Hydrolytic Oligomers of Rhodium(III): A Multinuclear NMR Study of the Doubly Hydroxo-Bridged Dimer and Trimer in Aqueous Solution

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Received March 5, 1992

Metastable oligomeric hydrolysis products of rhodium(III) have been chromatographically separated and studied by means of multinuclear NMR (^{103}Rh, ^{17}O, and ^{1}H). Two of these species, a dimer and a trimer, have been characterized in solution. For the dimer a centrosymmetric structure with a double hydroxo bridge was established, $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_4]^{4+}$, giving a single ^{103}Rh NMR signal (9997.4 ppm at 298 K). ^{17}O NMR showed three signals resulting from oxygen in H_2O coordinated cis and trans to the plane of the bridge (−122.2, −130.6 ppm) and from bridging OH (−320.1 ppm). From low-temperature studies of the hexaaquarhodium(III) ion in solutions with varying H:D ratios, the ^{1}H NMR chemical shift difference between H_2O and HDO coordinated in the first hydration sphere of rhodium(III) was found to be 0.17 ppm. Similar studies on the dimer allowed us to differentiate ^{1}H NMR signals for protons at the three sites (cis H_2O, trans H_2O, and bridging OH) on the basis of the observation of split signals for H_2O/HDO isotopic pairs. Our NMR data for the trimer are consistent with a linear bis(μ-hydroxo)-bridged structure, $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_2(\mu\text{-}OH)_2Rh(OH_2)_4]^{5+}$, with two ^{103}Rh NMR signals at 9967.1 and 10004.3 ppm due to the terminal and central Rh sites, respectively. The two-bond spin–spin coupling constant of this species is $^{2}J_{Rh,Rh}$ = 1.5 Hz.

Introduction

The kinetic inertness of complexes of the low-spin d^6 ions rhodium(III) and iridium(III), and similarly of the d^3 chromium-(III) ion, has allowed chromatographic separation of some of their simpler oligomers formed on hydrolysis.[1-4] A variety of techniques have been used to probe the structure and chemistry of these hydroxo-bridged species.[5] In the case of chromium(III), structures for dimers with monohydroxo[4] and dihydroxo[2] bridges, for a trimer,[2] and for a tetramer[2] have been proposed on the basis of their relative resistance to acid cleavage, their pK_a values, and also crystallographic data for the dihydroxo-bridged dimer.[6] The trimer is believed to consist of a compact triangular arrangement of chromium atoms linked by three mono(μ-hydroxo) groups and a central μ_3-hydroxo bridge.[2] However, arguments in favor of a linear structure with two bis(μ_2-hydroxo) bridges have been forwarded.[5,7] Decisive structural investigations of these species by NMR have been hindered by the paramagnetic nature of chromium(III), and the failure to obtain a suitable salt of the trimer has so far prevented crystallographic characterization. ^{17}O NMR studies of the iridium(III) system have allowed the solution structures of the monohydroxo- and dihydroxo-bridged dimers to be elucidated.[3]

Ion-exchange chromatography has recently been used to separate metastable hydrolytic oligomers of rhodium(III), whereby the crystal structure of dimer **1** could be determined.[1] In the present study, our aim has been to structurally characterize the lower oligomers of rhodium(III) in aqueous solution using a combination of ^{103}Rh, ^{17}O, and ^{1}H NMR methods, thus allowing comparison with the related iridium(III) and chromium(III) systems, for which metal NMR is not informative. Previous studies using ^{103}Rh NMR have demonstrated its capability to differentiate and identify rhodium(III) complexes in solution, despite the inherently low sensitivity of the method.[8]

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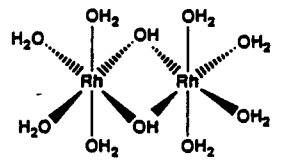

Experimental Section

Separation and Preparation of Rhodium(III) Oligomeric Hydroxo Complexes. The aging and elution characteristics of rhodium(III) were found to be substantially the same as those described earlier.[1] Typically, the dry acid-free salt[8] $Rh(ClO_4)_3\cdot 6H_2O$ (3.0 g, 5.8 mmol) was dissolved in 120 mL of 1 M NaOH, and after ca. 45 min at 25 °C the hydrolysis reaction was quenched by addition of 1 M $HClO_4$ to give a final pH = 1.7. The solution was diluted with 0.02 M $HClO_4$ to give $c_{Rh(III)} \sim 10$ mM and absorbed onto a 3 × 20 cm column of Sephadex SP C25 (Pharmacia) in the H^+ form. Fractions containing different Rh(III) species were eluted with increasing concentrations of $NaClO_4$ in 0.02 M $HClO_4$. In fractions 1 and 2, the $[Rh(OH_2)_6]^{3+}$ ion and the dimer $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_4]^{4+}$, respectively, could be identified from their UV–vis spectra.[1,9] A third fraction was obtained with 2 M $NaClO_4$. Higher oligomers remaining on the column eluted very slowly with a saturated $LiClO_4$ solution and were not collected. The dilute eluates obtained were kept at 4 °C. The hydroxides of the oligomers in fractions 2 and 3 were precipitated by dropwise addition of each eluate to an equal volume of a 0.25 M aqueous pyridine solution at 0 °C under rapid stirring.[6] The precipitates were collected in a refrigerated centrifuge, washed twice with cold distilled water, and finally washed with acetonitrile prior to drying and storage at −20 °C.

Solution Preparation. (i) ^{103}Rh and ^{17}O NMR. The following solutions were prepared: (1) $Rh(ClO_4)_3\cdot 6H_2O$ (0.1 g) in 3 mL of 1 M $HClO_4$, (2) fraction 2 oligomer hydroxide (0.37 g) in 2.5 mL of 2 M $HClO_4$, (3) fraction 3 oligomer hydroxide (0.21 g) in 2 mL of 1 M $HClO_4$, (4) a

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Table I. ^{103}Rh NMR Chemical Shifts (δ/ppm) at 298 K for Aqueous Solutions Containing $[Rh(OH_2)_6]^{3+}$, the Rhodium(III) Dimer and Trimer, and Mixtures of These Species[a]

	solution no.[a]				
assignment	1	2	3	4	5
$[Rh(OH_2)_6]^{3+}$	9915.8				9913.7
trimer (terminal)			9967.1 (2)[b]	9966.4 (2)	9964.0 (2)
dimer		9997.4		10000.7	9996.7
trimer (central)			10004.3 (1)	10003.6 (1)	10001.4 (1)

[a] See Experimental Section. [b] Approximate relative intensities of the trimer signals are given in parentheses.

nonequilibrium mixture containing 2 mL of solution 3 and 0.5 mL of solution 2, (5) $Rh(ClO_4)_3 \cdot 6H_2O$ (0.1 g) in 2.5 mL of solution 4, and (6) fraction 3 oligomer hydroxide (0.56 g) in 2.5 mL of 3 M $HClO_4$. In all cases, dissolution in $HClO_4$ of the respective precipitates was rapid and complete, and concentrated solutions of the metastable oligomers suitable for ^{103}Rh and ^{17}O NMR could be obtained. ^{17}O enrichment of the dimer (solution 2, 2.0 mL) was achieved by the addition of 7 μL of $H_2{}^{17}O$-enriched water (ISO-YEDA Co. Ltd., 12% $H_2{}^{17}O$; cf. natural abundance of $H_2{}^{17}O$ = 0.037%), followed by equilibration for 100 h at 25 °C, giving 0.07 atom % ^{17}O totally. After ^{17}O NMR measurements, the enrichment was enhanced by the addition of a further 14 μL of $H_2{}^{17}O$-enriched water, i.e. 0.14 atom % ^{17}O altogether.

(ii) ^{1}H NMR. Two solutions were prepared for low-temperature measurements: (7) $Rh(ClO_4)_3 \cdot 6H_2O$ (0.03 g, 0.06 mmol) in 0.6 mL of acetone-h_6 and 22 μL of D_2O (1.2 mmol) and (8) fraction 2 oligomer hydroxide (0.013 g) in 0.6 mL of acetone-d_6, 25 μL of H_2O, 75 μL of D_2O, and 25 μL of 11 M $DClO_4$.

NMR Measurements. A Bruker AM 400 spectrometer in unlocked mode was used for all measurements.

^{103}Rh NMR spectra were recorded at 12.6 MHz for samples in 10-mm NMR tubes using pulse widths of 10 μs (representing a flip-angle $\alpha = 13°$, as measured for ^{103}Rh in aqueous $[Rh(OH_2)_6]^{3+}$) and a pulse repetition time of 1.5 s. Experiments were conducted at two probe temperatures, 276 and 298 K, the chemical shifts being referenced to $\Xi(^{103}Rh) = 3.16$ MHz using the high-frequency positive-shift sign convention.[10]

^{17}O NMR spectra were recorded at 54.2 MHz for samples in 10-mm NMR tubes. For an aqueous solution of $Rh(ClO_4)_3 \cdot 6H_2O$ ($c_{Rh(III)}$ = 1.03 M, c_{HClO_4} = 0.07 M) the 90° pulse width for ^{17}O was found to be 16.5 μs, and T_1 = 6.3 ms. For measurements on the hydrolytic oligomers of rhodium(III), 90° pulses were used with short pulse repetition times, normally 0.1 s. The probe temperature was 308 K. Chemical shifts were referenced to external distilled water at 298 K (δ = 0 ppm). The spectra were corrected for baseline roll by polynomial fitting to the observed spectra.

^{1}H NMR spectra were recorded at 400 MHz for solutions in 5-mm NMR tubes with probe temperatures ranging from 240 to 190 K. Chemical shifts were referenced to the internal acetone solvent signal at 2.04 ppm, corresponding to TMS at 0 ppm.

Results and Discussion

^{103}Rh NMR Studies. Solution 1, containing the $[Rh(OH_2)_6]^{3+}$ ion, gave a single signal at 9915.8 ppm at 298 K. Solutions of the fraction 2 and 3 oligomers from two separate preparations were studied at two probe temperatures, 276 and 298 K, respectively. The fraction 2 solutions gave a single ^{103}Rh NMR signal at 9997.4 ppm at 298 K (9965.2 ppm at 276 K), as expected for a symmetric dimer. However, solution 3 gave two signals with a peak area ratio 1:2 at 10 004.3 and 9967.1 ppm, respectively, at 298 K (9962.8 and 9928.7 ppm at 276 K), consistent with a trimeric rhodium(III) complex. The ^{103}Rh NMR results from the two preparations were identical with respect to both the relative intensities of the signals and the ^{103}Rh chemical shifts, allowing for a temperature dependence[8] of between +1.5 and +2 ppm K^{-1}. The ^{103}Rh NMR shifts for solutions studied at 298 K are summarized in Table I. Spectra of the pure solutions of the dimer and trimer were rerecorded after ^{17}O NMR measurements, during which the samples were held at 35 °C for approximately 12 h; no noticeable degradation had occurred. The variations in ^{103}Rh chemical shifts of cationic species with solution composition (anion concentration) and temperature have been discussed previously.[8] Hence, to avoid ambiguous assignment of signals having small chemical shift differences, spectra were recorded for two nonequilibrium mixtures containing (1) the dimer and trimer (solution 4) and (2) $[Rh(OH_2)_6]^{3+}$, the dimer, and the trimer (solution 5; see Figure 1). This allowed observation of the shifts of all three species under the same experimental conditions and confirmed that the two signals in the spectrum of the trimer originated from two different Rh sites in the same complex, in the ratio 1:2. A high-resolution spectrum of a concentrated solution of the trimer (solution 6) was recorded at 298 K; using Gaussian resolution enhancement, the signals at 9996.7 and 9962.1 ppm were found to be split into a triplet (1:2:1) and a doublet (1:1), respectively; see Figure 2. The observed spin–spin coupling was interpreted in terms of an AX_2 spin system ($I(^{103}Rh) = {}^1/_2$) in which A gives rise to a triplet and the two equivalent X nuclei give rise to a doublet. The three alternative structures shown for the trimer,[5] the "linear" isomer **2**, the "bent" isomer **3**, and the "cyclic" isomer **4**, are all compatible with the observed ^{103}Rh NMR spectrum.

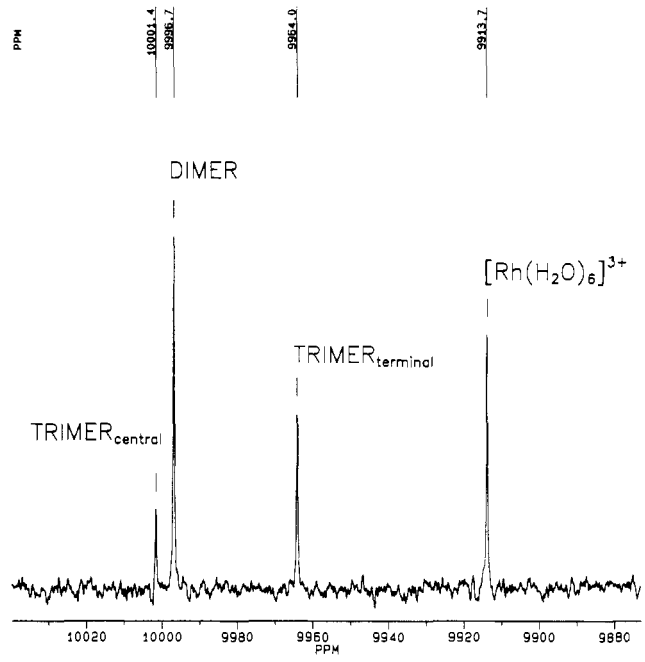

Figure 1. ^{103}Rh NMR spectrum of a nonequilibrium solution containing $[Rh(OH_2)_6]^{3+}$, the dimer, and the trimer (solution 5), recorded at 298 K.

The parameters used for ^{103}Rh NMR measurements were chosen[11] to give maximum sensitivity for aqueous $[Rh(OH_2)_6]^{3+}$, for which the spin–lattice relaxation time (T_1) was determined to 25 s. Differences in the T_1 values between the two types of ^{103}Rh nuclei in the trimer could result in an error in their NMR intensity ratio. However, unreasonably large differences would be required[11] to give an apparent peak intensity ratio, A:X = 1:1 or 1:3. Thus, the splitting pattern and the observed intensity ratio (A:X = 1:2) between the two signals allowed us to confirm both the nuclearity and the AX_2 structure of the trimer. The measured two-bond coupling constant is $^2J_{Rh,Rh}$ = 1.5 Hz; see Figure 2. To our knowledge, this is the first measured Rh–Rh two-bond spin–spin coupling constant. The previously reported one-bond Rh–Rh coupling constants, $^1J_{Rh,Rh}$ = 4–17 Hz,[12] were

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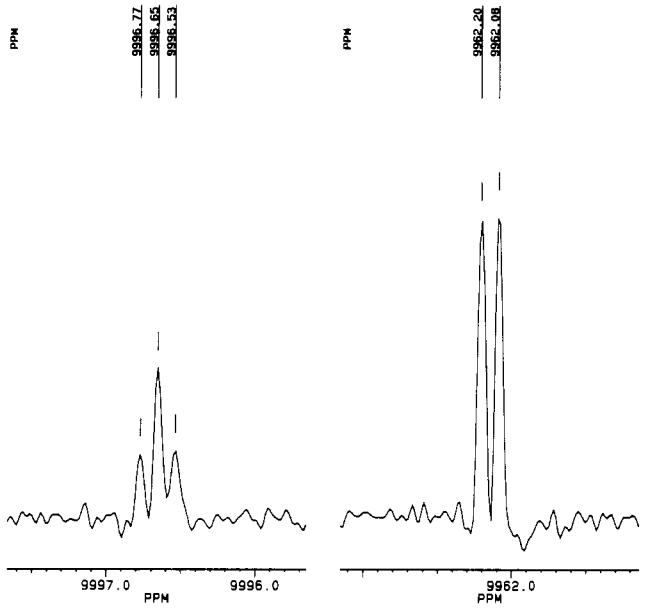
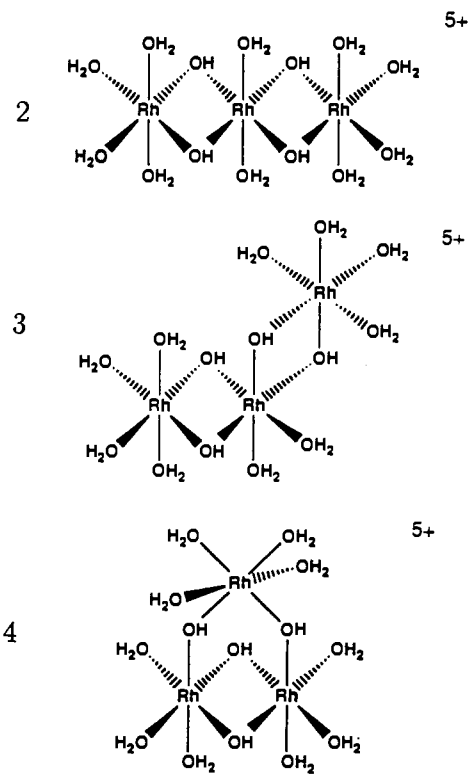


Figure 2. Expansion of the ^{103}Rh NMR spectrum of a solution containing the trimer (0.56 g of hydroxide of fraction 3 in 2.5 mL of 3 M $HClO_4$) after Gaussian resolution enhancement showing the splitting of the signals due to two-bond spin–spin coupling between the terminal and central ^{103}Rh nuclei. The measured coupling constant is $^2J_{Rh,Rh}$ = 1.5 Hz.



obtained for species containing rhodium in lower oxidation states, where direct Rh–Rh bond formation is possible.

^{17}O NMR Studies. The ^{17}O NMR spectra recorded at 308 K for three aqueous solutions containing $[Rh(H_2O)_6]^{3+}$, the dimer, and the trimer (natural abundance of ^{17}O), respectively, are summarized in Figure 3.

By integration of the ^{17}O signals from the ClO_4^- ion, bulk water, and coordinated H_2O (−141.8 ppm) in the spectrum of $[Rh(H_2O)_6]^{3+}$ (solution 1; see Figure 3A), the hexacoordination in the first hydration sphere of rhodium(III) could be confirmed from the known total concentrations. The observed chemical shift for coordinated H_2O in $[Rh(OH_2)_6]^{3+}$ is in good agreement with a previous measurement of the ^{17}O NMR chemical shift of

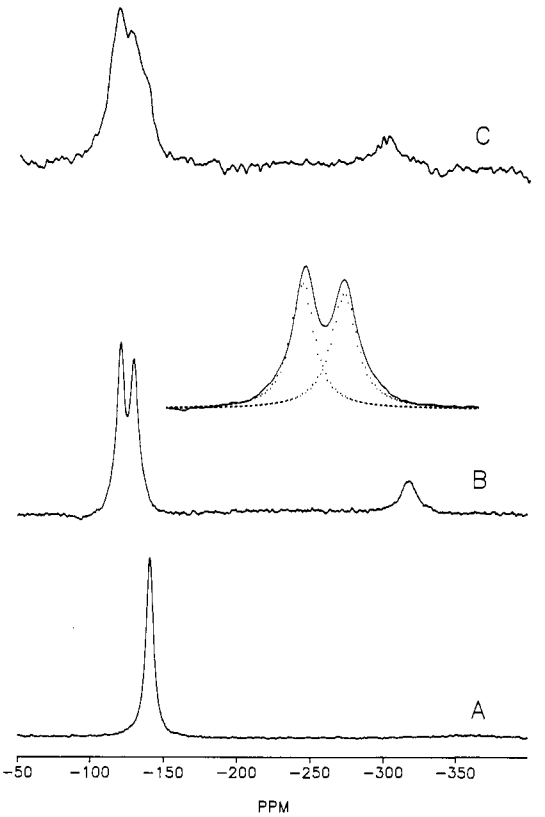


Figure 3. Summary of the natural-abundance ^{17}O NMR spectra recorded at 308 K for (A) $[Rh(OH_2)_6]^{3+}$ (solution 1), (B) the pure dimer (solution 2), and (C) the pure trimer (solution 6). Lorentzian line shapes fitted to the coordinated H_2O region of the dimer are inset in part B. Peaks due to the ClO_4^- anion (+294 ppm) and bulk water (~8 ppm) are not shown. All spectra have been corrected for baseline roll by polynomial fitting.

water coordinated trans to water (−141 ppm) in *cis*/*trans*-$[RhCl_2(OH_2)_4]^+$ complexes (−99 ppm trans to Cl).[13] Although a well-defined second hydration sphere of hydrogen-bonded water molecules is formed around the highly polarizing rhodium(III) ion,[14,15] these oxygen atoms are in rapid exchange with bulk water on the time scale of the ^{17}O NMR experiment and are therefore not observed as a separate ^{17}O NMR signal.

The ^{17}O NMR spectrum of the dimer (solution 2) consists of two signals in the coordinated H_2O region (−122.2 and −130.6 ppm; see Figure 3B), tentatively assigned (by analogy with the ^{17}O NMR spectrum of the *cis*/*trans*-$[RhCl_2(OH_2)_4]^+$ complexes above) to H_2O coordinated cis and trans, respectively, to the plane of the double hydroxo bridge.

Lorentzian curve shapes were fitted to the spectrum of the dimer using the LabCalc program.[16] The intensity ratios between the signals due to coordinated H_2O and bridging OH, 4.2 (±0.4):1, and between the two signals from coordinated H_2O, 1.0 (±0.1):1, are compatible with the bis(μ-hydroxo)-bridged dimeric structure **1** in solution. The intensity ratio of ^{17}O NMR signals from coordinated H_2O has been used to establish the solution structure of the analogous bis(μ-hydroxo) Ir(III) dimer.[3] The structural unit proposed above for the rhodium(III) dimer has previously been found in the solid bis(μ-hydroxo) Rh(III) and

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(16) LabCalc, Galactic Industries Corp., 395 Main St., Salem, NH 03079-9891.

Cr(III) dimers[1,6] and more recently in the crystal structure of the heterometallic Rh(III)–Cr(III) bis(μ-hydroxo) dimer.[17]

The strong kinetic trans-activating effect of the hydroxo ligand is well established.[18] It was reasoned that a bridging OH ligand ought to have a similar trans-activating effect, and hence H_2O molecules coordinated trans to the plane of the bis(μ-hydroxo) bridge should be more labile than their cis counterparts. In order to test this assumption, the solution containing the dimer was enriched to double the total ^{17}O content, and after equilibration at 298 K for 100 h, the ^{17}O NMR spectrum was recorded. The enrichment procedure was then repeated with a further doubling of the total ^{17}O content, and the ^{17}O NMR spectrum was recorded after 24-h equilibration. After both enrichments, comparison of the intensities of the signals from the coordinated H_2O and bridging OH groups using the ClO_4^- signal as an internal standard showed that (1) the total intensity of the coordinated H_2O corresponded to the expected $H_2{}^{17}O$ concentration at equilibrium and (2) the bridging OH groups were not enriched in ^{17}O. Enrichment of the ClO_4^- ion was not expected on the basis of the long oxygen lifetime in this oxyanion. No selective enrichment of the signals from coordinated H_2O was observed, thus preventing assignment of water coordinated cis or trans to the OH groups on the basis of the kinetic trans effect. Moreover, in the crystal structure of the bis(μ-hydroxo)-bridged dimer,[1] no significant difference was observed in the Rh–O bond lengths between the cis- and trans-coordinated H_2O molecules. The observed lability of both types of coordinated H_2O in the dimer is remarkable when compared to the very slow rate of exchange in $[Rh(OH_2)_6]^{3+}$.[19] The fact that no noticeable enrichment of oxygen occurred in the bridging OH groups reflects the stability of the bis(μ-hydroxo) bridge.

Two ^{17}O NMR signals were observed in the spectrum of the trimer (solution 6, Figure 3C), a broad complex band at −118 ppm and a single peak at −303 ppm, which have been assigned by analogy with the bis(μ-hydroxo)-bridged dimer and the hexaaquarhodium(III) ion as resulting from oxygen in coordinated H_2O and bridging OH groups, respectively. By inspection of structures **2**–**4**, the following maximum number of ^{17}O NMR signals can be expected: 3, 3, and 4 in the coordinated water region and 1, 2, and 2, respectively, in the bridging OH region. Fourier deconvolution[16] was used to synthetically narrow the line widths of the overlapping peaks in the coordinated water region, resulting in three resolved peaks. The broader signal due to bridging OH was satisfactorily fitted with a single Lorentzian line form (Figure 3C). These observations are consistent with the linear structure **2**. However, due to uncertainties caused by the pronounced baseline roll and the large line widths, the alternative structures **3** and **4** cannot be completely excluded on the basis of this spectrum.

Two distinct regions have been observed for signals due to oxygen coordinated to rhodium(III): (1) coordinated H_2O between −118 and −142 ppm, with the lower limit corresponding to H_2O in the first hydration sphere of $[Rh(OH_2)_6]^{3+}$; (2) bridging OH at −303 and −320 ppm. The assignment of the former region to coordinated H_2O is supported by similar observations for Ir(III) species: ^{17}O NMR signals due to coordinated water in the monohydroxo-bridged dimer at −145 ppm, in the dihydroxo-bridged dimer at −137 and −143 ppm, and in the hexaaquairidium(III) ion at −152 ppm.[3] However, no signals due to bridging OH were observed for the Ir(III) system, possibly since spectra were only recorded between 1000 and −200 ppm. In contrast, for the bis(μ-hydroxo)-bridged Mo(III) dimer, the signals for cis- and trans-coordinated H_2O and bridging OH are observed at −42, −19, and 124 ppm, respectively. The large differences in the chemical shifts of the bridging OH groups in the Mo(III) and Rh(III) dimers is probably related to their different bonding characters; in the Mo(III) dimer, a direct Mo–Mo interaction is believed to occur.[20]

^{1}H NMR Studies. The $[Rh(OH_2)_6]^{3+}$ Cation. At room temperature, the ^{1}H NMR spectrum of an aqueous solution containing $[Rh(OH_2)_6]^{3+}$ consists of single broad signal, since the protons in the first hydration sphere of rhodium(III) are in rapid exchange with the bulk water protons on the ^{1}H NMR time scale. Upon addition of acetone, the solution can be cooled without freezing until the protons of the first hydration sphere enter the slow-exchange regime to give a signal separate from the bulk water signal. As well as preventing freezing at low temperature, the addition of acetone contributes to a decrease in the proton exchange rate by reducing the bulk, or noncoordinated, water concentration.[21] For a solution of $Rh(ClO_4)_3{\cdot}6H_2O$ without excess water in pure acetone-h_6, two spectral features were observed in the slow-exchange regime at 210 K in addition to the acetone signal at 2.0 ppm: (1) a broad signal at 5.3 ppm, which was assigned to protons in bulk water molecules; (2) a complex set of signals centered at 9.2 ppm, which were attributed to protons of coordinated H_2O in the first hydration sphere of rhodium(III). The fact that a bulk water signal was observed in this solution provides evidence for ligand exchange of water by acetone in the first coordination sphere of rhodium(III). Hence, in addition to the signals from H_2O in the $[Rh(OH_2)_6]^{3+}$ ion, we observed signals probably originating from H_2O coordinated cis and trans to acetone in complexes of the type $[Rh(OH_2)_{6-n}(OC(CH_3)_2)_n]^{3+}$. When more water was added, the ^{1}H NMR spectra showed a shift in complex distribution in favor of the hexaaquarhodium(III).

A low-temperature spectrum of $Rh(ClO_4)_3{\cdot}6H_2O$ in acetone-h_6 with D_2O added, such that $(H,D)_2O_{tot}$:Rh $\sim$ 26, is given in Figure 4A. A pair of signals are observed in the coordinated water region, the relative intensities of which were found to vary with the H_2O:D_2O ratio. It was concluded that these signals (9.19 and 9.02 ppm) originated from coordinated HDO and H_2O molecules, respectively, in the first hydration sphere of the hexaaquarhodium(III) ion. The signal due to protons in bulk water is observed at 5.3 ppm. Similar results have been obtained for hexaaquaaluminum(III), where the isotopic shift between signals from coordinated HDO and H_2O was 0.07 ppm,[22] again with HDO at higher chemical shifts than H_2O. In the present case the isotopic shift is larger, 0.17 ppm. As in the aluminum(III) system, an exchange of H and D was observed between the solvent acetone and water in the first hydration sphere of the cation (and finally the bulk water).

The Dimer and Trimer. ^{1}H NMR spectra of a solution of the dimer in acetone-d_6/$DClO_4$ (solution 8) were recorded as a function of temperature. Sufficient $(H,D)_2O$ was added, as judged from the coordinated water signals, to ensure that no direct coordination of acetone occurred. We can thus assume the first coordination sphere around the dimer in the mixed solvent to be representative of that in a true aqueous solution. At 240 K, in addition to signals from protons in acetone (2.0 ppm) and bulk water (6.3 ppm), a split signal due to an HDO/H_2O isotopic pair was observed at 8.2 ppm, from slowly exchanging protons in either cis- or trans-coordinated water molecules in the dimer. When the solution was cooled to 220 K, a new signal was observed at 3.6 ppm. This signal did not show isotopic splitting and can therefore be assigned to the bridging OH groups (bridging OD gives no signal in ^{1}H NMR). When the solution was further cooled to 190 K, a second isotopically split signal, the cis or trans counterpart to the coordinated water signal previously observed

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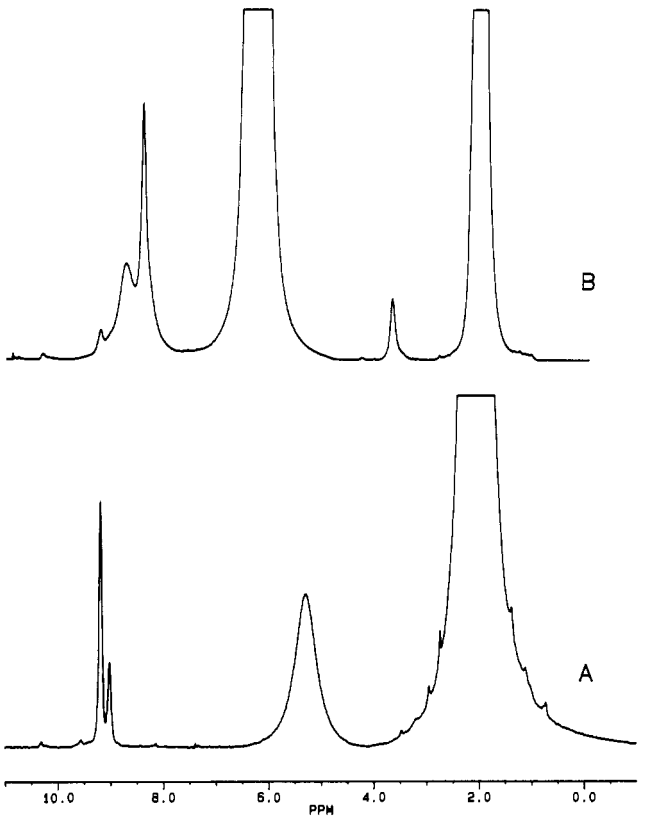

Figure 4. ^{H} NMR spectra recorded at 215 K for (A) $Rh(ClO_4)_3 \cdot 6H_2O$ in acetone-h_6 with added D_2O (solution 7) and (B) the dimeric hydroxide dissolved in $DClO_4$/acetone-d_6 (solution 8). The spectra are referenced to internal acetone at 2.04 ppm.

at 8.2 ppm (now at 8.4 ppm), was resolved at 8.7 ppm. The bridging OH signal was shifted to 3.7 ppm. Thus, the two types of coordinated water protons appear to have different rates of exchange with the bulk water, with bridging OH protons exchanging at an intermediate rate. The ^{1}H NMR spectrum at 190 K is given in Figure 4B. Signals corresponding to isotopic pairs were identified by recording solutions with varying HDO:H_2O ratios, showing that the split signals for coordinated water in the dimer follow the same order as observed for hexaaquarhodium(III), with HDO protons at higher chemical shifts than H_2O. The ^{1}H NMR chemical shifts given for coordinated water in the dimer (Figure 4B) refer to the HDO isotopomer. The minor isotopic-pair signal at 9.2 ppm probably results from HDO in the hexaaquarhodium(III) ion, present as a degradation product in these acidic solutions, since its relative intensity was found to vary for several duplicate solutions. In the above experiments, it was not possible to differentiate between ^{1}H NMR signals due to cis- and trans-coordinated water on the basis of their relative intensities, since they are present in equal numbers in the dimer.

Solutions of the trimer with sufficiently high water:acetone ratios to prevent coordination of acetone to the cation froze during low-temperature ^{1}H NMR experiments. However, for solutions with lower water:acetone ratios, measurements could be performed at 220 K. A complex signal centered at ~8.4 ppm was observed from the coordinated water in the trimer, with splitting due to direct coordination of acetone to rhodium(III), in analogy with the hexaaquarhodium(III) ion. However, a more useful observation for the structural interpretation of the trimer was that only a single signal due to bridging OH was observed (4.3 ppm).

The low-temperature ^{1}H NMR signals due to protons in the trimer, dimer, and hexaaquarhodium(III) ions can be summarized as follows: (1) HDO and H_2O in the first hydration sphere of hexaaquarhodium(III) at 9.19 and 9.02 ppm, respectively; (2) HDO coordinated to rhodium(III) oligomers from 8.4 to 8.7 ppm; (3) bridging OH at 3.7 ppm (dimer) and 4.3 ppm (trimer). In comparison, signals for HDO and H_2O in hexaaquaaluminum(III) have been observed at 10.2 ppm, signals for water in oligomeric species from 8 to 9.5 ppm, and signals for bridging OH at ~4.8 ppm.[21] The observation of the ^{1}H NMR signals of bridging OH in the rhodium(III) and aluminum(III) systems at lower chemical shifts than that of the free hydroxide ion is indicative of an increased electron density around the proton in the bridging ligand.

The Structure of the Rhodium(III) Trimer. The observed ^{103}Rh NMR spectra of the trimer indicate that only a single AX_2 isomer is present; the narrow signals and the demonstrated kinetic inertness of the bis(μ-hydroxo) bridge for the dimer exclude the possibility of fast intramolecular rearrangement between the three possible isomeric forms of the trimer: **2**–**4**. On the basis of the combined experimental evidence from ^{1}H and ^{17}O NMR studies, which indicate the presence of only one type of OH bridge, we conclude that the probable structure for the trimer is the linear bis(μ-hydroxo)-bridged isomer, **2**. There have been no previous observations of the proposed linear isomer **2**, whereas the bent isomer **3** and the cyclic isomer **4** have been observed in the solid state, though mostly in combination with multidentate ligands, which can be expected to pose steric restrictions on the resulting structures.[5] We have so far failed to obtain a suitable solid phase of the trimer for a decisive crystallographic investigation.

The hydrated metal ions of rhodium(III) and chromium(III) have been shown to be isostructural in aqueous solution,[14,15] and in the present study the hydrolytic dimers are found to have comparable solution structures. Therefore, the difference in the trimers, where rhodium(III) appears to form a linear bis(μ-hydroxo)-bridged structure and chromium(III) a "compact" triangular structure, is unexpected. However, in preliminary acid cleavage and dissolution experiments of hydrated rhodium(III) oxide followed by ^{103}Rh NMR, the trimer was not found to be present in significant concentrations.[15b] The dominant species was found to be the dimer, which slowly degraded to the monomer. In contrast, the trimer of chromium(III) has been found to be stable to acid cleavage.[23] These observations support the proposed structural differences for the trimeric species.

Conclusions

The combination of chromatographic separation of metastable Rh(III) species, followed by ^{103}Rh, ^{17}O, and ^{1}H NMR studies on concentrated solutions, has allowed us to determine the structure of the bis(μ-hydroxo)-bridged rhodium(III) dimer **1** and to propose the linear structure of the bis(μ-hydroxo)-bridged rhodium(III) trimer **2** in aqueous solution. The methods used could be extended to characterize the tetramer and higher hydrolytic oligomers, although solutions containing these species have proved difficult to obtain in sufficiently high concentrations for ^{103}Rh and ^{17}O NMR.

Acknowledgment. We acknowledge the Swedish Natural Science Research Council (NFR) for continuing financial support and a research studentship (M.C.R.) OKs Miljöstiftelse for a supporting grant, the Swedish Institute for a fellowship (I.T.), and Dr. István Bányai for stimulating discussions.

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