# Substitution of methanol-d$_4$ for the coordinated water in the trinuclear complexes, $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ ($M_3 = Ru_3$, $Rh_3$ or $Ru_2Rh$) in methanol-d$_4$

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(Received January 29, 1993)

## Abstract

The $^1H$ NMR spectra of acetate methyl signals of the titled three complexes in $CD_3OD$ change with time due to successive substitution of $CD_3OD$ for the coordinated water molecules. The first-order rate constants for the first methanol-d$_4$ substitution of the triruthenium(III) and trirhodium(III) complexes are $7.7\times10^{-4}$ s$^{-1}$ (298.2 K) ($\Delta H^\ddagger = 103\pm6$ kJ mol$^{-1}$ and $\Delta S^\ddagger = +41\pm12$ J K$^{-1}$ mol$^{-1}$ at 0–21 °C) and $1.3\times10^{-3}$ s$^{-1}$ (298.2 K) ($\Delta H^\ddagger = 102\pm9$ kJ mol$^{-1}$ and $\Delta S^\ddagger = +42\pm32$ J K$^{-1}$ mol$^{-1}$ at 0–10 °C) per one metal ion, respectively, which are greater by approximately 2 and 6 orders of magnitude, respectively, than the water exchange reactions of the hexaaqua complexes of these metal ions. The *trans* effect of the central oxide ion is considered as a major factor responsible for the labilization. The first-order rate constants for the mixed-metal rhodium–diruthenium complex at 298.2 K are $9.9\times10^{-5}$ ($\Delta H^\ddagger = 109\pm4$ kJ mol$^{-1}$ and $\Delta S^\ddagger = +44\pm9$ J K$^{-1}$ mol$^{-1}$) and $7.9\times10^{-5}$ s$^{-1}$ ($\Delta H^\ddagger = 103\pm3$ kJ mol$^{-1}$ and $\Delta S^\ddagger = +22\pm6$ J K$^{-1}$ mol$^{-1}$ at 10.1–35.3 °C) at ruthenium and rhodium centers, respectively, which are *c.* 10 times smaller than the corresponding values for the homonuclear complexes. The slower rates in the mixed-metal complex indicate that electronic configuration in the molecular orbital based on (metal–d$\pi$)–(oxygen–p$\pi$) interactions plays some role in controlling the substitution rate. On the basis of the activation parameters, a dissociative mechanism is proposed for all these reactions.

## Introduction

Ligand substitution properties of simple mononuclear trivalent metal complexes have been extensively studied [1–4]. For the first-transition series, substitution lability is discussed mainly in terms of electronic configurations (ligand field activation energy) [5, 6] and mechanisms (whether dissociative or associative) mainly in terms of metal ion sizes [3, 4, 7]. Recently, a good linear correlation between the water exchange rate constant of hexaaqua complexes in aqueous solution and that of the acetylacetonate exchange of tris(acetylacetonato) complexes in acetylacetone solvent has been pointed out for a series of trivalent metal ions [8]. The tris(acetylacetonato) complexes are available for a wider variety of metal(III) ions [9] including various second-row transition metal ions, and it has been suggested that the acetylacetonate exchange reactions may be used as a more general measure of the metal ion lability [8, 9]. Among the trivalent metal ions whose water and acetylacetonate exchange studies are available, Ru(III) and Rh(III) ions appear to be the most inert ones [7–10][†].

It has been increasingly recognized that metal ions have a versatile field of a wide variety of di- and polynuclear complexes (or clusters) [12], whose various characteristics are quite different from those of the mononuclear species. As one of the most fundamental aspects, it is important to understand their ligand substitution properties. In order to understand the effect

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[†] Ir(III) is probably the most inert trivalent metal ion so far studied [11].

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of di- and polynuclear moieties on the ligand substitution properties, it is preferable to choose metal ions, of which the mononuclear complexes are well understood with respect to their ligand substitution behavior. Although some kinetic studies on the ligand substitution properties of di- and polynuclear complexes have been reported [13–25]*, such comparison can be made in only a limited case**.

The $\mu_3$-oxo-hexakis($\mu$-acetato)tri(ligand)trimetal(III) ions, $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ ($L = H_2O$, pyridine (py), etc.) (Fig. 1) occur in a wide variety of trivalent metal ions [26] such as vanadium(III), chromium(III), manganese(III), iron(III), cobalt(III) [27], ruthenium(III), rhodium(III), iridium(III) and gallium(III) [28]. The direct metal–metal bond is absent in these complexes (metal–metal distance is *c.* 3.3 Å) [26]. The ligand substitution properties of the mononuclear complexes of these metal ions are well understood [1, 4, 7]. Although the pyridine exchange reactions of the ruthenium trimers have been studied [22], the comparison of the rate constants with those of the mononuclear ruthenium complexes is not straightforward. We have found during a study of the mixed ruthenium–rhodium complex, $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$, that the substitution of $CD_3OD$ for the water ligands can be monitored quantitatively by 400 Hz $^1H$ NMR spectroscopy in $CD_3OD$ [29]. This type of substitution reaction can be reasonably compared with water exchange reactions of the mononuclear complexes of the corresponding metal ions. Thus we have carried out variable temperature studies of the $CD_3OD$ substitution for the water ligands for the series of trinuclear complexes, triruthenium(III), rhodium(III)–diruthenium(III) and trirhodium(III). A remarkable labilization, as compared with the mononuclear complex of these metal ions, and also the effect of mixing different metal ions have been revealed.

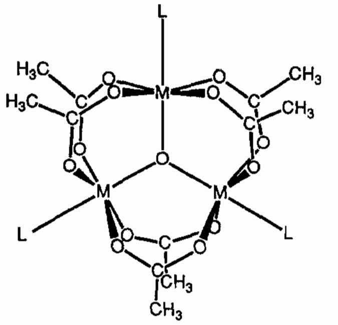

Fig. 1. Structure of the trinuclear complexes, $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$.

## Experimental

### *Materials*

The three complexes, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]ClO_4$, $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]ClO_4$ and $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]ClO_4$, were prepared and recrystallized as described previously [29]. Deuterated methanol (99% deuterated) and $CD_3OD$ from Aldrich were used as received.

### *Kinetic measurements*

These were carried out with a JEOL JNM-GX-400 FT-NMR spectrometer. The complex was dissolved in the cooled solvent (*c.* −20 °C) (*c.* $1\times10^{-3}$ M), and the sample solution was quickly placed in the NMR cell compartment which was kept at the desired temperature. The temperature was controlled by the attached variable temperature controller, and was calibrated within the accuracy of ±0.2 °C using the chemical shift difference between the methyl and hydroxy signals of methanol. The reaction was monitored at a certain time interval, and the relative integrated intensity of the individual peak was obtained to evaluate the rate constants.

## Results

### *Preliminary observations*

The $^1H$ NMR spectra in the acetate methyl region of the three complexes, $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ ($M_3 = Ru_3, Rh_3, Ru_2Rh$), changed their patterns with time in $CD_3OD$. The changes were interpreted by considering the successive substitution of $CD_3OD$ for the terminal aqua ligands. Figure 2 shows the change for the triruthenium complex, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$. Although the complex contains an odd number of d-electrons, the acetate methyl signals (at around 1.11 ppm) shifted only moderately from the position expected for diamagnetic compounds [30]. Six peaks were observed during the change. The peak at the highest magnetic field ($\delta = 0.76$) corresponds to the original triaqua complex, and the one at the lowest field ($\delta = 1.44$) to the fully substituted tri(methanol-$d_4$) complex as it is the only peak observed after a prolonged time. The remaining four peaks can be grouped into two sets, two peaks in each set with a 1:2 integrated intensity ratio. The set at the higher magnetic field ($\delta = 0.92$, 1.03) should belong to the mono(methanol-

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*Some examples of the kinetic studies of di- and polynuclear complexes are available for Mo dimers [13, 14], Re dimers [14], Mo and W di- and trimers [15–18], Mo tetramers [19], $Mo_2W$ complex [20], Ru(III) dimers [21], Ru trimers [22], $Ir_3$(III,III,IV) trimer [23], Pt dimers [24], and Pt(II) tetramer [25].

**One such case is the acetate exchange reactions of the tetranuclear platinum(II) complex, $Pt_4(CH_3COO)_8$ [25]. This complex undergoes a rapid ligand exchange reaction, which is explained by a strong *trans* effect of the metal–metal bond.

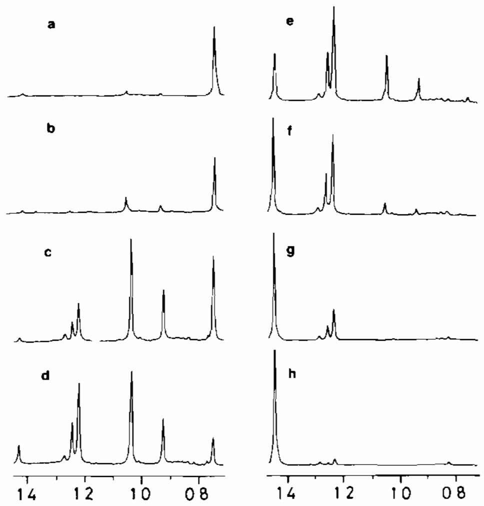

Fig 2 Time dependence of the $^1H$ NMR spectrum of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3](ClO_4)$ in $CD_3OD$ in the acetate methyl region: (a) 580 s after the dissolution at 0 °C, (b) 80 min at 0 °C, (c) 9 min after the dissolution at 21 °C, (d) 20 min at 21 °C, (e) 38 min at 21 °C, (f) 70 min at 21 °C, (g) 2 h at 21 °C, (g) 4 h at 21 °C.

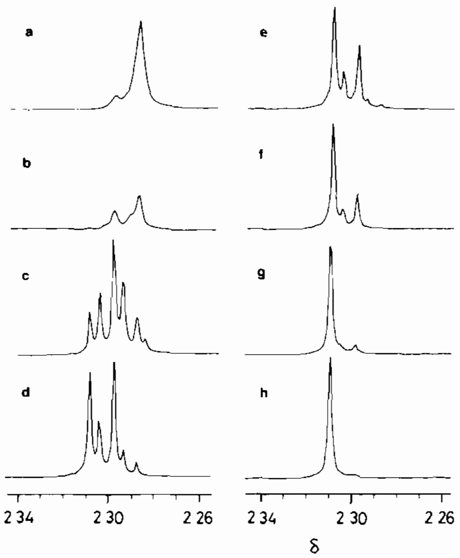

Fig. 3. Time dependence of the $^1H$ NMR spectrum of $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3][ClO_4)$ in $CD_3OD$ in the acetate methyl region: (a) 6 5 min after the dissolution at 0 °C, (b) 49 min at 0 °C, (c) 15 min after the dissolution at 21 °C, (d) 28 min at 21 °C, (e) 38 min at 21 °C, (f) 53 min at 21 °C, (g) 100 min at 21 °C, (g) 3 h at 21 °C.

$d_4$) complex: the peak with the smaller intensity corresponds to the acetate bridging between two aqua ruthenium(III) ions ($(H_2O)Ru\text{–}Ru(OH_2)$) and the other with the larger intensity to the one bridging between the $CD_3OD$–ruthenium(III) and the aqua-ruthenium(III) ($(CD_3OD)Ru\text{–}Ru(OH_2)$). A similar assignment can be made for the other set ($\delta = 1.22$, 1.24) which should belong to the di(methanol-$d_4$) complex. Figure 3 shows the change with time in the $^1H$ NMR spectrum of 'diamagnetic'* $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ in $CD_3OD$. The signals appeared within a much narrower range. Six peaks were again observed, which were assigned similarly. The change in the $^1H$ NMR spectrum, and the peak assignment of the 'diamagnetic'* mixed-metal complex, $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ in $CD_3OD$, was reported previously [29]. Unlike those of the $Ru_3$ and $Rh_3$ complexes, the acetate methyl signal of the $Ru_2Rh$ complex did not show appreciable shift by the different monodentate ligand at the opposite site; for example, the methyl signals of $(H_2O)Ru(\mu\text{-}CH_3COO)_2Ru(H_2O)$ moieties from the two different complexes, $[\{Ru(H_2O)\}_2\{Rh(H_2O)\}(O)(CH_3COO)_6]^+$ and $[\{Ru(H_2O)\}_2\{Rh(CD_3OD)\}(O)(CH_3COO)_6]^+$ were observed as a single peak.

The assignments of all the acetate methyl signals observed during the changes are summarized in Table 1.

*Kinetic analysis for the two homonuclear complexes*

Figure 4 shows the change in relative intensities ($R$ (%)) of four sets of peaks of the $Ru_3$ complex with time. A similar result was also obtained for the $Rh_3$ complex. It is clear that successive substitution of $CD_3OD$ for aqua ligands takes place.

$$[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+ \ (A)$$
$$\xrightarrow{k_1} [M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_2(CD_3OD)]^+ \ (B)$$
$$\xrightarrow{k_2} [M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)(CD_3OD)_2]^+ \ (C)$$
$$\xrightarrow{k_3} [M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(CD_3OD)_3]^+ \ (D)$$

($M = Ru$ or $Rh$)

The concentration of each species is defined as [X] which is equal to $0.01R_x[M_3]_{total}$ ($R_x$, relative integrated intensity of X in %), where X = A, B, C or D. For the first step, eqn. (1) holds.

$$-\ln[A] = k_1 t - \ln\{[M_3]_{total}\} \qquad (1)$$

The plot of ln[A] against $t$ gave a good straight line (Figs. 5 and 6), from the slope of which $k_1$ was evaluated. The second and the third steps were analyzed less accurately at 21 °C. Nevertheless, the rate constants, $k_2$ and $k_3$, were evaluated with reasonable certainty by using a non-linear least-squares computer simulation to the observed time dependence of the change in the

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*The term, 'diamagnetic', is used here for the compounds that have no unpaired electron and not for those with negative magnetic moments. In fact, the $Rh_3$ and the mixed $Ru_2Rh$ complex show small positive magnetic moments [31].

TABLE 1. Peak positions ($\delta$ vs. TMS) of the acetate methyl signals of the trinuclear complexes, $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_n(CD_3OD)_{3-n}]^+$ in $CD_3OD$

| $M_3$ | Site | | |
|---|---|---|---|
| | $(H_2O)M\text{-}M'(H_2O)$ | $(H_2O)M\text{-}M'(CD_3OD)$ | $(CD_3OD)M\text{-}M'(CD_3OD)$ |
| $Ru_3$ | 0.76 ($n=0$)<br>0.92 ($n=1$) | 1.03 ($n=1$)<br>1.22 ($n=2$) | 1.24 ($n=2$)<br>1.44 ($n=3$) |
| $Rh_3$ | 2.284 ($n=0$)<br>2.287 ($n=1$) | 2.293 ($n=1$)<br>2.297 ($n=2$) | 2.304 ($n=2$)<br>2.308 ($n=3$) |
| $Ru_2Rh$[a] | 1.92 (Ru–Ru)<br>2.37 (Ru–Rh) | 1.96 (Ru–Ru)<br>2.36 (M = Ru, M′ = Rh)<br>2.40 (M = Rh, M′ = Ru) | 2.00 (Ru–Ru)<br>2.39 (Ru–Rh) |

[a] Splitting due to the difference in the monodentate ligand at the opposite site was not observed (see text)

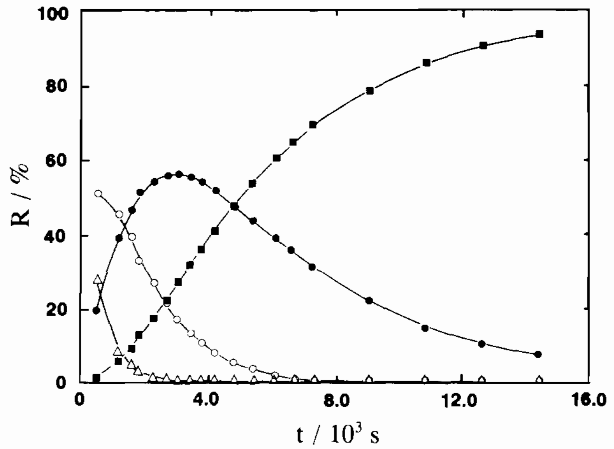

Fig. 4. Time dependence of the relative integrated intensities ($R$ (%)) of the signals of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3](ClO_4)$ in $CD_3OD$ at 21 °C: (△) peak at $\delta=0.76$, (○) sum of the peaks at 0.92 and 1.03, (●) sum of the peaks at 1.22 and 1.24, (▲) peak at 1.44

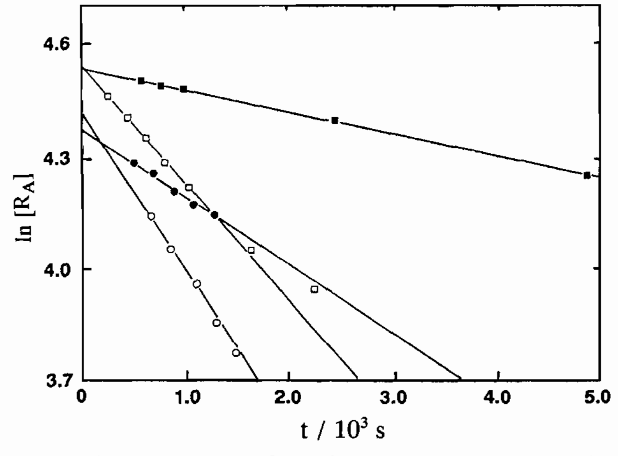

Fig. 5. First-order plots of the decrease in the concentration of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3](ClO_4)$ (A) estimated from the relative integrated intensity of the $^1H$ NMR signal at $\delta=0.76$ in $CD_3OD$ at. (■) 0, (●) 7, (□) 10.5, (○) 14 °C

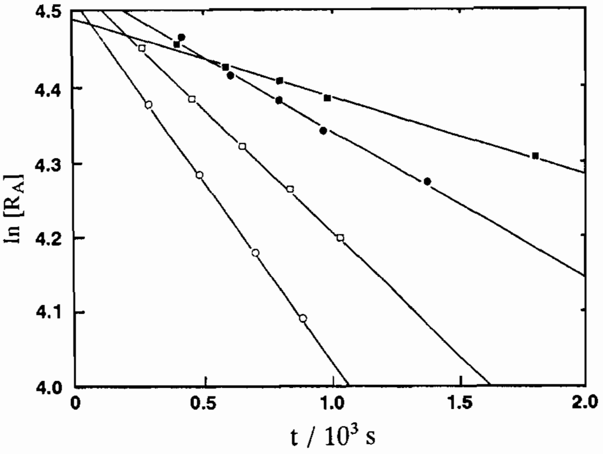

Fig. 6. First-order plots of the decrease in the concentration of $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3](ClO_4)$ (A) estimated from the relative integrated intensity of the $^1H$ NMR signals at $\delta=2.284$ in $CD_3OD$ at (■) 0, (●) 5, (□) 7.5, (○) 10 °C

ratio of various species (Fig. 3 for the $Ru_3$ complex). Rate constants ($k_1$, $k_2$ and $k_3$) were converted into those per metal ion ($k_{1a}=k_1/3$, $k_{2a}=k_2/2$, $k_{3a}=k_3$), and are listed in Table 2, together with the activation parameters for $k_{1a}$.

### *Kinetic analysis for the rhodium–diruthenium complex*

Reaction scheme (Fig. 7) given here uses somewhat different notations, for convenience, from those adopted in the previous paper [29]. Because of the failure to observe the splitting of the NMR peak due to the difference in the monodentate ligand at the opposite site, evaluation of the rate constants is not straightforward and rate constants other than $k_{11}$ and $k_{21}$ were difficult to estimate.

The relative intensities ($R$ (%)) of the signals of the acetate methyl groups bridging between two $Ru(H_2O)$ moieties and between $Ru(H_2O)$ and $Rh(H_2O)$ are expressed as $I$(Ru–Ru) and $I$(Ru–Rh), respectively. The first-order plots, ln($I$(Ru–Ru)) or ln($I$(Ru–Rh)) versus

TABLE 2. Rate constants and activation parameters for the substitution of deuterated methanol for the water in $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ (M = Ru or Rh) in $CD_3OD$

| | Temp. (°C) | $10^{-4}\ k_{na}$ [a] ($s^{-1}$) | $\Delta H^\ddagger$ (kJ $mol^{-1}$) | $\Delta S^\ddagger$ (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|
| M = Ru | | | | |
| $k_{1a}$ | 0.0 | 0.19 | 103 ± 6 | +41 ± 12 |
| | 7.0 | 0.57 | | |
| | 10.5 | 1.06 | | |
| | 14.0 | 1.44 | | |
| | 21.0 | 5.5 | | |
| $k_{2a}$ | 21.0 | 3.2 | | |
| $k_{3a}$ | 21.0 | 2.1 | | |
| M = Rh[b] | | | | |
| $k_{1a}$ | 0.0 | 0.33 | 102 ± 9 | +42 ± 32 |
| | 5.0 | 0.66 | | |
| | 7.5 | 1.11 | | |
| | 10.0 | 1.63 | | |
| $k_{2a}$ | 21.0 | 4.4 | | |
| $k_{3a}$ | 21.0 | 3.9 | | |

[a] Rate constants per one metal ion ($k_{1a}=k_1/3$, $k_{2a}=k_2/2$, $k_{3a}=k_3$). [b] $k_{1a}$ at 21.0 °C calculated from the activation parameters is $8.9\times10^{-4}$ $s^{-1}$

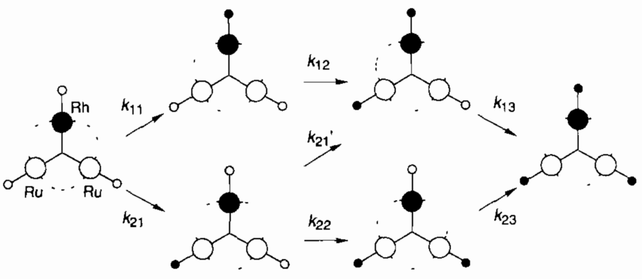

Fig. 7. Diagram of the successive substitution of $CD_3OD$ for water in $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ in $CD_3OD$.

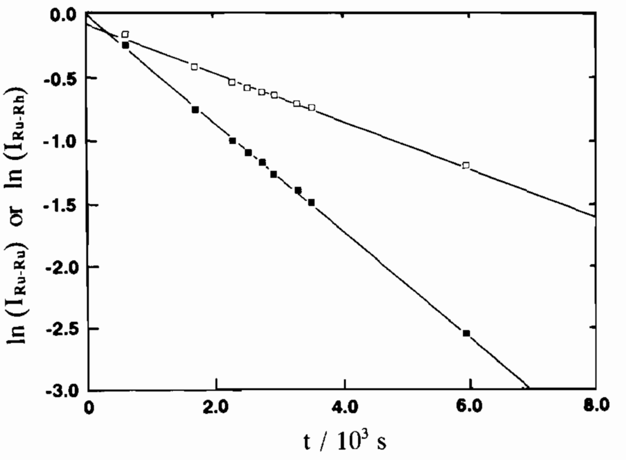

Fig. 8. First-order plots of the decrease in relative integrated intensity of the $^1H$ NMR signals of $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3](ClO_4)$ in $CD_3OD$ at 30.5 °C: (□) peak at 1.92 ppm ($I$(Ru–Ru)), (■) peak at 2.37 ppm ($I$(Ru–Rh)).

TABLE 3. Rate constants and activation parameters for the first substitution of deuterated methanol for the water in the mixed-metal complex, $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ in $CD_3OD$[a]

| Temp. (°C) | $k_{11a}$ (per Ru) | $k_{21a}$ (Rh) |
|---|---|---|
| 10.1 | $9.3\times10^{-6}$ | $1.0\times10^{-5}$ |
| 21.0 | $6.0\times10^{-5}$ | $5.1\times10^{-5}$ |
| 30.5 | $2.15\times10^{-4}$ | $1.90\times10^{-4}$ |
| 35.3 | $4.9\times10^{-4}$ | $4.07\times10^{-4}$ |
| $\Delta H^\ddagger$ (kJ $mol^{-1}$) | 109 ± 4 | 103 ± 3 |
| $\Delta S^\ddagger$ (J $K^{-1}$ $mol^{-1}$) | +44 ± 9 | +22 ± 6 |

[a] Rate constants per metal ion are given ($k_{11a}=k_{11}$, $k_{21a}=k_{21}/2$).

$t$, gave good straight lines (Fig. 8). The rate constants, $k_{11}$ and $k_{21}$, were obtained from the slopes of the plots taking the following points into consideration. The decrease of $I$(Ru–Ru) should correspond to the disappearance of the tri(aqua) and the $\{Ru(H_2O)\}_2$-$Rh(CD_3OD)$ species. Since the latter species may be neglected in the initial part of the reaction, $k_{21}$ is evaluated from the slope of the plot ln($I$(Ru–Ru)) versus $t$. The good straight line over more than two half-lives indicates that the values of $k_{22}$ and $k_{21}'$ are close to those of $k_{21}$ and $k_{11}$, respectively. The initial decrease of $I$(Ru–Rh) should be related to the two processes corresponding to $k_{11}$ and $k_{21}$. While the former process results in complete loss of the corresponding NMR peak, the latter process leaves half of the peak intensity (corresponding to the $Ru(H_2O)$–$Ru(CD_3OD)$–$Rh(CD_3OD)$ species). If the subsequent disappearance of the $Ru(H_2O)$–$Ru(CD_3OD)$–$Rh(CD_3OD)$ species was slow, then the plot would show a concaved curve. The plot is practically linear for more than two half-lives, indicating that $k_{22}$ is of a similar magnitude to $k_{21}$ and/or $k_{11}$. From the slope of the plot, at least in the initial part, the value $k_{11}+k_{21}$* can be evaluated.

The rate constants per metal ion, $k_{11a}$ ($=k_{11}$) and $k_{21a}$ ($=k_{21}/2$) are summarized in Table 3 together with corresponding activation parameters.

## Discussion

### *Effect of the trinuclear assembly*

The rate constants for the trinuclear complexes are compared with those of the solvent exchange reactions of the mononuclear complexes of Ru(III) and Rh(III) (Table 4) [7, 10, 32–35]. It is assumed here that the rate constant for the substitution of $CD_3OD$ for the water ligands in the trinuclear complexes is approximate to that of the water exchange reaction of the same complexes, since the dissociative mechanism is assigned

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*In the previous paper [29], it was erroneously stated that the slope corresponds to $k_{11}+(1/2)k_{21}$.

TABLE 4. Kinetic data on the solvent exchange and complex formation reactions of Ru(III) and Rh(III)

| Complex | System | $k$ ($s^{-1}$) (298.2 K)[a] | $\Delta H^{\ddagger}$ (kJ $mol^{-1}$) | $\Delta S^{\ddagger}$ (J $K^{-1}$ $mol^{-1}$) | Reference |
|---|---|---|---|---|---|
| (i) *Ruthenium(III)* | | | | | |
| $[Ru(H_2O)_6]^{3+}$ | $H_2O$-exchange | $3.5\times10^{-6}$ | $89.8\pm4$ | $-48.3\pm14$ | 7 |
| $[Ru(OH)(H_2O)_5]^{2+}$ | $H_2O$-exchange | $5.9\times10^{-4}$ | $95.8\pm7.9$ | $+14.9\pm24.4$ | 7 |
| $[Ru(NH_3)_5(H_2O)]^{2+}$ | $H_2O$-exchange | $2.3\times10^{-4}$ | $91.5\pm1.3$ | $-7.7\pm4.4$ | 32 |
| 'Ru$_3$' | $H_2O \rightarrow CD_3OD$ | $7.7\times10^{-4}$ | $103\pm6$ | $+41\pm12$ | this work |
| 'Ru$_2$Rh' | $H_2O \rightarrow CD_3OD$ | $9.9\times10^{-5}$ | $109\pm4$ | $+44\pm9$ | this work |
| $Ru(acac)_3$ | Hacac-exchange | $1.4\times10^{-11}$ | $115\pm8$ | $-67\pm19$ | 33 |
| (ii) *Rhodium(III)* | | | | | |
| $[Rh(H_2O)_6]^{3+}$ | $H_2O$-exchange | $2.2\times10^{-9}$ | $131\pm23$ | $+29\pm69$ | 10 |
| $[Rh(OH)(H_2O)_5]^{2+}$ | $H_2O$-exchange | $4.2\times10^{-5}$ | | | 10 |
| $[Rh(NH_3)_5(H_2O)]^{3+}$ | $H_2O$-exchange | $8.4\times10^{-6}$ | $103.3\pm1.3$ | $+3.4\pm4.6$ | 34 |
| 'Rh$_3$' | $H_2O \rightarrow CD_3OD$ | $1.3\times10^{-3}$ | $102\pm9$ | $+42\pm32$ | this work |
| 'Ru$_2$Rh' | $H_2O \rightarrow CD_3OD$ | $7.9\times10^{-5}$ | $103\pm3$ | $+22\pm6$ | this work |
| $Rh(acac)_3$ | Hacac-exchange | $4.8\times10^{-13}$ | $118\pm2$ | $-85\pm6$ | 35 |

[a] Rate constants per one metal ion are given. Those not available at 298.2 K were calculated by using reported activation parameters.

here (*vide infra*). The Rh$_3$ complex, $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$, undergoes $CD_3OD$ substitution for the water ligands with a first-order rate constant that is nearly $10^6$ times larger than that of the water exchange reaction of $[Rh(H_2O)_6]^{3+}$ [10]. The difference is less remarkable in the case of the Ru$_3$ complex, but a $2\times10^2$ acceleration is still observed as compared with the water exchange of $[Ru(H_2O)_6]^{3+}$ [7]. It is clear that the Ru and Rh ions in the trinuclear complexes are considerably more labile than those in the mononuclear complexes.

It is concluded that the labilization of the metal ions in the trinuclear complexes is due to the *trans*-labilization effect of the central oxide ion. It is generally known that the deprotonation of the coordinated water molecule considerably accelerates the liberation of the neighboring ligands ('conjugate base mechanism') [1–5]. Further deprotonation to oxide ion is expected to cause even stronger labilization. In fact, the oxo–metal bond is known to strongly labilize the ligand *trans* to it, and is considered as an extreme of the conjugate base mechanism [9, 15a]. The $\mu_3$-oxide may not be as effective as terminal oxide or hydroxide, but may still have a considerable labilizing effect. As Table 4 shows, the rate constant of the Ru$_3$ complex is very close to that of the conjugate base form of the hexa(aqua)ruthenium(III) ion, namely $[Ru(OH)(H_2O)_5]^{2+}$ [7], while the Rh$_3$ complex reacts faster by more than one order of magnitude than $[Rh(OH)(H_2O)_5]^{2+}$ [10]*.

The substitution rate constants of the two complexes appear to decrease slightly from the first step to the second and to the third steps (Table 2). The extent of the decrease is small, however, and it would be more reasonable to conclude that the substitution takes place almost independently at each site of the trinuclear complexes. For the ligand substitution reactions of some trinuclear molybdenum(IV) and tungsten(IV) complexes, it was concluded that the three metal centers behave almost independently [15b, 17, 19, 36].

The present mixed Rh–Ru complex does not show appreciable regioselectivity in its terminal ligand substitution. The substitution rate constants are almost identical between the two different reaction sites, the Ru and the Rh centers. The Ru(III) center in $[Ru(H_2O)_6]^{3+}$ is more labile by more than three orders of magnitude than the Rh(III) center of $[Rh(H_2O)_6]^{3+}$ [7, 10]. The difference becomes smaller in their conjugate bases, $[M(OH)(H_2O)]^{2+}$ (M = Ru or Rh), namely the labilizing effect of the coordinated hydroxide is more significant for the rhodium complex. In the trinuclear complexes, the central oxide ion labilizes both the Ru and the Rh ions to a different extent diminishing the original difference in reactivities of the two metal ions found for the hexaaqua complexes. It is unlikely that the absence of regioselectivity is an intrinsic consequence of mixing two metal ions. In fact, the mixed molybdenum–tungsten complex, $[MoW_2(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$, shows remarkable regioselectivity; substitution of $CD_3OD$ is at least 10 times faster at the Mo site than that at the W sites [15c].

Terminal ligand substitutions at the Ru and the Rh centers in the heterometal complex, $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$, are nearly one order of magnitude slower than those in the homonuclear complexes. The reason for the reactivity difference is not clear at the

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[*] Effect of possible deprotonation of the aqua ligand of the present trinuclear complexes on the rate constants would be small, since the deprotonation is less favorable in methanol and the substitution takes place at a different metal center from the deprotonation site. In fact, a similar trinuclear complex, $[Mo_3(\mu_3\text{-}O)_2(CH_3COO)_6(H_2O)_3]^{2+}$ showed very small $[H^+]$ dependence in its substitution of ethanol-$d_4$ for coordinated $H_2O$ (A. Nagasawa, unpublished observation).

present stage. The reactivity should be related to the electronic configuration of the trinuclear units. The electronic structures of these complexes have been discussed in terms of the molecular orbital based on the metal d$\pi$–oxygen p$\pi$ interactions [29, 30, 37]. The number of electrons involved in the molecular orbital would affect the lability of the individual metal ions. The hitherto unknown $RuRh_2$ derivative should give highly relevant information on this point.

*Mechanism of the substitution reactions*

It is known for some aqua complex ions that the conjugate base pathway ($[M(OH)(H_2O)_5]^{2+}$) proceeds through a more dissociative mechanism as compared with their parent complexes, $[M(H_2O)_6]^{3+}$, and is characterized by large $\Delta H^\ddagger$, positive $\Delta S^\ddagger$ and positive $\Delta V^\ddagger$ values [7, 10, 38, 39]. Significantly large $\Delta H^\ddagger$ and positive $\Delta S^\ddagger$ values for the reactions of the trinuclear complexes point to a dissociative mechanism, which is consistent with the assignment of the conjugate-base-type mechanism. A similar conclusion was previously made for the terminal ligand substitution reactions (substitution of $CD_3OD$ for the aqua ligands and the pyridine exchange) of $[Mo_3(\mu_3\text{-}CCH_3)(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^{2+}$ ($L = H_2O$, py) and related complexes on the basis of the activation parameters, dependence of the rate on the type of leaving ligands and in the case of the pyridine exchange the independence of the rate on py concentration [15b]. The pyridine exchange reaction of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$, which is much slower than the present $CD_3OD$ substitution reaction and indicates strong leaving ligand dependence, is reported to proceed through a dissociative mechanism [22a]. It seems that the dissociative mechanism is a common feature for the terminal ligand substitution of the oxo-centered trinuclear complexes.

## Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 03231105) on Priority Area of 'Molecular Approaches to Non-equilibrium Processes in Solutions' and a Grant-in-Aid for Scientific Research (No. 01430009) from the Ministry of Education, Science and Culture, Japan. Thanks are due to the Instrument Center, the Institute for Molecular Science, for the use of the JNM-GX-400 FT-NMR spectrometer.

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