ show 16 resonances in the range $-13$ to 25 ppm, implying a 2-fold axis of symmetry through the $\mu$-oxo bridge. The spectra did not change at 25 °C over 3 h. The $^1H$ NMR and ESI-MS results clearly show that bisammine complex $1^{4+}$ is stable in these solutions at room temperature for at least several hours.

The mass spectrum of $(1^{4+})(PF_6)_4$ measured immediately after dissolving the complex in methanol showed oligomeric ions and $[1^{4+} + (4 - n)X]^{n+}$ ($n = 2, 3$), as for acetonitrile and acetone solvents except for a new peak at $m/z$ 292.7. This new peak was assigned to the complex $[(bpy)_2-(NH_3)Ru^{II}ORu^{III}(NH_3)(bpy)_2]^{3+}(1^{3+})$, in which one ruthenium ion has been reduced to $Ru^{II}$.[14] Another ion, observed at $m/z$ 287, can be assigned to the $NH_3$ elimination ion $[1^{3+} - NH_3]^{3+}$ formed by collision-induced dissociation (CID) of the residual gas in the skimmer, because increase of the skimmer acceleration potential from 40 to 50 V causes a steep increase of the $[1^{3+} - NH_3]^{3+}$ peak and simultaneous decrease of the $1^{3+}$ ion. The reduced complex, $1^{3+}$, increased on letting the methanol solution stand for 3 h, and no substitution product of the $NH_3$ ligands was detected. Consequently, $1^{4+}$ is reduced to $1^{3+}$ in methanol, but substitution of the $NH_3$ ligands does not proceed in either complex.

**$[(bpy)_2(OH)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{3+}$ ($3^{3+}$).** Thirty-two resonances having the same intensities were observed in each $^1H$ NMR spectra of $(3^{3+})(ClO_4)_3$ measured in $CD_3CN$ and acetone-$d_6$, suggesting that the solution contains a complex with four magnetically inequivalent bpy ligands. The spectra remained unaltered at room temperature over 2 h.

The ESI-MS spectrum of $(3^{3+})(ClO_4)_3$ obtained immediately after dissolving the complex in acetonitrile shows the ions $[3^{3+} + (3 - n)X]^{n+}$ ($X = ClO_4^-$; $n = 1-3$) and a dimeric $[23^{3+} + 3X]^{3+}$. Although small ion peaks corresponding to $[3^{3+} + AN - NH_3 + (3 - n)X]^{n+}$ ($AN = CH_3CN$; $n = 2, 3$) were also detected in the higher mass region, these are more likely to be $NH_3$ elimination ions from the solvent adduct $[3^{3+} + AN + (3 - n)X]^{n+}$ by CID, as in the spectrum of $(1^{4+})(PF_6)_4$, in view of the NMR results described previously. No change of the mass spectrum was observed after letting the solution stand for 2 h. The complex in acetone showed a similar spectrum to that in acetonitrile.

Figure 2a shows the ESI-MS spectrum of $(3^{3+})(ClO_4)_3$ obtained immediately after dissolving the complex in methanol. The parent peaks $[3^{3+} + (3 - n)X]^{n+}$ were principally observed. The exchange ion of the hydroxyl ligand by $CH_3O^-$ $[3^{3+} - HO^- + CH_3O^- + X]^{2+}$ was also detected,

(14) It is possible that this ion is a ligand substituted ion $[1^{4+} - NH_3 + OH^-]^{3+}$. To characterize the triply charged $m/z$ 292.7 ion, a deuterium-labeled experiment was performed. $(1^{4+})(PF_6)_4$ was dissolved in $CH_3OD$ and allowed to stand for several minutes, and the ESI mass spectrum was then obtained. The spectrum showed that the triply charged ion had shifted higher by 1.8 Da. A mass shift of 1.4 Da is expected for the structure $[(bpy)_2(ND_3)Ru^{III}ORu^{III}(OD)(bpy)_2]^{3+}$, and a 2.0 Da shift, for the structure $[(bpy)_2(ND_3)Ru^{II}ORu^{III}(ND_3)(bpy)_2]^{3+}$. Consequently, the $m/z$ 292.7 signal was assigned to $1^{3+}$.
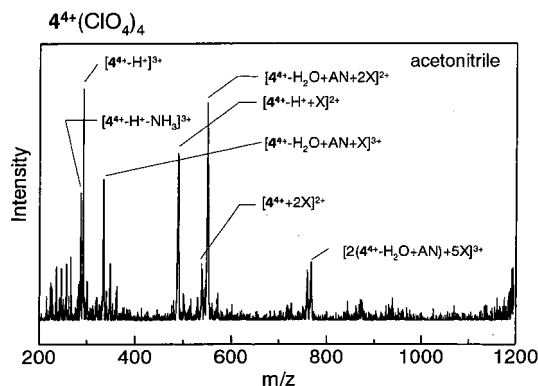
**Figure 2.** ESI-MS spectra of $(3^{3+})(ClO_4)_3$ obtained (a) immediately after dissolving the complex in methanol and (b) after standing for 2 h. $X = ClO_4^-$

but substitution of the $NH_3$ ligand was not observed. The spectrum of the solution after standing for 2 h (Figure 2b) shows an increase of the exchange products $[3^{3+} - OH^- + CH_3O^- + (3 - n)X]^{n+}$ ($n = 1-3$) together with their $NH_3$ elimination ions by CID, that is, $[3^{3+} - HO^- + CH_3O^- - NH_3 + (3 - n)X]^{n+}$. The mononuclear complex formed by breakage of the oxo-bridge, $[(bpy)_2Ru^{II}(OCH_3)(CH_3OH)]^+$ ($m/z$ 477), was also detected. Near $m/z$ 300 were overlapping peaks from $3^{3+}$ and the $NH_3$-elimination ion $[3^{3+} - HO^- + CH_3O^- - NH_3]^{3+}$ formed by CID. The doubly charged ions of these species with one counterion attached also overlap each other in the vicinity of $m/z$ 500. However, most of the ions in the spectrum were identifiable as hydroxyl ligand substitution products. The substitution reaction of the hydroxyl ligand with $CH_3O^-$ already should therefore go through. Ligand substitution of $3^{3+}$ by methanol was also followed using $^1H$ NMR; a set of 32 resonances was gradually converted to a different set of 32 resonances, supporting the formation of $[(bpy)_2(OCH_3)Ru^{III}ORu^{III}(NH_3)-(bpy)_2]^{3+}$. The spectrum obtained after 24 h consisted entirely of the ions of mononuclear complexes formed from decomposition of the dimer complex.

These results indicate that the $NH_3$ ligand of $3^{3+}$ is not changed in the solutions at room temperature. The hydroxyl ligand is stable in acetone and acetonitrile but is slowly substituted by $CH_3O^-$ in methanol.
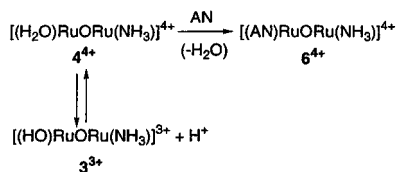
**$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{4+}$ ($4^{4+}$).** High-intensity ions of $[4^{4+} - H_2O + AN + (4 - n)X]^{n+}$ ($X = ClO_4$, $n = 1-3$) and dimeric ions were observed in the spectrum of $(4^{4+})(ClO_4^-)_4$ obtained immediately after dissolving the complex in acetonitrile, while the parent peaks of $4^{4+}$ were

**Figure 3.** ESI-MS spectrum of ($4^{4+}$)(ClO$_4^-$)$_4$ measured immediately after dissolving the complex in acetonitrile. AN = acetonitrile and X = ClO$_4^-$.

**Scheme 1**



not detected (Figure 3). The deprotonated ions from the aqua ligand, $[3^{3+} + (3 - n)X]^{n+}$ ($n = 2, 3$), were also observed as strong peaks. The spectrum obtained after 20 min consisted entirely of $[4^{4+} - H_2O + AN + (4 - n)X]^{n+}$ ions, indicating that substitution of the aqua and the hydroxyl ligands with AN was complete. The proton NMR spectrum of ($4^{4+}$)(ClO$_4$)$_4$ in acetonitrile-$d_3$ showed only one set of 32 resonances, probably attributable to $[(bpy)_2(CD_3CN)$-Ru$^{III}$ORu$^{III}$(NH$_3$)(bpy)$_2]^{4+}$ because the measurement required about 30 min. These results indicate that the reaction of $4^{4+}$ in acetonitrile proceeds according to the mechanism in Scheme 1. Immediately after dissolving in acetonitrile, deprotonation of the aqua ligand and the substitution reaction with the solvent molecule proceed competitively to form both $3^{3+}$ and $[(bpy)_2(AN)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{4+}$ ($6^{4+}$), and finally, all the complexes are converted to $6^{4+}$. As we have already shown, the hydroxyl ligand of $3^{3+}$ is not substituted by acetonitrile. Consequently, the transformation from $3^{3+}$ to $6^{4+}$ should proceed via protonation of $3^{3+}$, that is, regeneration of $4^{4+}$. It is clear that the aqua ligand is much more easily replaced than the hydroxyl ligand.

In methanol, the ligand substitution reaction also proceeds efficiently. ESI-MS detected the substituted product $[(bpy)_2(CH_3O)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{3+}$ and the ion $3^{3+}$. The spectrum obtained after 2 h showed only the ions of the substituted products, and all complexes were converted to the mononuclear complexes after 24 h, as with the case of $3^{3+}$.

In acetone, the spectrum showed that $[4^{4+} - H_2O + (4 - n)X]^{n+}$ ($n = 2-3$) were the most abundant ions probably deriving from elimination of the acetone molecule (Ac) by CID from $[4^{4+} - H_2O + Ac + (4 - n)X]^{n+}$ as a result of the low capability of acetone for coordination. In fact, the parent ions $[4^{4+} - H_2O + Ac + (4 - n)X]^{n+}$ ($n = 2-3$) were observed as small peaks in the range $m/z$ 200–600. The ions corresponding to $3^{3+}$ were also detected, and an
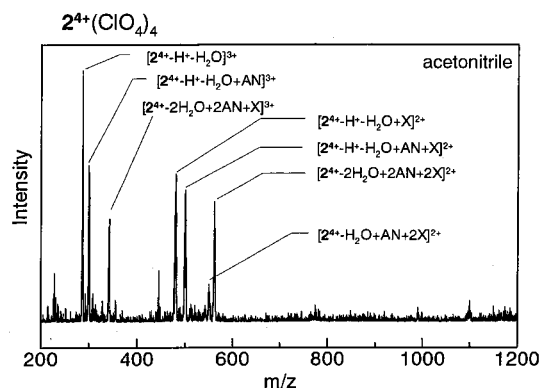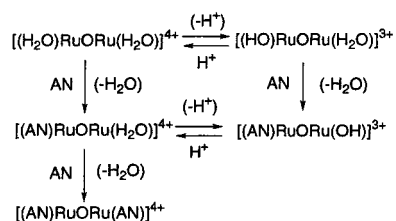
**Figure 4.** ESI-MS spectrum of ($2^{4+}$)(ClO$_4^-$)$_4$ measured immediately after dissolving the complex in acetonitrile. AN = acetonitrile, and X = ClO$_4^-$.

increase in $[3^{3+} + (3 - n)X]^{n+}$ ($n = 2, 3$) was observed after standing for 2 h. There might be an equilibrium between $[(bpy)_2(Ac)Ru^{III}ORu^{III}(NH_3)(bpy)_2]^{4+}$ and $4^{4+}$.

**$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ ($2^{4+}$) and $[(bpy)_2$-$(H_2O)Ru^{III}ORu^{IV}(OH)(bpy)_2]^{4+}$ ($5^{4+}$).** Figure 4 illustrates the ESI-MS spectrum of ($2^{4+}$)(ClO$_4$)$_4$ immediately after dissolving the complex in acetonitrile. No parent peaks attributable to $2^{4+}$ were detected, and two major ion groups were observed, the single-ligand-substituted and deprotonated ions $[2^{4+} - H^+ - H_2O + AN + (3 - n)X]^{n+}$ ($n = 2, 3$) and the double-ligand-substituted ions $[2^{4+} - 2H_2O + 2AN + (4 - n)X]^{n+}$ ($n = 2, 3$). The $m/z$ 293 and 489 ions $[2^{4+} - H^+ + (3 - n)X]^{n+}$ ($n = 2, 3$) and $m/z$ 551 ion $[2^{4+} - H_2O + AN + 2X]^{2+}$ were also observed at low intensities.[15] Detection of these ions indicates that substitution of the aqua ligands by acetonitrile runs competitively with the deprotonation reaction. The mass spectrum obtained after standing for 30 min showed only the ion peaks $[2^{4+} - 2H_2O + 2AN + (4 - n)X]^{n+}$, attributable to $[(bpy)_2(AN)Ru^{III}ORu^{III}(AN)$-(bpy)$_2]^{4+}$. These results are consistent with the $^1$H NMR spectrum measured for 30 min after ($2^{4+}$)(ClO$_4$)$_4$ was dissolved in acetonitrile-$d_6$, because only one set of 16 resonances was observed. ESI-MS of ($2^{4+}$)(ClO$_4$)$_4$ in acetonitrile was performed at −20 °C. The parent complex ion $2^{4+}$ was observed at low intensity. Although the double-ligand-substituted ions $[2^{4+} - 2H_2O + 2AN + (4 - n)X]^{n+}$ were also observed, the peaks of $[2^{4+} - H^+ - H_2O + AN + (3 - n)X]^{n+}$ were stronger. The spectrum taken after standing for 1 h was essentially unchanged. The substitution mechanism of $2^{4+}$ in acetonitrile is summarized in Scheme 2. This scheme is based on the described results combined with those obtained for $3^{4+}$ and $4^{4+}$: substitution with acetonitrile and deprotonation of the aqua ligands occur simultaneously to give $[(bpy)_2(AN)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ and $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH)(bpy)_2]^{3+}$, of which the parent peak was not observed in the ESI-MS spectra because of CID. The ion $[(bpy)_2(AN)Ru^{III}ORu^{III}(OH)(bpy)_2]^{3+}$ was probably produced from both complexes. This complex might not be directly converted to $[(bpy)_2(AN)Ru^{III}ORu^{III}$-

(15) Peaks attributable to $[2^{4+} - H^+ - H_2O + (3 - n)X]^{n+}$ are probably formed by CID of $[2^{4+} - H^+ - H_2O + AN + (3 - n)X]^{n+}$ or $[2^{4+} - H^+ + (3 - n)X]^{n+}$.

**Scheme 2**

$$[(H_2O)RuORu(H_2O)]^{4+} \underset{H^+}{\overset{(-H^+)}{\rightleftharpoons}} [(HO)RuORu(H_2O)]^{3+}$$

AN $\Big\downarrow$ $(-H_2O)$                    AN $\Big\downarrow$ $(-H_2O)$

$$[(AN)RuORu(H_2O)]^{4+} \underset{H^+}{\overset{(-H^+)}{\rightleftharpoons}} [(AN)RuORu(OH)]^{3+}$$

AN $\Big\downarrow$ $(-H_2O)$

$$[(AN)RuORu(AN)]^{4+}$$

$(AN)(bpy)_2]^{4+}$, but it is in equilibrium with $[(bpy)_2(AN)$-$Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$, of which the aqua ligand can be substituted by acetonitrile at ambient temperature to give $[(bpy)_2(AN)Ru^{III}ORu^{III}(AN)(bpy)_2]^{4+}$.

In acetone, the spectrum of complex $2^{4+}$ showed a weak parent complex ion. The main ions appearing in the spectrum were $[2^{4+} - 2H_2O + (4 - n)X]^{n+}$ ($n = 2, 3$), $[2^{4+} - H^+ - H_2O + (3 - n)X]^{n+}$ ($n = 2, 3$), and $[2^{4+} - H_2O + (4 - n)X]^{n+}$ ($n = 2, 3$). These were most likely formed via acetone elimination by CID, respectively, from $[(bpy)_2(Ac)$-$Ru^{III}ORu^{III}(Ac)(bpy)_2]^{4+}$ ($7^{4+}$), $[(bpy)_2(Ac)Ru^{III}ORu^{III}(OH)$-$(bpy)_2]^{3+}$ ($8^{3+}$), and $[(bpy)_2(Ac)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$ ($9^{4+}$). Four sets of resonances were observed in the $^1H$ NMR spectrum of a saturated acetone-$d_6$ solution of $(2^{4+})(ClO_4)_4$, and the integrated values of the resonances indicate that 80% of the total amount of the complexes is $7^{4+}$, 15% is $8^{3+}$, and the remainders are $2^{4+}$ and $9^{4+}$. Neither the ESI-MS nor $^1H$ NMR spectra changed on standing for 5 h, suggesting that these complexes are in equilibrium with each other.

The ESI-MS spectrum of complex $(2^{4+})(ClO_4)_4$ in methanol showed the doubly substituted ions $[2^{4+} - 2H_2O + 2CH_3O^-]^{2+}$ and $[2^{4+} - 2H_2O + CH_3O^- + CH_3OH + (3 - n)X]^{n+}$ ($n = 1-3$) as main peaks and the reduced ion peaks $[2^{3+} - 2H_2O + CH_3O^- + (2 - n)X]^{n+}$ ($n = 1, 2$). The ion $[2^{4+} - 2H_2O + CH_3O^- + (3 - n)X]^{n+}$, which should be formed by CID, was also observed. The spectrum of the complex obtained after dissolving in methanol for 30 min showed an increase in the reduced ion; the mononuclear ion $[(bpy)_2Ru^{II}(OCH_3^-)]^+$ ($m/z$ 445) was also observed. This indicates that one of the $Ru^{III}$ metals in the complex was reduced to $Ru^{II}$ after the ligand exchange by methanol and then decomposed to the mononuclear complex. The ESI-MS of the complex at $-20\ °C$ (Figure 5a) mainly yielded the ions resulting from exchange of both $H_2O$ ligands. At low temperature, the reduced ion decreased significantly, and no mononuclear complex was detected.

These results indicate that the aqua ligands in $2^{4+}$ are rapidly substituted by solvent molecules but that substitution of the hydroxyl ligand formed by deprotonation from the aqua ligand is very slow. Exchange of the hydroxyl ligand probably proceeds by protonation of the ligand. This also explains the fact that the ligand substitution reaction of $2^+$ proceeded more quickly in the protic solvent methanol.

Our experiments have shown that both aqua ligands of $2^{4+}$ are quickly substitutable especially in methanol. Even with the low-temperature ESI-MS, neither the parent ion nor single-ligand-substituted ion could be detected. The difference in reactivities between $2^{4+}$ and its oxidized form $5^{4+}$ is
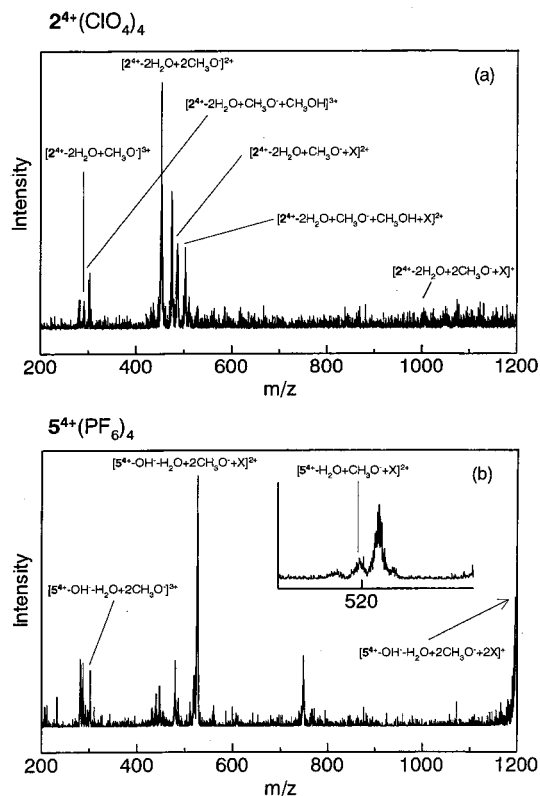


**Figure 5.** ESI-MS spectra of (a) $(2^{4+})(ClO_4)_4$ and (b) $(5^{4+})(PF_6)_4$ obtained immediately after dissolving the complex in methanol at $-20\ °C$. X = (a) $ClO_4^-$ or (b) $PF_6^-$.

interesting, so we studied the ESI-MS of complex $5^{4+}$ in methanol. From the spectrum obtained immediately after dissolving $(5^{4+})(PF_6^-)_4$ in methanol at $-20\ °C$ (Figure 5b), the parent ion of $5^{4+}$ was not detected, and the doubly substituted ions $[5^{4+} - OH^- - H_2O + 2OCH_3^- + (3 - n)X]^{n+}$ dominated the observation. However, we detected the single-ligand substituted and deprotonated ion $\{[(bpy)_2$-$(CH_3O^-)Ru^{III}ORu^{IV}(OH)(bpy)_2]+X\}^{2+}$ (X = $PF_6^-$) as a small peak at $m/z$ 519. This peak disappeared after standing for 30 min. These results indicate that the hydroxyl ligand in the oxidized complex $5^{4+}$ is less labile to displacement than the aqua ligands in $2^{4+}$ and $5^{4+}$. It is noteworthy that substitution of either the hydroxy ligand or the aqua ligand in $5^{4+}$ with $H_2^{18}O$ has been assumed to be very slow at ambient temperature,[2e,2i,4] while the ligand substitution of $5^{4+}$ is rapid in methanol even at $-20\ °C$.

Unfortunately, we were unable to follow substitution reactions of $2^{4+}$ and $5^{4+}$ in $^{18}O$-labeled water using ESI-MS techniques, because ionization did not occur in aqueous solution.

**Dependence of the Ligand Substitution Reactions on the Ligand Species and Valence of Ruthenium.** The results described here clearly show that liberation of the ligands of the $\mu$-oxo ruthenium dimers in solution depends strongly on the ligand species: an aqua ligand is easily substituted with any solvents, but an $NH_3$ ligand is inert against all the nucleophiles used at room temperature. Although a hydroxyl ligand can be substituted, its protonation (i.e., conversion to the aqua ligand) is required. The hydroxyl ligand of $5^{4+}$ is

also more stable than both aqua ligands of $2^{4+}$ in methanol. Two possible reasons are that the $Ru^{IV}-O$ bond is stronger than that of $Ru^{III}-O$, and that an aqua ligand is more labile towards displacement than a hydroxyl ligand.

In conclusion, ESI-MS techniques are valuable for determining the structure of $\mu$-oxo ruthenium dimers, and probably similar paramagnetic complexes, in organic solutions. The combination of ESI-MS with $^1$H NMR can give important information on reactions of these complexes.

**Supporting Information Available:** Proton NMR data of the characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0109445