High-Pressure Oxygen-17 NMR Study of the Dihydroxo-Bridged Rhodium(III) Hydrolytic Dimer. Mechanistic Evidence for Limiting Dissociative Water Exchange Pathways

Alexander Drljaca, Achim Zahl, and Rudi van Eldik*

Institute for Inorganic Chemistry, University of Erlangen-Nürnberg,
Egerlandstrasse 1, 91058 Erlangen, Germany

Rate constants and activation parameters for water exchange on the Rh(III) hydrolytic dimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ were determined using ^{17}O NMR spectroscopy as a function of temperature (308−323 K) and pressure (0.1−150 MPa). This represents the first variable-pressure ^{17}O NMR study conducted on a polynuclear metal aqua ion. Two pathways for water exchange with similar rates were found for H_2O coordinated at positions cis (k_{cis}) and trans (k_{trans}) to the bridging OH groups on the Rh(III) centers. The bridging OH groups were not found to exchange with the bulk solvent, indicating that they are substitution inert on the time scale of these experiments. The kinetic parameters for water exchange on the fully protonated Rh(III) dimer at $[H^+] = 1.0$ M and $\mu = 2.0$ M are as follows: $k_{trans}^{298} = 8.5 \times 10^{-7}$ s^{-1}, $\Delta H^*_{trans} = 150 \pm 2$ kJ mol^{-1}, $\Delta S^*_{trans} = +141 \pm 7$ J K^{-1} mol^{-1}, $\Delta V^*_{trans} = +8.5 \pm 0.8$ cm^3 mol^{-1} (+8.5 ± 0.6 cm^3 mol^{-1} at $[H^+] = 2.0$ M and $\mu = 3.0$ M); $k_{cis}^{298} = 5.4 \times 10^{-7}$ s^{-1}, $\Delta H^*_{cis} = 159 \pm 8$ kJ mol^{-1}, $\Delta S^*_{cis} = +168 \pm 24$ J K^{-1} mol^{-1}, $\Delta V^*_{cis} = +10.1 \pm 0.3$ cm^3 mol^{-1} (+10.9 ± 1.0 cm^3 mol^{-1} at $[H^+] = 2.0$ M and $\mu = 3.0$ M). In comparison to the water exchange for $[Rh(H_2O)_6]^{3+}$, the introduction of bridging OH groups in the dimer was found to labilize the bound waters but not to the same extent as deprotonation of the monomer. Assuming an expansion of the ground-state partial molar volume of 3−5 cm^3 mol^{-1} due to the labilizing effect of bridging OH groups in the dimer, the kinetic results suggest a limiting dissociative pathway, D, for water exchange in both the cis and trans positions. It is postulated that dissociation of a more labile trans water molecule in the Rh(III) dimer will lead to a five-coordinate intermediate which can undergo a rapid Berry pseudorotation to account for the similarity in rate and activation parameters for exchange of both cis and trans water molecules.

Introduction

Variable-pressure ^{17}O NMR techniques have been extremely useful in obtaining information on the rates and mechanisms of water exchange reactions for a range of metal aqua ions, in particular those where hydrolysis is kinetically important. The following series of trivalent hexaaqua ions and their conjugate bases have been studied: $[Ga(H_2O)_6]^{3+}$,[1] $[Fe(H_2O)_6]^{3+}$,[2,3] $[Cr(H_2O)_6]^{3+}$,[4] $[Ru(H_2O)_6]^{3+}$,[5] $[Rh(H_2O)_6]^{3+}$,[6] and more recently $[Ir(H_2O)_6]^{3+}$,[7] where the rates for water exchange and activation volumes for the corresponding monodeprotonated aqua ions were found to increase by 100−20000-fold and 6−12 cm^3/mol, respectively, over those of the fully protonated aqua ions. These results suggest a common trend where the introduction of a hydroxide group leads to a labilization of the primary coordination sphere of the metal ion and a change in mechanism creating a more dissociative transition state for water exchange.

Water exchange studies on polynuclear metal aqua ions are limited. Richens et al.[8] used ^{17}O NMR spectroscopy to investigate water exchange on a Mo(IV) trimer, $[Mo_3O_4(H_2O)_9]^{4+}$, where the six H_2O ligands trans to the μ_2-O were found to exchange about 10^5 times faster than those trans to the μ_3-O. However, since only the conjugate base pathway was observed, it was not possible to determine the effect of deprotonation. A further study conducted on $[Mo_3S_4(OH_2)_9]^{4+}$ found that H_2O ligands trans to μ-S undergo water exchange 10^5 times faster than those which are trans to μ_3-S.[9]

Recently, variable temperature water exchange kinetics were measured on the substitutionally inert hydrolytic Cr(III) and Rh(III) dimers $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ [10] and $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ [11] using conventional ^{18}O-labeling techniques. In each case, two pathways for exchange were observed due to waters positioned cis (k_{slow}) and trans (k_{fast}) to the bridging hydroxides. The trans-labilizing effect of bridging OH groups on the fully protonated Cr(III) and Rh(III) dimers was found to be marginally greater than the effect of cis labilization such that k_{fast} was 3−6-fold faster than k_{slow}. Furthermore, when the water exchange rates for the fully protonated $[Cr(H_2O)_6^{3+}]$−Cr(III) dimer[4,10] and $[Rh(H_2O)_6^{3+}]$−Rh(III) dimer[6,11] pairs are compared, it can be concluded that the introduction of bridging

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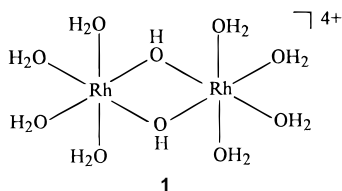(9) Richens, D. T.; Pittet, P.-A.; Merbach, A. E.; Humanes, M.; Lamprecht, G. J.; Ooi, B.-L.; Sykes, A. G. *J. Chem. Soc.*, *Dalton Trans.* **1993**, 2305.
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OH groups into the dimer cations does have a labilizing effect resulting in faster water substitution rates compared those of with the corresponding hexaaqua ions. For the Cr(III) and Rh-(III) cases, rate increases of 20−200- and 200−600-fold, respectively, were observed.

It has been well established that pressure effects on rate can provide useful criteria in the determination of mechanisms for solvent exchange reactions.[12,13] Reported here is an extension of the ^{18}O-labeling study (acid and temperature dependent)[11] on the Rh(III) hydrolytic dimer (**1**)[14] to high pressures (up to

$$
\left[\begin{array}{c}
H_2O \quad\quad H \quad\quad OH_2 \\
\ \ \ \ \ \ \ \ \ \ O \\
H_2O \diagdown \ \ | \ \ \diagup OH_2 \\
\ \ \ \ \ \ Rh \ \ \ \ \ \ Rh \\
H_2O \diagup \ \ | \ \ \diagdown OH_2 \\
\ \ \ \ \ \ \ \ \ O \\
H_2O \quad\quad H \quad\quad OH_2
\end{array}\right]^{4+}
$$

1

150 MPa) using a specially designed ^{17}O NMR high-pressure probe[15] to clarify the mechanism of water exchange. The advantage of using ^{17}O NMR spectroscopy to monitor the exchange kinetics over ^{18}O mass spectrometry (used previously on the Cr(III) and Rh(III) dimers)[10,11] is that each exchange process may be individually studied (i.e., separate NMR signals for the cis and trans water molecules), whereas with the ^{18}O technique a composite exponential function is fitted to a single set of isotope fraction vs time data to extract the individual rate constants. This work represents the first ^{17}O NMR variable-pressure study conducted on a hydrolytic polynuclear metal aqua ion.

Experimental Section

Materials. Analytical grade reagents were used throughout, and water was deionized and distilled prior to use. Crystals of the monomer $[Rh(H_2O)_6](ClO_4)_3$ and dimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4](dmtos)_4\cdot 8H_2O$ (dmtos = mesitylene-2-sulfonate) were prepared using previously described methods.[14,16] The ^{17}O enrichment and subsequent crystallization procedure of the Rh(III) monomer and dimer were carried out by literature methods using 10.2% $H_2^{17}O$ (Enritech).[6,11] In the case of the dimer, the ^{17}O enrichment of the complexed water was 5.1%, assuming complete exchange. Chromatographic and spectrophotometric analyses[14] showed that the enriched monomer and dimer crystals and the dimer solutions during the NMR experiments were pure and had not undergone polymerization or cleavage. The Rh content of the crystals was determined spectrophotometrically[17] and corresponded to that expected for the above formulas, indicating in the case of the dimer that mesitylene-2-sulfonic acid had not coprecipitated with the product. The solutions for NMR measurements were prepared by weighing such that (a) [dimer] = 0.1 M, [H$^+$] = 1.0 M (HClO$_4$), and ionic strength μ = 2.0 M, (b) [dimer] = 0.1 M, [H$^+$] = 2.0 M (HClO$_4$), and μ = 3.0 M, and (c) [Rh(H$_2$O)$_6^{3+}$] = 0.1 M, pH = 0 or 2.5 (HClO$_4$), and μ = 2.0 M in the case of the monomer. The ionic strength was adjusted with NaClO$_4$ where required.

pK_a Measurements. The values of pK_{a1} for the Rh(III) dimer (**1**) at 298.1 and 323.1 K and at μ = 2.0 M were 2.26 ± 0.03 and 1.92 ± 0.04, respectively, as determined from changes in the UV spectrum with [H$^+$] according to a literature method.[11] Absorbance changes were measured at the peak maximum of 242 nm on a Shimadzu UV−vis

scanning spectrophotometer (UV-2101PC) over nine acid standards, 0.0010 < [H$^+$] < 0.90 M, with [Rh]$_{total}$ = 9.40 × 10^{-4} M.

NMR Measurements. The ^{17}O NMR spectra were recorded at a resonance frequency of 54.24 MHz on a Bruker AVANCE DRX400WB spectrometer equipped with a superconducting BC-94/89 magnet system. At atmospheric pressure, the kinetic measurements were performed at three different temperatures (308.1, 323.1, 338.1 K) on a commercial 5 mm Bruker broad-band probe thermostated with a Bruker B-VT 3000 variable-temperature unit. The temperature dependence of the transverse relaxation rates was obtained over 10 temperatures (290−350 K). The spectra with spectral widths of 22−43.5 kHz and 2−8K data points were obtained using a pulse width of 16 μs in the quadrature detection mode.

A homemade high-pressure probe described in the literature[15] was used for the variable-pressure experiments which were conducted at 323.1 ± 0.5 K and at ambient pressure and 30, 50, 60, 90, 100, 120, and 150 MPa. Some modifications of the RF circuit were necessary to use the sample coil in a double-tuned manner. The ^{17}O NMR experiments were performed unlocked, but the sample was shimed on the corresponding proton FID, so that significant line broadening due to field inhomogeneity caused by the high-pressure probe was excluded. A standard 5 mm NMR tube cut to a length of 45 mm was used for the sample solutions. The pressure was transmitted by a movable macor piston, and the temperature was controlled with a Pt-100 resistor as described elsewhere.[15] The signal-to-noise ratio was ca. a factor of 4 less for the high-pressure probe than for the standard Bruker probe.

Each kinetic run consisted of 25−35 spectra and was followed for up to 3 half-lives. A single spectrum consisted of 1000−10 000 scans, and an exponential filter (50 Hz) was applied before Fourier transformation to improve the signal-to-noise ratio. The experimental time taken for one spectrum was short compared to the kinetic half-lives. Line widths and integrations were determined from Lorentzian line shape analyses of the two overlapping bound-H$_2$O signals. The transverse relaxation times were obtained by line width measurements after correction for the applied line broadening according to $1/T_2 = \pi\Delta\nu_{1/2}$.

The measured dimer spectrum was in agreement with that previously reported[11,18] with overlapping resonances due to coordinated waters observed at −126.7 and −135.8 ppm and a bridging hydroxo group observed at −324.4 ppm. Spectra of [Rh(H$_2$O)$_6$]$^{3+}$ were recorded at pH = 0 and 2.5 to check the effect of deprotonation, and the resonance due to the bound water was found at −144.1 ppm. All signals are reported relative to bulk water and referenced to the ClO$_4^-$ anion at 288 ppm.

Results and Discussion

The kinetics of water exchange on [(H$_2$O)$_4$Rh(μ-OH)$_2$Rh-(H$_2$O)$_4$]$^{4+}$ were followed by measuring the depletion of the complex and enrichment of the bulk solvent in ^{17}O label with time using ^{17}O NMR spectroscopy. The exchange kinetics were studied at 323.1 K and at two different acidities, [H$^+$] = 1.0 M (μ = 2.0 M) and [H$^+$] = 2.0 M (μ = 3.0 M), to check the influence of the presence of small amounts of the monodeprotonated form of the dimer. At 323 K and μ = 2.0 M, the measured pK_{a1} for the Rh(III) dimer is 1.9 (see Experimental Section), which suggests that under these conditions only ca. 1% of the monodeprotonated form of the dimer is present at [H$^+$] = 1.0 M. Assuming the rate accelerations attributed to this deprotonation are 6- and 13-fold at 323 K, as determined by a previous study,[11] then the fast and slow exchanges contribute 6 and 11%, respectively, to the measured rate at [H$^+$] = 1.0 M. Since at 323 K the values of pK_{a1} for the Rh(III) dimer are 1.2[11] and 1.9 at μ = 1.0 and 2.0 M, respectively, the value of pK_{a1} at μ = 3.0 M is expected to increase. It follows that, at this ionic strength and [H$^+$] = 2.0 M, the contributions

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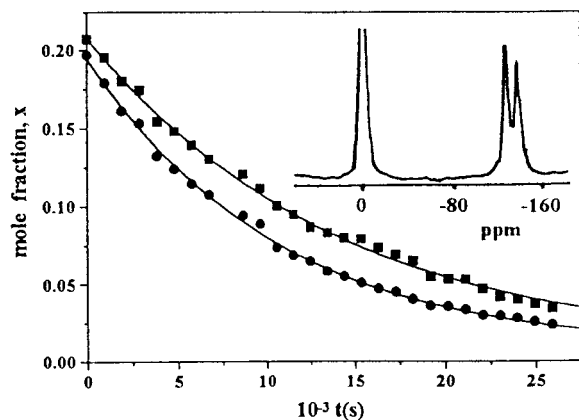
Figure 1. Mole fraction x of bound trans (●) and cis (■) $H_2^{17}O$, as a function of time, monitored by ^{17}O NMR spectroscopy at $T = 323.1$ K for an aqueous solution of $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ (5.1% ^{17}O) in 1.0 M $HClO_4$ ([dimer] = 0.1 M; μ = 2.0 M; P = 0.1 MPa). The upper right inset shows the spectrum 0.5 h after dissolution obtained using a commercial 5 mm Bruker broadband probe.

to the measured water exchange rate will be significantly less than 6 and 11%, respectively. Thus, under the selected conditions, the presence of the monodeprotonated form of the dimer is not expected to significantly affect the measurements conducted on the fully protonated dimer.

This study provides an opportunity to study an aqua ion where the hydroxide groups have been fixed and are not free to rotate or scramble as is the case for terminal hydroxides on deprotonated monomeric aqua ions. The inset to Figure 1 shows a typical ^{17}O NMR spectrum of the Rh(III) dimer recorded at ambient pressure and 323.1 K. Two low-frequency coordinated water signals at -126.7 and -135.8 ppm, assigned by analogy with the ^{17}O NMR spectra of *cis-* and *trans-*$[RhCl_2(OH_2)_4)]^+$ complexes[18] with coordinated waters positioned trans and cis to the bridging hydroxide groups, respectively, were found to diminish with time, indicating exchange of the ^{17}O label from the Rh(III) dimer complex. There was no change in intensity of the signal due to the bridging OH groups at -324.4 ppm under the conditions of the study, indicating that these groups are substitutionally inert on the time scale of these experiments. These observations are consistent with a preliminary study on the Rh(III) dimer where the exchange rate was determined via ^{17}O NMR spectroscopy at $[H^+] = 0.17$ M and $T = 323.2$ K.[11] The intensity ratio among the various ^{17}O signals was 4:4:2 (cis H_2O:trans H_2O:bridging OH), indicating that all oxygen positions on the dimer had been labeled and that the solution structure was in agreement with that reported previously.[18]

Transverse Relaxation Rates. The temperature dependence of the ^{17}O transverse relaxation rate was obtained from line-width measurements on a 0.1 M $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ solution where $[HClO_4] = 1.0$ M and $\mu = 2.0$ M (NaClO$_4$). The relaxation rate ($1/T_{2Q}$) was found to decrease with increasing temperature, which is consistent with a quadrupolar relaxation mechanism. An Arrhenius temperature dependence according to eq 1 was assumed for the quadrupolar relaxation rate.

$$1/T_{2Q} = (1/T^b_{2Q})^{298} \exp\{(E_Q^b/R)[(1/T) - (1/298.15)]\} \quad (1)$$

Figure 2 shows the variation of $1/T_{2Q}$ with temperature for the resonances at -126.7 and -135.8 ppm and a least-squares fit of the data to eq 1 which gives values of $(1/T_{2Q})^{298}$ and E_Q of 1498 ± 22 s^{-1} and 23.6 ± 0.8 kJ mol^{-1}, respectively, for the resonance at -126.7 ppm and 1892 ± 36 s^{-1} and $22.3 \pm$
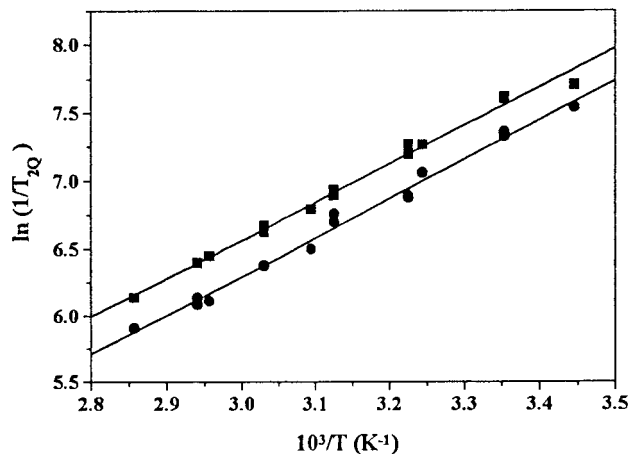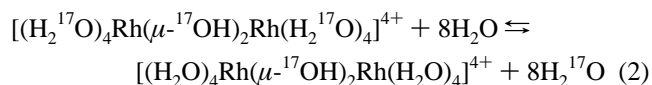

Figure 2. Temperature dependence of the transverse relaxation rate, $1/T_{2Q}$, of the bound-water ^{17}O NMR signals at postions trans (●) and cis (■) to the bridging hydroxide groups at [dimer] = 0.1 M, $[HClO_4]$ = 1.0 M, and μ = 2.0 M.

0.9 kJ mol^{-1}, respectively, for the resonance at -135.8 ppm. These values fall into the same range as those observed for other octahedral diamagnetic aqua ions including $[Al(H_2O)_6]^{3+}$,[19] $[Ga(H_2O)_6]^{3+}$,[1] $[Ru(H_2O)_6]^{2+}$,[5] and $[Rh(H_2O)_6]^{3+}$,[6] where $380 < (1/T_{2Q})^{298} < 2300$ s^{-1} and $16.0 < E_Q < 23.5$ kJ mol^{-1}. However, these values are strongly ionic strength (viscosity) dependent and the previous studies were conducted at different ionic strengths. The difference in the observed relaxation rates arises from the different quadrupolar coupling constants for the two coordinated water sites.[20]

Variable-Temperature Kinetics. The rate law for the isotopic exchange reaction[21] on the dimer (eq 2) is given by eq 3, where k represents the rate constant for the exchange of a

$$[(H_2^{17}O)_4Rh(\mu\text{-}^{17}OH)_2Rh(H_2^{17}O)_4]^{4+} + 8H_2O \rightleftharpoons$$
$$[(H_2O)_4Rh(\mu\text{-}^{17}OH)_2Rh(H_2O)_4]^{4+} + 8H_2^{17}O \quad (2)$$

$$-dx/dt = k(x - x_\infty)/(1 - x_\infty) \quad (3)$$

particular water molecule[22,23] at positions either cis or trans to the bridging OH groups and x and x_∞ are the mole fractions of cis or trans $H_2^{17}O$ coordinated to the Rh centers at the time of sampling and at exchange equilibrium, respectively. The mole fraction x of coordinated $H_2^{17}O$, obtained by integration of the ^{17}O signals as a function of time, was fitted to eq 4, which was

$$x = x_\infty + (x_0 - x_\infty) \exp[-kt/(1 - x_\infty)] \quad (4)$$

derived by integration of eq 3 setting $x = x_0$ at $t = 0$ and $x_\infty = 4 \times$ [dimer]/[bulk $H_2^{17}O$] = $4 \times 0.1/55.5$. The adjustable parameters were k and x_0.

The value of x_0 is related to the number of water molecules of crystallization n through eq 5,

$$n = (8/x_0) - ([\text{bulk } H_2^{17}O]/[\text{dimer}]c) - 8 \quad (5)$$

where c is the $H_2^{17}O$ content of the dimer.

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Table 1. Temperature and Pressure Dependence of the Rate Constants for Water Exchange on $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(H_2O)_4]^{4+}$ at Positions Cis and Trans to the Bridging Hydroxo Groups

temp (K)	pressure (MPa)	$10^5 k_{trans}$ (s^{-1})	$10^5 k_{cis}$ (s^{-1})
	Experimental Conditions: [Dimer] = 0.1 M, [HClO$_4$] = 1.0 M, μ = 2.0 M		
308.1	0.1	0.633 ± 0.015	0.480 ± 0.010
323.1	0.1	9.37 ± 0.11	7.12 ± 0.10
	30	8.01 ± 0.45	6.71 ± 0.46
	60	7.13 ± 0.48	5.66 ± 0.37
	90	6.49 ± 0.31	5.24 ± 0.23
	120	6.23 ± 0.29	4.51 ± 0.14
	150	5.72 ± 0.11	4.03 ± 0.11
338.1	0.1	124 ± 2.9	130 ± 3.5
	Experimental Conditions: [Dimer] = 0.1 M, [HClO$_4$] = 2.0 M, μ = 3.0 M		
323.1	0.1	8.07 ± 0.54	4.07 ± 0.23
	50	7.10 ± 0.57	3.35 ± 0.24
	100	6.12 ± 0.41	2.89 ± 0.18
	150	5.00 ± 0.29	2.17 ± 0.10

Table 2. Activation Parameters and Rate Constants at 298 K for the Water Exchange Processes at the Cis and Trans H$_2$O Positions on the Fully Protonated Rh(III) Dimer

parameter	cis H$_2$O	trans H$_2$O
k^a (s^{-1})	5.39×10^{-7}	8.46×10^{-7}
$\Delta H^{*\,a}$ (kJ mol^{-1})	159 ± 8	150 ± 2
$\Delta S^{*\,a}$ (J K^{-1} mol^{-1})	$+168 \pm 24$	$+141 \pm 7$
$\Delta V^{*\,b}$ (cm^3 mol^{-1})	$+10.5 \pm 0.6$	$+8.5 \pm 0.8$
$\Delta V^{*\,c}$ (cm^3 mol^{-1})	$+10.9 \pm 1.0$	$+8.5 \pm 0.6$
k^d (s^{-1})	4.86×10^{-7}	12.6×10^{-7}
$\Delta H^{*\,d}$ (kJ mol^{-1})	64 ± 9	119 ± 4
$\Delta S^{*\,d}$ (J K^{-1} mol^{-1})	-150 ± 30	$+41 \pm 12$

[a] Present study at $\mu = 2.0$ M and [HClO$_4$] = 1.0 M. [b] Present study at $\mu = 2.0$ M, [HClO$_4$] = 1.0 M, and $T = 323.1$ K. [c] Present study at $\mu = 3.0$ M, [HClO$_4$] = 2.0 M, and $T = 323.1$ K. [d] Previous ^{18}O-labeling study at $\mu = 1.0$ M (NaClO$_4$).[11]

The average n value found is 7.7 ± 0.5, which is consistent with the literature value of eight waters of crystallization.[14]

A typical plot of the experimental ^{17}O NMR data and the fitted curve (from eq 4) are shown in Figure 1, and the results of the analysis at three temperatures, two acid concentrations, and over eight pressures are summarized in Table 1. Successful fits were obtained in each case as indicated by small and random distributions of residuals with time. The temperature dependence of the rate constants (Table 1) obtained over three temperatures (308.1, 323.1, 338.1 K) was least-squares-fitted to eq 6, leading to the rate constants and activation parameters listed in Table 2.

$$k = (k_B T/h) \exp[(\Delta S^*/R - (\Delta H^*/RT)] \qquad (6)$$

Rate constants for water exchange of the trans (k_{trans}) and cis (k_{cis}) waters on the Rh(III) dimer at $T = 298$ K (Table 2) and [H$^+$] = 1.0 M were 8.46×10^{-7} and 5.39×10^{-7} s^{-1}, respectively. These results compare favorably with those obtained in the previous ^{18}O study at $T = 298$ K (Table 2) for the fully protonated dimer where $k_{cis} = 4.86 \times 10^{-7}$ s^{-1} and $k_{trans} = 12.6 \times 10^{-7}$ s^{-1}.[11] Note that in the ^{18}O study the measurements were made at $\mu = 1.0$ M, whereas the present study was conducted at $\mu = 2.0$ M. Furthermore, the two rate constants had to be extrapolated from a biexponential decay function in the former study.

The values of k_{cis} and k_{trans} are rather similar, suggesting as a first approximation that the bridging OH groups in the dimer equally labilize the coordinated H$_2$O at both positions (i.e., the
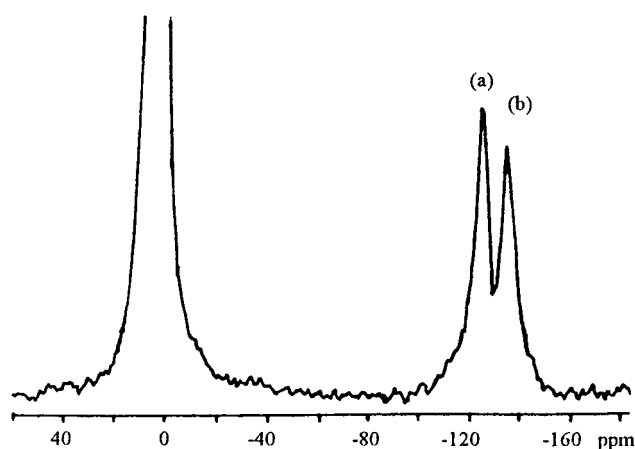
Figure 3. Typical ^{17}O NMR spectrum of the Rh(III) dimer recorded at high pressure (150 MPa) with a homemade high-pressure probe[15] at [dimer] = 0.1 M, [HClO$_4$] = 1.0 M, and $T = 323.1$ K. Shown are the signals due to bulk water and bound water at positions trans (a) and cis (b) to the bridging hydroxo groups.

effect of trans labilization seems to be very small) although, intuitively, we would expect the waters in the trans positions to be labilized significantly more than those in the cis positions as has been shown in numerous previous studies.[1,2,4–7] This similarity in exchange rates is supported by the low-temperature X-ray crystal structure of the Rh(III) dimer where the Rh−O distances trans to the bridging OH group [2.042(2) and 2.038-(2) Å] are very similar to those in the cis positions [2.020(2) and 2.026(2) Å].[11] In direct comparison to the H$_2$O exchange rates on [Rh(H$_2$O)$_6$]$^{3+}$, it can be argued that the introduction of bridging OH groups on the fully protonated Rh(III) dimer labilizes the coordinated waters, but not to the same extent as deprotonation of the monomer does, since at 298 K the values of k_{trans} and k_{cis} (8.5×10^{-7} and 5.4×10^{-7} s^{-1}) fall between the water exchange rates for [Rh(H$_2$O)$_6$]$^{3+}$ (2.2×10^{-9} s^{-1}) and [Rh(H$_2$O)$_5$OH]$^{2+}$ (4.2×10^{-5} s^{-1}).[6] In the present study, the ^{17}O NMR spectra of enriched [Rh(H$_2^{17}$O)$_6$]$^{3+}$ (pK_a = 3.4) were recorded at pH = 0 and 2.5 in an attempt to establish a separate site of deprotonation; however, at each pH, only one signal due to bound water (at the same position) was observed. A similar effect was observed in the previous investigation on the Rh(III) dimer[11] where a pH-dependent NMR study failed to provide evidence for the site of deprotonation. This is understandable since it has been shown that proton exchange on [Rh(H$_2$O)$_6$]$^{3+}$ is $\approx 10^{13}$ times faster than water exchange.[6,24]

Variable-Pressure Kinetics. The quality of the ^{17}O NMR spectra obtained at high pressures using the specially designed high-pressure probe[15] is demonstrated by a typical spectrum at 150 MPa shown in Figure 3. Water exchange rate constants for waters in the cis and trans positions on the Rh(III) dimer obtained over four and six pressures at [H$^+$] = 2.0 and 1.0 M, respectively, and 323.1 K are listed in Table 1 and were found to decrease with increasing pressure. Values of k_{cis} and k_{trans} were then fitted to eq 7 with the activation volume, ΔV^*, and

$$\ln k_i = \ln k_0 - \Delta V_i^* P/RT \qquad (i = \text{cis, trans H}_2\text{O}) \quad (7)$$

the rate constant at zero pressure, k_0, as adjustable parameters. The natural logarithm of the exchange rate constants as a function of pressure are shown in Figure 4 together with weighted least-squares fits of eq 7. The obtained activation

(24) Banyai, I.; Glaser, J.; Read, M. C.; Sandström, M. *Inorg. Chem.* **1995**, *34*, 2423.
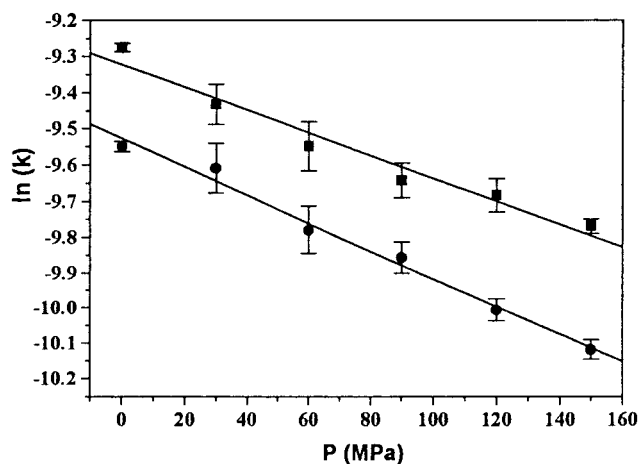
Figure 4. Rate constants for the exchange of trans (■) and cis (●) water molecules on the Rh(III) dimer as a function of pressure at $T = 323.1$ K, where [dimer] = 0.1 M, [HClO$_4$] = 1.0 M, and $\mu = 2.0$ M.

volumes are given in Table 2. The similarities in rate constants (Table 1) and activation volumes (Table 2) for the variable-pressure water exchange reactions conducted at two different acid concentrations, [H$^+$] = 1.0 and 2.0 M, suggest a negligible contribution from the monodeprotonated dimer to the observed exchange rates. The data for k_{cis} suggest that solvent exchange in the cis position of the dimer is more sensitive to the acid concentration than exchange in the trans position. This is in full agreement with the expected labilization effect of deprotonation on the Rh(III) dimer, viz. the cis position being affected most.

Mechanistic Interpretation. The positive volumes of activation for the exchange of coordinated water molecules trans and cis to bridging OH groups on the Rh(III) dimer of +8.5 and +11 cm^3 mol^{-1}, respectively (Table 2), approach those for a limiting dissociative pathway and are entirely consistent with the large positive entropies of activation (+141 and +168 J K^{-1} mol^{-1}, respectively). This contrasts with findings of the previous ^{18}O-labeling study on the dimer, where the values for ΔS^* of −150 and +41 J K^{-1} mol^{-1} for the cis and trans bound waters, respectively, could not be conclusively used to assign a mechanism for water exchange.[11] The differences in rate constants and inconsistencies in activation parameters between the two studies (Table 2) on the Rh(III) dimer are most likely related to differences in data acquisition techniques for monitoring the release of either the ^{17}O or the ^{18}O label into the bulk solvent. While with the ^{18}O method a single set of data for the fraction of isotope released from the complex over time is obtained and accordingly fitted to a composite (two exponential) rate function, in the present case we were able to observe each water exchange process individually.

The activation volumes for the Rh(III) dimer (Table 2) are larger than the highest positive value obtained so far for a monodeprotonated hexaaqua ion of +7.0 cm^3 mol^{-1} for [Fe(H$_2$O)$_5$OH]$^{2+}$, which was assigned to an I$_d$ mechanism.[2] For the previous trivalent metal hexaaqua ions studied [Fe(III), Cr(III), Ru(III), Rh(III), Ir(III)],[1,2,4−7] the introduction of hydroxide groups via deprotonation has led to significantly more positive activation volumes over the fully protonated ions. This can be explained by the strong electron-donating ability of OH$^-$ which strengthens its bond to the metal center, thus weakening and labilizing the remaining metal−H$_2$O bonds, and favors a more dissociative activation process. In the case of water exchange on the Rh(III) dimer, the large positive activation volumes result from the two bridging OH groups, which favor a dissociative

mechanism. Furthermore, the water groups in the cis and trans positions to these bridging hydroxides were found to be apparently equally labilized, which is consistent with the similar Rh−O bond lengths for the cis and trans water molecules.[11]

It is clear from the water exchange rate constants that the OH group in [Rh(H$_2$O)$_5$OH]$^{2+}$ ($k_{ex} = 4 \times 10^{-5}$ s^{-1})[6] has a greater labilizing effect than those in [(H$_2$O)$_4$Rh(μ-OH)$_2$Rh-(H$_2$O)$_4$]$^{4+}$ ($k_{ex} = 5 \times 10^{-7}$ and 8×10^{-7} s^{-1}). However, for [Rh(H$_2$O)$_5$OH]$^{2+}$ an activation volume of +1.5 cm^3 mol^{-1} was obtained[6] and accordingly assigned an I mechanism, whereas for the Rh(III) dimer values of +8.5 and +11 cm^3 mol^{-1} for waters exchanging in the trans and cis positions, respectively, were obtained. These differences in activation volumes may be explained by an expansion of the ground-state partial molar volume which could occur when these aqua ions are labilized by the introduction of OH groups. Such ground-state expansion of the trans metal−water bond is expected to be significantly larger for the monomeric Rh(III) species than for the dihydroxy-bridged dimer, since in the latter case each hydroxo ligand affects two Rh(III) centers. However, at present no structural data are available that allow a direct comparison of bond lengths in complexes of the type [M(H$_2$O)$_6$]$^{3+}$ and [M(H$_2$O)$_5$OH]$^{2+}$. Semiempirical calculations with SAM1 using AMPAC Version 5.0 (a computer program allowing simulation of bond length data) on [Fe(H$_2$O)$_6$]$^{3+}$ and [Fe(H$_2$O)$_5$OH]$^{2+}$ clearly showed a significant decrease of ca. 0.25 Å in the Fe−O bond length on deprotonation of a coordinated water molecule, accompanied by a ca. 0.15 Å lengthening in the Fe−O distance trans to the Fe−OH bond (see Note Added in Proof). Such a bond expansion can easily lead to a partial molar volume increase of ca. 10 cm^3 mol^{-1} in the ground state. If we now consider that the activation volume for limiting dissociative water exchange is +13.5 cm^3 mol^{-1}, as has been semiempirically estimated by Swaddle,[25] and ground-state expansions of ca. 10 and ca. 5 cm^3 mol^{-1} occur on the more labile Rh(H$_2$O)$_5$OH^{2+} and dihydroxy-bridged Rh(III) dimer, respectively, then the activation volumes required to reach the dissociative transition state will be ca. 3 cm^3 mol^{-1} in the former case and ca. 8 cm^3 mol^{-1} in the latter case. These values are close to those found experimentally and therefore suggest that water exchange induced by hydroxo groups follows a limiting dissociative pathway in both cases.

The interpretation presented above carries implications for the mechanistic interpretation of the small positive volumes of activation reported for water exchange on pentaaqua hydroxo ions of Cr(III), Ru(III), Rh(III), and Ir(III), for which an I mechanism was postulated.[7] Since the ground-state partial molar volume of such hydroxo species can be considerably larger due to the trans-labilizing influence of the hydroxo ligand, the actual activation volume required to reach a limiting D transition state can be much smaller than the predicted value of +13.5 cm^3 mol^{-1}.[25] It follows that these small positive activation volumes could be typical for a limiting D mechanism under the influence of strong ground-state labilization.
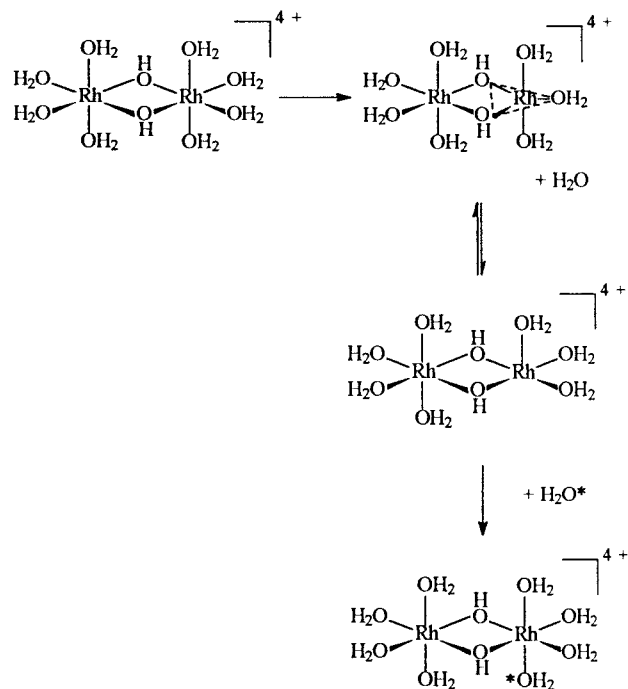
An alternative interpretation which accounts for the observed data in terms of a limiting D mechanism exists where the volume of activation may be explained in terms of an "early" or "late" transition state along the reaction coordinate of the volume profile. In the case of strong trans labilization due to coordinated hydroxide groups, such as for Rh(H$_2$O)$_5$OH^{2+}, the lower activation barrier will induce an "early" (reactant-like) transition state which will be characterized by a small positive volume of activation. For the case where trans labilization is less

(25) Swaddle, T. W. *Inorg. Chem.* **1983**, *22*, 2263.

important, such as for the dihydroxo-bridged Rh(III) dimer, the activation barrier for solvent exchange will be higher and result in a "later" (product-like) transition state which will be characterized by a more positive volume of activation. Therefore the extent of trans labilization will tune the "early" or "late" nature of the transition state and consequently the absolute magnitude of the volume of activation. However, more structural information (from either crystallographic X-ray measurements or theoretical calculations; see Note Added in Proof) is required, especially on the series of pentaaqua hydroxo ions of Fe(III), Cr(III), Rh(III), Ru(III), and Ir(III), to enable a more quantitative interpretation of the activation volume data.

The proposed limiting D mechanism for water exchange on the Rh(III) dimer is consistent with the similarity in exchange rates observed for waters positioned cis and trans to the plane of the bridging hydroxo groups. A dissociation of the trans water molecule (which is expected to be more labile than the cis water molecule) will lead to a 5-coordinate intermediate of trigonal bipyramidal geometry which can, for instance, undergo a rapid Berry pseudorotation[26] to form a square pyramidal configuration, thus allowing an entering solvent molecule to bind in the cis position. The Berry pseudorotation mechanism for the Rh(III) dimer is outlined in Scheme 1. Alternatively, the bridging hydroxo groups can occupy axial and equatorial positions, respectively, resulting in the formation of a trigonal bipyramidal geometry that allows the entering water molecule to occupy either the cis or the trans position. Due to these possible rapid intramolecular rearrangements, the cis and trans water molecules become equivalent in terms of the solvent exchange process on the time scale of the latter process. It is noteworthy that this will only be the case for a limiting D mechanism where the formation of a five-coordinate intermediate is possible, which is entirely consistent with the obtained water exchange rates and activation parameters.

We conclude that the first study which investigates the effect of pressure on water exchange reactions on a polynuclear aqua ion, the dihydroxo-bridged Rh(III) dimer, has revealed evidence which supports the operation of a limiting dissociative mechanism. In addition, it was found rather surprisingly that water molecules bound both cis and trans to the hydroxo bridge undergo exchange with the bulk solvent at approximately the same rate. This is consistent with a rapid rearrangement of the 5-coordinate intermediate proceeding significantly faster than

(26) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH:Weinheim, Germany, 1991.

Scheme 1. Berry Pseudorotation Mechanism for the μ-Hydroxo-Bridged Rh(III) Dimer

solvent exchange, but slow enough to allow the cis and trans water molecules to be distinguished on the NMR time scale.

Note Added in Proof

In a recent theoretical study of the hydrolysis of ferric ion in water using density functional analysis (Martin, R. L.; Hay, P. J.; Pratt, L. R. *J. Phys. Chem. A* **1998**, *102*, 3565), the following bond distances (Å) were calculated:

$Fe(H_2O)_6^{3+}$:	$Fe-OH_2 = 2.060$
$Fe(H_2O)_5OH^{2+}$:	$Fe-OH_2 = 2.103-2.150$
	$Fe-OH = 1.760$

These results support some of the arguments used in the present manuscript.