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Article

Water Exchange from the Oxo-Centered Rhodium(III) Trimer $[Rh_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^+$: A High-Pressure ^{17}O NMR Study

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Water exchange from the oxo-centered rhodium(III) trimer, $[Rh_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^+$, was investigated using variable-temperature (272.8–281.6 K) and variable-pressure (0.1–200 MPa) ^{17}O NMR spectroscopy. The exchange reaction was also monitored at three different acidities (pH = 1.8, 2.9, and 5.7) in which the molecule is in the fully protonated form ($pK_a = 8.3$ (±0.2), $I = 0.1$ M, $T = 298$ K). The temperature dependence of the pseudo-first-order rate coefficient for water exchange yields the following kinetic parameters: $k_{ex}{}^{298} = 5 \times 10^{-3}\ s^{-1}$, $\Delta H^{\ddagger} = 99$ (±3) kJ mol^{-1}, and $\Delta S^{\ddagger} = 43$ (±10) J $K^{-1}mol^{-1}$. The enhanced reactivity of the terminal waters, some 6 orders of magnitude faster than water exchange from $Rh(H_2O)_6{}^{3+}$, is likely due to trans-labilization from the central oxide ion. Also, another contributing factor is the low average charge on the metal ions (+0.33/Rh). Variation of reaction rate with pressure results in a $\Delta V^{\ddagger} = +5.3$ (±0.4) $cm^3\ mol^{-1}$, indicative of an interchange-dissociative (I_d) pathway. These results are consistent with those published by Sasaki et al. who proposed that water substitution from rhodium(III) and ruthenium(III) oxo-centered trimers follows a dissociative mechanism based on highly positive activation parameters (Sasaki, Y.; Nagasawa, A.; Tokiwa-Yamanoto, A.; Ito, T. *Inorg. Chim. Acta* **1993**, *212*, 175–182).

Introduction

Activation volumes have been used to assign mechanisms for water exchange to bulk solution for a large number of mononuclear main group and transition-metal cations. Most notably are the variable-pressure ^{17}O NMR studies by Merbach et al., which revealed the progressive changeover in the water substitution mechanism for divalent 3d octahedral metal ions.[2,3] As the number of d electrons increases and ionic radii decreases across the period, the water-substitution mechanism switches from interchange-associative (I_a) to interactive-dissociative (I_d), which was inferred from a change in sign of the activation volumes. Rotzinger[4,5] confirmed this result by calculating activation volumes at the Hartree−Fock and CAS−SCF levels. The determination of activation volumes has also proved useful in the mechanistic assignment of water exchange from $Rh(H_2O)_6{}^{3+}$.[6] One would predict a dissociative activation mode for a low spin $t_{2g}{}^6$ metal ion because the approach of a ligand would be electrostatically disfavored. However, the activation volume determined from high-pressure ^{17}O NMR measurements was $-4.2\ cm^3\ mol^{-1}$, indicative of an I_a water substitution pathway.[6] The results from this particular study led to a debate in which the validity of activation volumes for the use of mechanistic assignment was questioned.[7] However, the proposed I_a mechanism for water exchange was further substantiated through the calculation of the activation volume using quantum-mechanical methods and was attributed to the strength of the Rh−OH_2 bonds.[8,9] As these examples

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[†] Department of Chemistry, U. C. Davis.

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(1) Sasaki, Y.; Nagasawa, A.; Tokiwa-Yamanoto, A.; Ito, T. *Inorg. Chim. Acta* **1993**, *212*, 175−182.

(2) Helm, L.; Merbach, A. E. *Coord. Chem. Rev.* **1999**, *187*, 151−181.

(3) Dunand, F. A.; Helm, L.; Merbach, A. E. *Adv. Inorg. Chem.* **2003**, *54*, 1−69.

(4) Rotzinger F. P. *J. Am. Chem. Soc.* **1996**, *118*, 6760−6766.

(5) Rotzinger F. P. *J. Am. Chem. Soc.* **1997**, *119*, 5230−5238.

(6) Laurenczy, G.; Rapaport, I.; Zbinden, D.; Merbach, A. E. *Magn. Reson. Chem.* **1991**, *29*, S45−S51.

(7) Dhungana, S.; Crumbliss, A. L. *Chemtracts* **2001**, *14*, 42−47.

(8) De Vito, D.; Sidorenkova, H.; Rotzinger, F. P.; Weber, J.; Merbach, A. E. *Inorg. Chem.* **2000**, *39*, 5547−5552.

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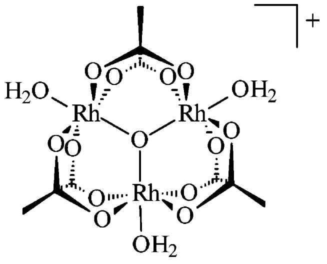
illustrate, high-pressure ^{17}O NMR has proven to be very useful for the mechanistic assignment of water exchange from simple mononuclear species.

Only recently, however, have high-pressure ^{17}O NMR techniques been extended to the study of water exchange from polynuclear aqua ions, such as the dihydroxo-bridged rhodium(III) dimer[10] ($[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_4]^{4+}$ abbreviated as $\mathbf{Rh_2}^{4+}$ in subsequent text) and the $\mathbf{GaAl_{12}}$ polyoxocation[11] ($GaO_4Al_{12}(\mu\text{-}OH)_{24}(H_2O)_{12}{}^{7+}$). Activation volumes for water exchange from $\mathbf{Rh_2}^{4+}$ ($\Delta V_{trans}^{\ddagger} = +8.5$ and $\Delta V_{cis}^{\ddagger} = +10.1$ cm^3 mol^{-1}) were near the dissociative limit estimated by Swaddle[12] ($\Delta V_{lim}^{\ddagger} \sim +13.5$ cm^3 mol^{-1} for octahedral trivalent 3d ions) and therefore indicate that water exchange for both the cis and trans water molecules follows a limiting dissociative (*D*) pathway. The high-pressure ^{17}O NMR study on the $\mathbf{GaAl_{12}}$ polyoxocation is particularly noteworthy in that an activation volume was measured not only for water exchange from this molecule but also for oxygen substitution of one of the hydroxyl bridges.

Particularly well suited for study are the oxo-centered carboxylate-bridged metal(III) trimers ($[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^+$ abbreviated as $\mathbf{M_3}^+$) because they are often used in catalysis,[13−15] but little is known about the substitution reactivity of the terminal ligands. Rates of water substitution and exchange from a small number of oxo-centered metal(III) trimers have been published,[1,16,17] but the pressure dependence on the rate has not yet been investigated, in part because of the rapid substitution reactivity of these complexes. Rate constants for water exchange or water substitution for $\mathbf{Ru_3}^+$, $\mathbf{Rh_3}^+$, and $\mathbf{Cr_3}^+$ are 1.08×10^{-3} s^{-1}, 1.3×10^{-3} s^{-1} (per substitution site), and 5.20×10^{-4} s^{-1} at 298 K, respectively.[1,16,17] In contrast, water exchange rates from the corresponding simple mononuclear species are 3−6 orders of magnitude slower (e.g., $Rh(H_2O)_6{}^{3+}$, $k_{ex}{}^{298} = 2.2 \times 10^{-9}$ s^{-1} and $Ru(H_2O)_6{}^{3+}$, $k_{ex}{}^{298} = 3.5 \times 10^{-6}$ s^{-1}).[6,18] One hypothesis to account for these large differences is that the increased lability of the terminal waters on the metal(III) trimers is due to trans-labilization from the planar μ_3-O. Also, a contributing factor is the reduced average charge on the metal ions (e.g., +0.33/Rh in $\mathbf{Rh_3}^+$ compared to +3 on $Rh(OH_2)_6{}^{3+}$).

It has been previously proposed that the mechanism of water substitution for $\mathbf{Rh_3}^+$ and other oxo-centered metal(III) trimers follows a *D* or an I_d pathway based on highly positive activation parameters and on the lack of dependence of the rate on the incoming ligand.[1,16] To confirm this hypothesis, we present here variable-pressure and temperature kinetic data for water exchange from $\mathbf{Rh_3}^+$. To our knowledge, this work is the first high-pressure ^{17}O NMR study of water exchange from an oxo-centered carboxylate-bridged metal(III) trimer.



($\mathbf{Rh_3}^+$)

Materials and Methods

Materials. Perchlorate crystals of $\mathbf{Rh_3}^+$ were acquired in two ways. First, $\mathbf{Rh_3}^+$ was purchased from Alfa Aesar in the acetate form, $[Rh_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]O_2CCH_3$. To purify the powder, 500 mg was dissolved in 20 mL of water, loaded onto a Dowex 50WX2-200 cation-exchange column, and eluted with ~50 mL of a 0.1 M $NaClO_4$ or 0.1 M $HClO_4$ solution. After several days of slow evaporation at room temperature, dark red plates formed and were collected and washed with ice-cold water. The structure of the trinuclear rhodium(III) perchlorate salt, $[Rh_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]ClO_4 \cdot 2H_2O$, was verified by matching lattice constants to published values using X-ray crystallography.[19] Second, the complex was synthesized by dissolving 500 mg of the rhodium active-hydroxide solid, $Rh(OH)_3 \cdot xH_2O$,[20,21] in excess acetic acid dissolved in DI water (10 mL) with continuous heating at 333 K overnight. After the reaction was quenched, the $\mathbf{Rh_3}^+$ solution was purified and crystallized as described above. Typical yields were in the range of 80%. Capillary-electrophoresis mass spectra ($m/z = 732.8$) indicate no difference in the rhodium(III) trimers obtained in these two ways.

Caution. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Appropriate care should be taken when handling metal perchlorate salts.

NMR Spectroscopy. ^{103}Rh and ^{17}O NMR spectra, acquired for characterization purposes, and ^{17}O variable-temperature kinetic experiments were conducted using a Bruker Avance NMR spectrometer based on an 11.7 T field located at the University of California Davis, NMR facility. Variable-pressure ^{17}O NMR experiments were performed on a Chemagnetics CMX-400 spectrometer equipped with a wide-bore 9.4 T magnet (Magnex Scientific).

(i) ^{103}Rh NMR. A ^{103}Rh NMR spectrum was collected on a stock batch of $\mathbf{Rh_3}^+$ perchlorate crystals to ensure their purity before ^{17}O NMR kinetic experiments were performed. The solution was prepared by dissolving 0.17 g of the $\mathbf{Rh_3}^+$ perchlorate salt in 2 mL of isotopically normal water to give $[\mathbf{Rh_3}^+] \sim 0.1$ M. The sample was placed in a 10-mm NMR tube containing a coaxial insert of 0.5 M $Rh(H_2O)_6{}^{3+}$ dissolved in $D_2O/HClO_4$ (3:1 pH < 0). The

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(9) De Vito, D.; Weber, J.; Merbach A. E. *Inorg. Chem.* **2004**, *43*, 858−864.

(10) Drljaca A.; Zahl A.; van Eldik, R. *Inorg. Chem.* **1998**, *37*, 3948−3953.

(11) Loring, J.; Yu, P.; Phillips B. L.; Casey, W. H. *Geochim. Cosmochim. Acta* **2004**, *68*, 2791−2798.

(12) Swaddle T. W. *Inorg. Chem.* **1983**, *22*, 2663−2665.

(13) Fouda, S. A.; Rempel, G. L. *Inorg. Chem.* **1979**, *18*, 1−8.

(14) Fish, R. H.; Fong, R. H.; Vincent, J. B.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1988**, *22*, 1504−1506.

(15) Ito, S.; Inoue, K.; Mastumoto, M. *J. Am. Chem. Soc.* **1982**, *104*, 6450−2.

(16) Powell, G.; Richens, D. T.; Powell, A. K. *Inorg. Chim. Acta* **1993**, *213*, 147−155.

(17) Fujihara, T.; Aonahata, J.; Kumakura, S.; Nagasawa, A.; Murakami, K.; Ito, T. *Inorg. Chem.* **1998**, *37*, 3779−3784.

(18) Rapaport, I.; Helm, L.; Merbach, A. E.; Bernhard, P.; Ludi, A. *Inorg. Chem.* **1988**, *27*, 873−9.

(19) Glowiak, T.; Kubiak, M.; Szymanska-Buzar, T. *Acta Crystallogr., Sect. B* **1977**, *B33*, 1732−7.

(20) Ayres, H. R.; Forrester, J. S. *J. Inorg. Chem.* **1957**, *3*, 365−6.

(21) Crimp, S. J.; Spiccia, L. *Aust. J. Chem.* **1995**, *48*, 557−66.

$Rh(H_2O)_6^{3+}/D_2O$ solution provided a chemical shift reference ($\delta = 9915.8$ ppm) and a lock signal.[22]

The ^{103}Rh NMR spectrum was recorded at 15.9 MHz via direct observation using a 10-mm broad-band probe. Because of the insensitivity of the ^{103}Rh nucleus, the $\pi/2$ pulse width could not be determined within a reasonable amount of time. Therefore, we used a conservative pulse width of 15 μs and a pulse-repetition time of 1.5 s, on the basis of previously published data,[22] to avoid signal saturation. A total of 25 000 scans were obtained over a spectral width of 28.7 kHz.

(ii) ^{17}O NMR. An ^{17}O NMR spectrum of $\mathbf{Rh_3}^+$ was obtained in which all oxygen ligands had been isotopically tagged. The tagged $\mathbf{Rh_3}^+$ was synthesized by dissolving 200 mg of $Rh(OH)_3 \cdot xH_2O$ in 2 mL of acidified $^{17}OH_2$ (~40%, pH ~ 0 using concentrated $HClO_4$) and was heated at 333 K for 8 days while a separate solution consisting of 1 mL acetic acid dissolved in 1 mL of $^{17}OH_2$ (~10%) was heated at 333 K for the same amount of time. The two solutions were then mixed together and heated at 333 K overnight to form the ^{17}O-tagged $\mathbf{Rh_3}^+$ complex. The $\mathbf{Rh_3}^+$ complex was then purified and isolated as described earlier. During the crystallization process, the tagged water molecules were replaced by isotopically normal water molecules from the eluent. To obtain a ^{17}O NMR spectrum in which all oxygens, including the bound waters, had been isotopically enriched, the crystals were dissolved in $^{17}OH_2$ (~10%) prior to running the spectrum. Because the molecule was not in isotopic equilibrium, the relative peak areas for the different functional groups give no information about the stoichiometry. However, assignments were made by comparing the chemical shifts to those already published for similar functional groups. The bulk water signal was broadened beyond detection by adding $Mn(ClO_4)_2 \cdot 6H_2O$ crystals to the $\mathbf{Rh_3}^+$ solution to give $[Mn^{2+}] = 0.25$ M.[23] The use of a paramagnetic shift reagent is common to broaden the bulk-water ^{17}O NMR signal because the transverse relaxation rate of the bulk-water resonance in the presence of $Mn(H_2O)_6^{2+}$ is much greater than the waters bound on $\mathbf{Rh_3}^+$ ($T_{2(\text{bound})} \gg T_{2(\text{bulk})}$).[24]

The ^{17}O NMR spectrum was recorded at 67.8 MHz in unlocked mode using a 10-mm broad-band probe with a pulse width of 20 μs ($\pi/2 \sim 60$ μs) and a delay of 5 ms. A total of 500 000 acquisitions were acquired over a spectral range of 99 kHz. All chemical shifts were referenced externally to tap water.

(iii) Variable-Temperature ^{17}O NMR. Samples were prepared by dissolving $\mathbf{Rh}_3^+$ perchlorate crystals in 2 mL of thermally equilibrated $^{17}OH_2$ (~15%) containing 0.25 M $Mn(H_2O)_6^{2+}$ to give $[\mathbf{Rh_3}^+] = 0.05$ M. The sample pH was acidic, pH = 1.8 (±0.1), because of carryover of $HClO_4$ from the $Mn(ClO_4)_2 \cdot 6H_2O$ crystals. For the variable-pH experiments, the solution pH was adjusted with solid $NaHCO_3$ until the desired pH was obtained. During the mixing, temperatures were controlled by agitating the sample inside a constant-temperature water bath. The time required to dissolve the crystals in $^{17}OH_2$ and to place the sample in the NMR spectrometer for data acquisition took no longer than 10 min, which was sufficiently short relative to the acquisition time that it could be safely ignored. A coaxial insert containing 0.51 M $TbCl_3$ in isotopically normal water was also placed inside the NMR tube to provide an external constant-intensity standard and a chemical-shift reference.[23,25] The waters bound to the Tb^{3+}(aq) ion are in rapid-exchange equilibrium with those in the bulk and appear at approximately −153 ppm relative to that of bulk water.

Oxygen-exchange experiments were performed by monitoring the height of the ^{17}O NMR signal from the bound water as a function of time. Peak heights were normalized to that of the Tb^{3+}(aq) external standard and were determined from a least-squares fit of the data to Lorentzian curves. Each kinetic run consisted of 30−60 spectra and was followed until the intensity counts of the bound water signal no longer increased. To calculate the pseudo-first-order rate coefficient for water exchange, the normalized peak heights from the bound water resonance were fit to the following three-parameter equation.

$$I_t = I_o + a(1 - e^{-k_{ex}t}) \tag{1}$$

The terms I_o and I_t refer to the normalized height of the bound water resonance at $t = 0$ (an adjustable parameter) and the normalized height during the course of the experiment, respectively. The term k_{ex} refers to the rate coefficient for water exchange, a is an adjustable parameter, which did not deviate appreciably from unity, and t is the elapsed time after mixing. The temperature dependence of the rate coefficient was investigated by repeating the experiment at four temperatures at ambient pressure: 281.6, 278.0, 276.3, and 272.8 K.

The experiments were conducted with a commercial 10-mm broad-band probe. Typically, 5000−20 000 scans over a spectral range of 99 kHz were recorded for each ^{17}O NMR spectrum. A pulse width of 20 μs, corresponding to a 31° tip angle for the bound waters on the Tb^{3+} ion, was used with a relaxation delay of 5 ms. The sample temperature was determined with a copper−constantan thermocouple placed inside a separate NMR tube but with similar geometry and with the same solvent mixture as the samples. We estimate the error in the temperature readings to be much less than ±0.5 K.

(iv) Variable-Pressure ^{17}O NMR. Samples for these experiments were prepared from two stock solutions. Crystals of $\mathbf{Rh_3}^+$ were dissolved in 1 mL isotopically normal water to give $[\mathbf{Rh_3}^+] = 0.057$ M, and the appropriate amount of $Mn(ClO_4)_2 \cdot 6H_2O$ and $NaClO_4$ crystals were weighed out to give $[Mn^{2+}] = 0.25$ M and $[NaClO_4] = 1.0$ M. A separate sample was prepared containing $[Mn^{2+}] = 0.25$ M and $[NaClO_4] = 1.0$ M in 1.3 mL $^{17}OH_2$ (~40%). The two stock solutions were prechilled to 267 K and were mixed in a cold room at 253 K yielding a solution with pH = 1.8 (±0.1). After mixing, the sample was immediately loaded into a quartz NMR tube (8 mm o.d.), sealed with a PTFE piston, and then frozen at 248 K for loading into the NMR probe. Once in the probe, the sample was allowed to thermally equilibrate for 40−60 min before acquiring data. Temperature equilibration tests indicate that it takes much less time than 40 min for the sample to melt and reach the desired target temperature (<15 min). Rates at ambient pressure using this approach are within a factor of 2 to those without the freezing step, indicating that temperature equilibration does not affect the value for the activation volume, which is determined by the variation with pressure of the rate (see below).

Because an external intensity standard could not be used for these experiments, the peak height of the bound water resonance was normalized to the height of the ClO_4^- signal at 309 ppm. The pseudo-first-order rate coefficient was calculated using eq 1, and the pressure dependence on the rate coefficient was investigated at

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[22] Read, M. C.; Glaser, J.; Sandström, M.; Toth, I. *Inorg. Chem.* **1992**, *31*, 4155−4159.

[23] Casey, W. H.; Phillips, B. L.; Karlsson, M.; Nordin, S.; Nordin, J. P.; Sullivan, D. J.; Neugebauer-Crawford, S. *Geochim. Cosmochim. Acta* **2000**, *64*, 2951−2964.

[24] Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307−320.

[25] Cossy C.; Helm L.; Merbach A. E. *Inorg. Chem.* **1988**, *27*, 1973−1979.

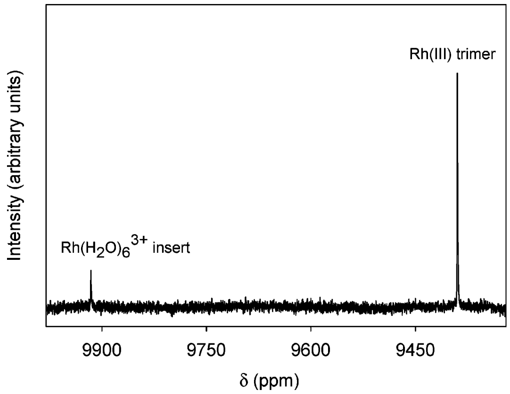

Figure 1. ^{103}Rh NMR spectrum of a ∼0.1 M solution of $\mathbf{Rh_3}^+$ (9389.8 ppm) containing a coaxial insert of 0.5 M $Rh(H_2O)_6^{3+}$ for chemical shift reference ($\delta = 9915.8$ ppm). The spectrum was acquired at 298 K.

five pressures, 0.1, 51, 92, 152, and 200 MPa, at a constant temperature of 270.9 K.

The experiments were conducted using a high-pressure probe assembly similar to that described by Jonas et al.[26] The pressure was generated manually with a large-volume syringe pump (High-Pressure Research Inc.) using water and was transferred to the sample with *n*-hexanes. The sample tube is fitted with an O-ring-sealed PTFE piston that allows the pressure to be transmitted to the sample. Experimental pressures were measured continuously with an electronic gauge (High-Pressure Research Inc.) and were controlled to within ±5 MPa. The sample temperature was controlled by circulating ethylene glycol from a constant-temperature bath through the thermostated jacket of the probe. Sample temperature was continuously monitored with a copper−constantan thermocouple symmetrically disposed from the sample inside the pressure chamber. The experimental temperature (270.9 K) was controlled to within ±0.4 K, which is a conservative estimate. The ^{17}O NMR spectra were acquired at 54.24 MHz and were collected using a pulse length of 20 μs ($\pi/3$), a sweep width of 100 kHz, and a recycle delay of 10 ms. A total of 40 000 scans was used to achieve an adequate signal-to-noise ratio. To remove baseline roll due to acoustic ringing, the first 90 μs of data were recalculated from the remainder of the free-induction decay using a linear-prediction algorithm. All peaks were fit to Lorentzian curves.

Potentiometric Measurements. The first pK_a of $\mathbf{Rh_3}^+$ (pK_{a1} = 8.3 (±0.2), $I = 0.1$ M, $T = 298$ (±0.1) K) was determined by titrating a 5 mM solution of $\mathbf{Rh_3}^+$ containing 100 mM $NaClO_4$ with 100 mM NaOH and back-titrating with 100 mM $HClO_4$. A pH-stat apparatus was used with a Metrohm combination electrode calibrated on the concentration scale using a 100 mM $HClO_4$ solution.

Results

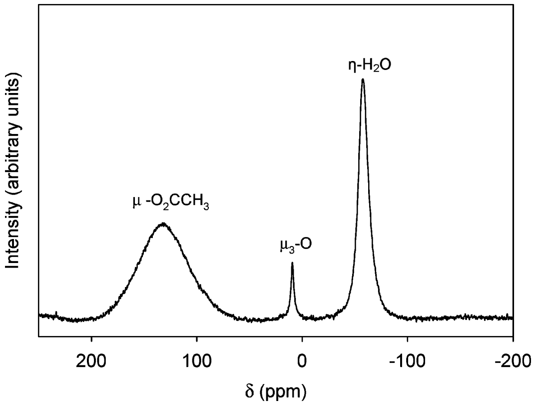

Figure 2. ^{17}O NMR spectrum of isotopically enriched $\mathbf{Rh_3}^+$ (enrichment ∼2−10%). ^{17}O NMR signals at −57, 9, and 131 ppm (relative to external tap water) are assigned to η-H_2O, μ_3-O, and μ-O_2CCH_3, respectively. The different oxygens in $\mathbf{Rh_3}^+$ were not in isotopic equilibrium so the relative peak areas do not correspond to the stoichiometry of the complex. The solution pH = 2.2 (±0.2) and the temperature was 276.3 K.

^{103}Rh and ^{17}O NMR Spectra. As expected, the ^{103}Rh NMR spectrum shows only one signal ($\delta = 9389.8$ ppm at 298 K) because of all three chemically equivalent rhodium(III) ions in the oxo-centered trimer with idealized D_{3h} symmetry (Figure 1). Because of increased shielding from the bridging groups, the rhodium(III) ions resonate at lower frequency relative to the external rhodium(III) standard, an aqueous solution of $Rh(H_2O)_6^{3+}$ ($\delta = 9915.8$ ppm). The ^{103}Rh chemical shift is comparable to those reported for other aqueous rhodium(III) clusters.[22,27] The ^{17}O NMR spectrum of the isotopically tagged $\mathbf{Rh_3}^+$ complex (Figure 2) shows three signals. The peak at −57 ppm is assigned to the ^{17}O-tagged bound waters (η-H_2O) on the $\mathbf{Rh_3}^+$ complex and is comparable to that found for the bound waters on other aqueous rhodium(III) compounds.[22,27] The broad resonance at 130 ppm is assigned to the six equivalent μ-O_2CCH_3 on the basis of chemical shifts reported for several uncoordinated carboxylates.[28,29] Tentatively, we assign the signal at 9 ppm to the planar μ_3-O because the chemical shifts of capping three-coordinate oxides have been reported at much higher chemical shifts in molybdenum(IV) and tungsten(IV) clusters.[30,31] However, no other signals besides the ClO_4^- signal at $\delta = 309$ ppm were observed downfield on the ^{17}O NMR spectrum.

Variable-Temperature Kinetics. After dissolution of isotopically normal $\mathbf{Rh_3}^+$ crystals in $^{17}OH_2$, a signal immediately appeared on the ^{17}O NMR spectrum at −57 ppm because of ^{17}O-tagged terminal waters, in addition to a peak at approximately −153 ppm because of bound waters on the Tb^{3+}(aq) ion (Figure 3).[25] Over the course of the experiment, the height of the bound water signal increased exponentially over time and was constant after 7−14 h (depending on temperature). The peak heights were normalized to the external Tb^{3+}(aq) standard and then were fit to eq 1 to extract the pseudo-first-order rate coefficient for water exchange. The experiment was repeated at four different temperatures (Figure 4) under ambient pressure to derive activation parameters.

The rate coefficients from these variable-temperature experiments yield the activation enthalpy ($\Delta H^{\ddagger}$) and entropy

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[26] Jonas, J. W.; Koziol, P.; Peng, X.; Reiner, C.; Campbell, D. *J. Magn. Reson. B* **1993**, *102*, 299−309.

[27] Spiccia, L.; Aramini, J. M.; Crimp, S. J.; Drljaca, A.; Lawrenz, E. T.; Tedesco, V.; Vogel, H. J. *J. Chem. Soc., Dalton Trans.* **1997**, *23*, 4603−4610.

[28] Richens, D. T.; Guille-Photin, C. *J. Chem. Soc., Dalton Trans.* **1990**, *2*, 407−12.

[29] Boykin, D. W.; Baumstark, A. L. In *^{17}O NMR spectroscopy in organic chemistry*; Boykin, D. W., Ed.; CRC Press: Boca Raton, FL, 1991.

[30] Richens, D. T.; Helm, L.; Pittet, P. A.; Merbach, A. E.; Nicolo, F.; Chapuis, G. *Inorg. Chem.* **1989**, *28*, 1394−402.

[31] Patel, A.; McMahon, M. R.; Richens, D. T. *Inorg. Chim. Acta* **1989**, *163*, 73−8.

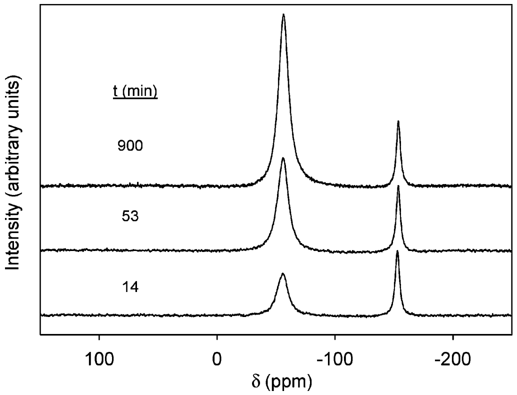

Figure 3. ^{17}O NMR spectra of $\mathbf{Rh_3}^+$ after injection of $^{17}OH_2$ as a function of time; $[\mathbf{Rh_3}^+] = 0.05$ M and $[Mn^{2+}] = 0.25$ M. The reported times in the figure refer to the time elapsed since injection and were recorded after acquisition of data was complete. The solution pH = 1.8 (±0.1), T = 276.3 K, and P = ambient.

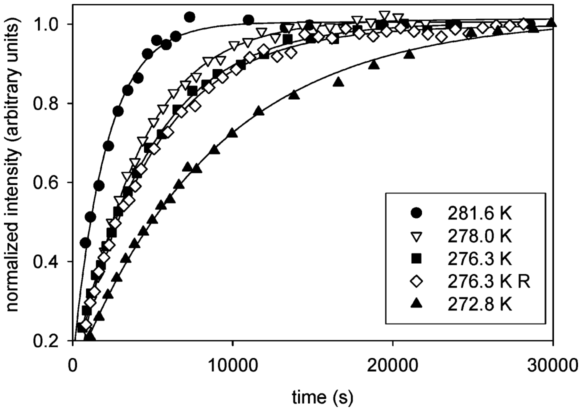

Figure 4. The normalized intensity of the bound water resonance on the ^{17}O NMR spectra as a function of time and temperature under ambient pressure (solution pH = 1.8 (±0.1)). The lines correspond to least-squares fits to eq 1.

($\Delta S^\ddagger$) via the Eyring equation (eq 2).

$$k_{ex} = \frac{k_B T}{h} e^{-((\Delta H^\ddagger - T\Delta S^\ddagger)/RT)} \tag{2}$$

The term k_{ex} represents the rate coefficient for exchange at atmospheric pressure, k_B is Boltzmann's constant, T is the experimental temperature in Kelvin, h is Planck's constant, and R is the gas constant.[32] A least-squares fit of the data to eq 2 gives $\Delta H^\ddagger = 99$ (±3) kJ mol^{-1} and $\Delta S^\ddagger = 43$ (±10) J K^{-1} mol^{-1}. Using eq 2 to estimate k_{ex}^{298} yields 5×10^{-3} s^{-1} and an error in $\ln(k_{ex}^{298})$ of ±1.2. This error is dominated by the error in $\Delta S^\ddagger$ (±10 J K^{-1} mol^{-1}) and is an overestimate. It is much larger than the experimental uncertainty of a single measurement. The temperature range was limited to below 281.6 K because at ambient temperature (298 K) the half-life for water exchange is less than 4 min. Nevertheless, over the temperature range of 281.6−272.8 K, the rate coefficients follow the Eyring equation (Figure 5).

Water exchange rates were also measured at three different pH conditions, pH = 1.8, 2.9,and 5.7 (pH < pK_a (8.3)). All

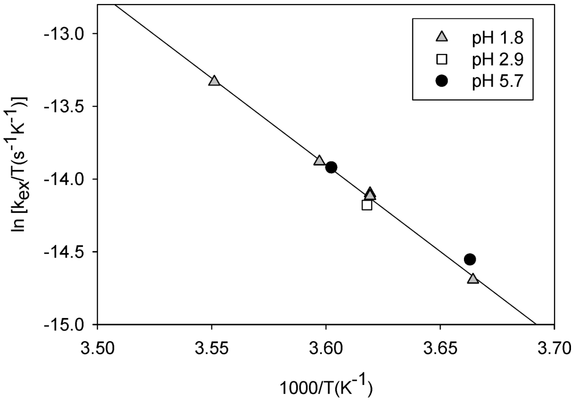

Figure 5. Temperature dependence of the pseudo-first-order rate coefficient for water exchange from $\mathbf{Rh_3}^+$ at 1 atmosphere.

Table 1. Rate Constants for Water Exchange from $[Rh_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^+$

experiment	temperature(K)	pH	pressure (MPa)	$10^{-4}\, k_{ex}$ (s^{-1})
variable temperature	281.6 (±0.5)	1.8 (±0.1)	0.1 (ambient)	4.6 (±0.2)
	278.0 (±0.3)	1.9 (±0.1)	0.1	2.61 (±0.04)
	277.6 (±0.3)	5.7 (±0.1)	0.1	2.50 (±0.05)
	276.4 (±0.3)	2.9 (±0.1)	0.1	1.92 (±0.05)
	276.3 (±0.3)	1.8 (±0.1)	0.1	2.08 (±0.04)
	276.3 (±0.3)	1.8 (±0.1)	0.1	2.04 (±0.04)
	273.0 (±0.5)	5.7 (±0.1)	0.1	1.3 (±0.1)
	272.8 (±0.3)	1.8 (±0.1)	0.1	1.14 (±0.02)
variable pressure	270.9 (±0.3)	1.7 (±0.1)	0.1	1.67 (±0.05)
	270.9 (±0.2)	1.8 (±0.1)	51 (±5)	1.49 (±0.04)
	270.9 (±0.4)	1.7 (±0.1)	92 (±5)	1.41 (±0.09)
	270.9 (±0.2)	1.7 (±0.1)	152 (±5)	1.17 (±0.03)
	270.9 (±0.3)	1.8 (±0.1)	200 (±5)	1.04 (±0.04)

rate coefficients follow the Eyring equation as shown in Figure 5, indicating no contribution from the partly deprotonated $\mathbf{Rh_3}^+$ at pH = 5.7 or from $\mathbf{Rh_3}^+$ with a protonated oxo-bridge at pH = 1.8. These variable pH results, while consistent with the rest of the kinetic data, were not used in the calculation of the activation parameters. Only experiments in which the solution pH was constant (solution pH = 1.8) were used in determining the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for water exchange. Rate constants for the variable-temperature and pH experiments are summarized in Table 1.

By comparison with the ^{17}O NMR spectrum of the tagged $\mathbf{Rh_3}^+$ complex shown in Figure 2, isotopic substitution into the μ_3-O, or the μ-O_2CCH_3 was not observed during these experiments even after nine weeks at an elevated temperature of 313 K. These functional groups are apparently inert to oxygen exchange at these experimental conditions.

Variable-Pressure Kinetics. The variation of reaction rate (k_{ex}) with pressure (P) can be related to the activation volume ($\Delta V^\ddagger$) by eq 3.[33]

$$\left(\frac{\partial \ln(k_{ex})}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT} \tag{3}$$

Assuming that the compressibility of activation is negligible as is typical for aqueous solutions, $\Delta V^\ddagger$ can be determined directly from eq 4[33−35]

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(32) Kelm, H.; Palmer, A. In *High-Pressure Chemistry*; Kelm, H., Ed.; D. Reidel: Dordrecht, The Netherlands, 1978.

(33) Richens, D. T. *The Chemistry of Aqua Ions*; John-Wiley: Chichester and New York, 1997.

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

(35) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479−1493.

$$\ln(k_{ex,P}) = \ln(k_{ex,P=0}) - P\Delta V^{\ddagger}/RT \qquad (4)$$

where the terms $k_{ex,P}$ and $k_{ex,P=0}$, refer to the rate coefficient for water exchange at the experimental pressure and at zero pressure, respectively. Because electrostriction effects can be ignored for water exchange reactions, $\Delta V^{\ddagger}$ can be related directly to intrinsic changes, such as bond breaking, during the formation of the activated complex.[33,34]

As shown in Figure 6, the rate coefficients for water exchange decrease with increasing pressure. A least-squares fit of the data to eq 4, with $k_{ex,P=0}$ as an adjustable parameter, gives $\Delta V^{\ddagger} = +5.3\ (\pm 0.4)\ \mathrm{cm^3\ mol^{-1}}$. Rate constants for these variable-pressure experiments are summarized in Table 1. The k_{ex} ($T = 270.9$ K) at atmospheric pressure is slightly greater, although less than a factor of 2, than expected on the basis of the reported activation parameters which would yield a $k_{ex} = 0.85 \times 10^{-4}\ \mathrm{s^{-1}}$. We attribute this error to a small systematic difference in accuracy between the indicated sample temperature in the high-pressure probe and in the commercial probe used for the ambient-pressure experiments. The target temperature, however, was constant (variability less than ±0.4 K) for each variable-pressure experiment. Since $\Delta V^{\ddagger}$ is derived from the isothermal slope of rate with pressure, the small difference in rates at ambient pressure can be ignored.

Discussion

Aqueous rhodium(III) ions are generally inert to substitution because of their large ligand-field-stabilization energies. The $Rh(OH_2)_6^{3+}$ ion, for example, is one of the most inert metal ions ($k_{ex}^{298} = 2.2 \times 10^{-9}\ \mathrm{s^{-1}}$) with an average lifetime for a bound water of roughly 14 years.[6] Upon deprotonation of $Rh(OH_2)_6^{3+}$, however, the rate of exchange is enhanced by a factor of 10^4 but is still sluggish ($k_{ex}^{298} \sim 10^{-5}\ \mathrm{s^{-1}}$).[6] Water exchange from $\mathbf{Rh_2}^{\mathbf{4+}}$ is also relatively slow for both the cis and trans water molecules ($k_{ex}^{298} \sim 10^{-7}\ \mathrm{s^{-1}}$), which interestingly have very similar rates of exchange.[10] The authors attributed this similarity to a rapid Berry pseudorotation after dissociation of one of the ligated waters from the complex.[10] In contrast, the rate of water exchange from $\mathbf{Rh_3}^{+}$ ($k_{ex}^{298} = 5 \times 10^{-3}\ \mathrm{s^{-1}}$) is some 6 orders of magnitude faster than $Rh(OH_2)_6^{3+}$ and is comparable to rates for other oxo-centered metal trimers that contain more labile metal(III) ions (e.g., $\mathbf{Cr_3}^{+}$ and $\mathbf{Ru_3}^{+}$ clusters).[1,16,17]

The enhanced reactivity of the bound waters on $\mathbf{Rh_3}^{+}$ derives from two related causes. First, electron donation from the central oxide ion reduces orbital overlap between the metal ions and the bound waters, which is evident in particularly long $Rh-OH_2$ bond lengths. The average $Rh-OH_2$ bond distance for the dihydrate salt of $\mathbf{Rh_3}^{+}$ is 2.12 Å,[19] which, to our knowledge, is the longest reported $Rh-OH_2$ bond for trivalent rhodium. The labilizing influence of an oxide ion is analogous to that of a bound hydroxyl[6,18,36,37] and has been observed for the aqueous vanadyl ion, $VO(OH_2)_5^{2+}$, although in this case the oxide is not bridging.[38,39] The axial water in this complex located trans from the bound oxide was found to exchange 10^6 times faster than waters at the equatorial positions, which correlates with the respective $V-OH_2$ bond distances. By analogy, labilization of the bound waters on $\mathbf{Rh_3}^{+}$ must reflect some electron donation from the μ_3-O, which is then manifested in long $Rh-OH_2$ bond lengths.

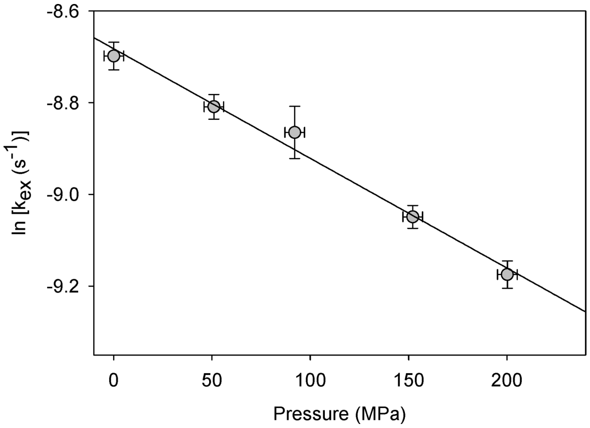

Figure 6. Pressure dependence of the pseudo-first-order rate coefficients for water exchange at 270.9 K. The line corresponds to a weighted least-squares fit to eq 4.

Second, the rapid reactivity of $\mathbf{Rh_3}^{+}$ may reflect a lower average charge density on each rhodium(III) (+0.33/Rh) relative to other rhodium(III) complex ions (e.g., $Rh(OH_2)_6^{3+} = +3$, $\mathbf{Rh_2}^{\mathbf{4+}} = +2$/Rh[40]). Low charge density would be expected to enhance the reactivity of the bound waters because the ion−dipole interaction is not as strong. Correspondingly, titration data indicate that the pK_a of $\mathbf{Rh_3}^{+}$ is considerably higher than that for other hydrolytic rhodium(III) ions (e.g., $Rh(OH_2)_6^{3+}$, p$K_a = 3.45$ and $\mathbf{Rh_2}^{\mathbf{4+}}$, p$K_a = 2.26$),[6,10] consistent with weaker $Rh-OH_2$ bonds.

The rate of water exchange from $\mathbf{Rh_3}^{+}$ ($k_{ex}^{298} = 5 \times 10^{-3}\ \mathrm{s^{-1}}$) is similar to the rate of water substitution by CD_3OD ($k_{ex}^{298} = 1.3 \times 10^{-3}\ \mathrm{s^{-1}}$) reported by Sasaki et al.[1] This similarity in reaction rates indicates that water substitution is largely independent of the identity of the incoming ligand, indicative of a dissociative activation pathway. A *D* (or I_d) mechanism was in fact already proposed by Sasaki et al. on the basis, in part, of positive $\Delta S^{\ddagger}$ values for $\mathbf{Rh_3}^{+}$ and other metal(III) trimers.[1,17] While a highly positive $\Delta S^{\ddagger}$ can often indicate a dissociative mechanism, it is not always reliable for mechanistic assignment because of the large experimental uncertainty from back extrapolation to $1/T = 0$. For this very reason, the determination of $\Delta V^{\ddagger}$ has become a major tool for assigning water exchange mechanisms. Our value for $\Delta V^{\ddagger}$ ($+5.3\ (\pm 0.4)\ \mathrm{cm^3\ mol^{-1}}$), when compared to the value estimated by Swaddle for a limiting *D* substitution ($\sim +13.5\ \mathrm{cm^3\ mol^{-1}}$ for 3d metal ions),[12] indicates that water exchange from $\mathbf{Rh_3}^{+}$ follows an I_d mechanism. Although the

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(36) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 4444−50.

(37) Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* **1981**, *20*, 4212−16.

(38) Wuethrich, K.; Connick, R. E. *Inorg. Chem.* **1968**, *7*, 1377−88.

(39) Kuroiwa, Y.; Harada, M.; Tomiyasu, H.; Fukutomi, H. *Inorg. Chim. Acta* **1988**, *146*, 7−8.

(40) Cervini, R.; Fallon, G. D.; Spiccia, L. *Inorg. Chem.* **1991**, *30*, 831−6.

Table 2. A Compilation of Rate Coefficients and Activation Parameters for Water Exchange from Several Aqueous Rhodium(III) Ions as Determined from ^{17}O NMR

complex	k_{ex}^{298} (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1}K^{-1})	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})	mechanism	source
$Rh(OH_2)_6^{3+}$	2.2×10^{-9}	131	29	−4.2	I_a	ref 6
$Rh(H_2O)_5(OH)^{2+}$	4.2×10^{-5}	103		+1.5	I	ref 6
$[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_4]^{4+}$						
trans H_2O	8.5×10^{-7}	150	141	+8.5	D	ref 10
cis H_2O	5.4×10^{-7}	159	168	+10.1	D	ref 10
$[Rh_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^+$	5×10^{-3}	99	43	+5.3	I_d	This Work

extent to which Swaddle's estimate applies to multinuclear complexes is still unknown, a dissociative mechanism is expected for a metal ion with saturated d_{xy}, d_{xz}, and d_{yz} orbitals because the approach of a seventh ligand is electrostatically unfavorable. Furthermore, the average bond angle between the bridging acetates and the bound water in the $\mathbf{Rh_3}^+$ is less than 90° (average angle ∼ 85°),[19] hindering the approach of a seventh ligand. An anonymous referee made a perceptive observation that this strain would be partly relieved by the departing bound water molecule, which would also favor a dissociative mechanism.

Activation volumes for water exchange from aqueous rhodium(III) ions are consistent with a range of mechanisms (see Table 2). On the basis of the negative value of $\Delta V^{\ddagger}$ for water exchange from $Rh(OH_2)_6^{3+}$, an I_a mechanism was assigned,[6] while water exchange for both the cis and trans water molecules from the $\mathbf{Rh_2}^{4+}$ was interpreted[10] to indicate a limiting *D* mechanism on the basis of highly positive $\Delta V^{\ddagger}$ values. The negative $\Delta V^{\ddagger}$ for water exchange from $Rh(OH_2)_6^{3+}$ was attributed to the strength of the Rh−OH_2 bonds because of the high charge density on the rhodium(III) cation, favoring an associative activation mode.[9] The limiting *D* mechanism assigned to water exchange from $\mathbf{Rh_2}^{4+}$ was explained in terms of labilization from the bridging hydroxyls; however, the reported bond lengths from crystal data (2.04−2.02 Å)[41] are much shorter than those reported for $\mathbf{Rh_3}^+$. On this basis, it came as a surprise to us that the $\Delta V^{\ddagger}$ value for water exchange from $\mathbf{Rh_3}^+$ was consistent with an I_d mechanism, rather than with *D*, considering the length of the Rh−OH_2 bonds and the bulkiness of the bridging acetates. Additionally, Fujihara et al. reported highly positive activation volumes for water substitution by dimethylacetamide from $\mathbf{Cr_3}^+$ using high-pressure UV−vis.[17] Swaddle suggested, however, that no exchange reactions are purely *D* or associative (*A*) but rather follow an infinite number of microscopic interchange pathways.[42] Our conclusion that water exchange from $\mathbf{Rh_3}^+$ follows an I_d mechanism falls in line with Swaddle's proposition.

Concluding Remarks

$\mathbf{Rh_3}^+$ can serve as a useful model for understanding the reactivity of oxo-centered carboxylate-bridged metal(III) trimers. Future experiments will be focused on understanding how water exchange rates are influenced by the nature of the bridging-carboxylates by synthesizing several oxo-centered carboxylate-bridged rhodium(III) trimers. Once synthesized, the rates of water exchange will be measured to correlate exchange rates to structural features within the clusters, such as Rh−OH_2 bond distances, while maintaining the average charge on the metal constant.

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(41) Drljaca, A.; Spiccia, L.; Krouse, H. R.; Swaddle, T. W. *Inorg. Chem.* **1996**, *35*, 985−90.

(42) Swaddle, T. W. *Comments Inorg. Chem.* **1991**, *12*, 237−58.