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Hydrolytic polymerization of rhodium(III). Characterization of various forms of a trinuclear aqua ion

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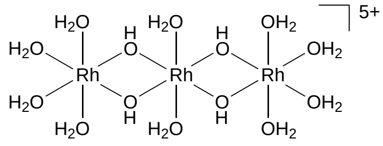
Solution studies of a trinuclear rhodium(III) aqua ion, using a variety of solution techniques (NMR, UV/VIS spectroscopy, charge per Rh determination and elution behaviour) have shown that this oligomer can exist in several structural forms. The form isolated, by ion-exchange chromatography following aging of Rh^{3+} solutions in base, does not have a linear (**1**) or bent (**2**) arrangement of rhodium(III) centres but consists of a triangular arrangement of such centres linked to each other by one μ-OH bridge (**4**). The fact that **4** exhibits two ^{103}Rh NMR signals at δ 9964 and 10 000 in a 2 : 1 ratio is rationalized in terms of the stabilization of a conformation with two rhodium environments through strong hydrogen-bonding between a terminal H_2O or OH ligand and a μ-OH bridging group. On heating this form is transformed into a new ion (**3**) which has a different UV/VIS spectrum and two ^{103}Rh NMR signals at δ 9671 and 9841 in a 1 : 2 ratio. The structure of this form is proposed to consist of a triangular arrangement of metal atoms, two magnetically equivalent rhodium(III) centres linked together by two μ-OH bridges and each linked to the third Rh^{III} *via* a single μ-OH bridge. The low pK_{a1} for this ion of 0.5 ± 0.1 is attributed to the formation of a strong hydrogen-bond between one of the μ-OH groups bridging the two equivalent rhodium(III) centres and the terminal OH group generated by deprotonation. The existence of a hydrogen-bond interaction in both **3** and **4** has literature precedent. At high pH, **3** is transformed into a new aqua ion, **5**, which exhibits a single ^{103}Rh NMR signal at δ 10 049 and a different UV/VIS spectrum to that of **3** and **4**. This is interpreted in terms of a symmetric structure in which the three rhodium(III) centres are linked by a single μ_3-OH group and pairs of Rh atoms are further linked by a μ-OH bridge. A variable-pH and -temperature kinetic study revealed that **4** undergoes an irreversible intramolecular condensation process which produces **3** or **5**, depending on the pH. The increase in rate with pH is consistent with the existence of two pathways, attributable to the reaction of singly and doubly deprotonated forms of **4**. The rate increase of *ca.* 100 fold matches those observed for related chromium(III) systems.

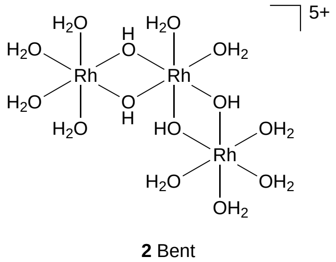
Recent studies of the polymerization of $[Rh(H_2O)_6]^{3+}$ have found that rhodium(III) oligomers form on addition of an excess of base to aqueous solutions of $[Rh(H_2O)_6]^{3+}$ and, following addition of acid to quench the polymerization process, can be separated using cation-exchange chromatography.[1,2] Solution and single-crystal X-ray studies have shown that a bis(μ-hydroxo) dimer is one of the oligomers formed.[1]

Glaser and co-workers[2] have taken advantage of the diamagnetic nature of Rh^{III} and have applied ^{103}Rh, ^{17}O and ^{1}H NMR spectroscopy to probe the structure of the products of polymerization of $[Rh(H_2O)_6]^{3+}$. The spectra of the rhodium(III) dimer were entirely consistent with the solid-state crystal structure of this oligomer. The ^{103}Rh NMR spectrum of a second oligomer isolated from reaction mixtures exhibited two signals in the ratio of 1 : 2 and has been proposed to be trinuclear with one of the three possible structures **1**–**3**. Oxygen-17 and ^{1}H NMR spectra were used to differentiate between these structures. A broad complex signal due to co-ordinated water observed at δ −118 in the ^{17}O NMR spectrum was resolved into three signals using Fourier deconvolution methods and it was concluded to indicate the presence of three water environments in the ion. Only one signal due to the bridging hydroxides was observed. Proton NMR studies of the trimer at 220 K showed a complex signal centred at δ ≈ 8.4 due to co-ordinated water and a single peak at δ 4.3 due to the bridging hydroxide. On the basis of this evidence the trinuclear rhodium(III) aqua ion was proposed to have a linear arrangement of Rh atoms (**1**).[2]

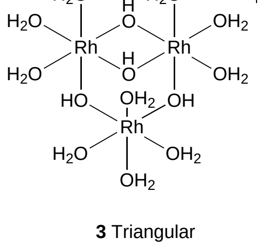
We report here our own investigations of the solution properties and the kinetics of intramolecular rearrangement of the trinuclear rhodium(III) aqua ion. These investigations have led to the conclusion that this aqua ion can exist in three forms, see Scheme 1, **3**–**5**, all based on the triangular arrangement of rhodium(III) centres.



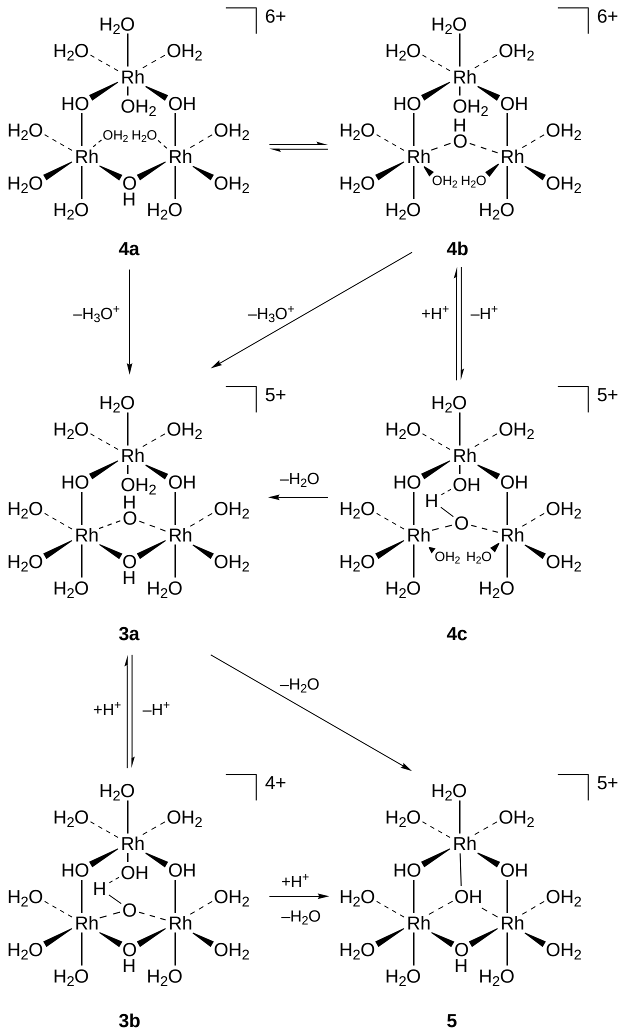
1 Linear



2 Bent



3 Triangular



Scheme 1 Interconversion between the triangular forms of the trinuclear rhodium(III) aqua ion

Experimental

Materials

The compound $RhCl_3 \cdot xH_2O$ prepared by the method of Dickson *et al.*[3] was converted into $[Rh(H_2O)_6][ClO_4]_3 \cdot 3H_2O$ by the method of Ayres and Forrester.[4] All materials were of LR grade or better and used as received, although for quantitative measurements AR reagents were used. Sodium perchlorate solutions of known concentration were made by neutralizing standardized solutions of NaOH with $HClO_4$. Rhodium analyses were carried out by the method of Ayres *et al.*[5]

Instruments and methods

The Cary 3 spectrophotometer system used for spectral measurements and kinetic studies was described previously[6] as has the procedure for measuring pH and for obtaining pH titration data, used to determine pK_a values.[7] Rhodium-103 NMR spectra were recorded on either a Bruker AM400 (298 K) spectrometer using a dedicated low-frequency probe tuned to 12.7 MHz or a DRX500 spectrometer (303 K) using a standard broadband probe tuned to 15.8 MHz. They were recorded unlocked and referenced to an external sample of $[Rh(H_2O)_6]^{3+}$ set to δ 9913.

Syntheses

Compound 4. Rhodium(III) oligomers were prepared by the method of Cervini *et al.*[1] and separated by cation-exchange chromatography on Sephadex SP C25. The third fraction (**4**) obtained in a yield of *ca.* 25% has been shown to be trinuclear by Glaser and co-workers.[2] The synthesis and characterization of the 'active' hydroxide of this form of the trinuclear rhodium(III) aqua ion has been reported elsewhere.[8]

Compound 3. On heating in acidic solution ($[HClO_4]$ 0.01–1.0 M, $T = 353$ K) for 24 h compound **4** is converted into **3**. Chromatographic analysis of these solutions showed only one band indicating total conversion into **3** and no evidence for cleavage to smaller oligomers or polymerization to higher oligomers. A more convenient synthesis of **3** uses the 'active' hydroxide of **4** as starting material. A sample of this hydroxide was dissolved in 1 M $HClO_4$ and the solution heated in an oil-bath at 353 K for 24 h to effect conversion into **3**. Cation-exchange chromatography of the resulting solution showed one main band. Small amounts (*ca.* 4%) of higher oligomers, present as impurity in the starting 'active' hydroxide (purity 96%), remained at the top of the column.

Elution behaviour and charge per Rh of rhodium(III) trimers

The elution behaviour of forms **3** and **4** of the trinuclear rhodium(III) aqua ion on Sephadex SP C25 was compared to that of the chromium(III) dimer, $[Cr_2(OH)_2(H_2O)_8]^{4+}$, and 'trimer', $[Cr_3(OH)_4(H_2O)_9]^{5+}$, as described by Cervini *et al.*[1] for rhodium(III) dimer. In both cases the rhodium(III) aqua ion was found to elute with or marginally after chromium(III) trimer but certainly after chromium(III) dimer. These experiments suggest a charge of around 5+ for **3** and **4**. This method of elution comparison has been successfully used to determine the charge of two iridium(III) dimers.[9] The charge per Rh of both forms of the aqua ion was determined as described in the literature for the rhodium(III) dimer.[1] The values averaged over three determinations were 1.65 ± 0.08 and 1.85 ± 0.08 for **3** and **4**, respectively.

pK_a Determination

The pK_a values for compound **4** were determined at 25 °C and $I = 1.0$ M ($NaClO_4$) by titration against standardized NaOH using a computer-controlled autoburette.[7] Titrations were started at pH ≈ 2 and stopped before precipitation of the 'active' hydroxide commenced (pH ≈ 5). The K_a values were obtained by fitting the potentiometric data using a standard equation allowing for three acid-dissociation processes and using a non-linear regression routine.[7] The pK_{a1} for **3** was determined from changes in the UV/VIS spectrum with pH at 228 nm.

Kinetic experiments

Solutions of compound **4** suitable for kinetic studies were prepared as described previously[1,2] except that elution from ion-exchange columns was carried out with 0.02 M $HClO_4$–1.98 M $NaClO_4$. The resulting solution was then diluted with water (1 : 1) to give a solution with $I = 1.0$ M (I was confirmed by literature methods[10]). Reaction mixtures were prepared at the desired temperature (328.2–348.2 K) by mixing known volumes of the trinuclear rhodium(III) aqua ion stock solution ($I = 1.0$ M) with a series of solutions containing varying proportions of $NaClO_4$. The final conditions were [trimer] = (1.7–6.7) × 10^{-4} M, $[HClO_4] = 0.002$–0.9 M and $I = 1.0$ M. In the analysis of kinetic data the final acid concentration was corrected for the temperature-dependent expansion of the solvent.

Initially the conversion of compound **4** into **3** or **5** was followed in the 200–500 nm range. The final spectrum of the solution was shown to be identical to that of pure solutions of **3** or **5**, the products observed at the lower and higher pH values, respectively. Cation-exchange chromatography showed that neither cleavage to smaller oligomers nor polymerization to higher oligomers had occurred. Parallel ^{103}Rh NMR spectral measurements over the same pH range but higher total $[Rh^{III}]$ confirmed the conversion of **4** into **3** or **5**. Absorbance data

Table 1 The UV/VIS spectral data for rhodium(III) aqua ions

Compound	λ_1/nm	ε_1/M^{-1} cm^{-1}	λ_2/nm	ε_2/M^{-1} cm^{-1}
$[Rh(H_2O)_6]^{3+}$ *	396	62	311	66
Dimer *	408	96	242	1750
3 (1 M $HClO_4$)	404	112	228	2400
(0.04 M $HClO_4$–1 M $NaClO_4$)			227	2230
4 (1 M $HClO_4$)	408	102	248	1970
5 (0.001 M $HClO_4$–1 M $NaClO_4$)	406	170	244	2200

* Ref. 1.

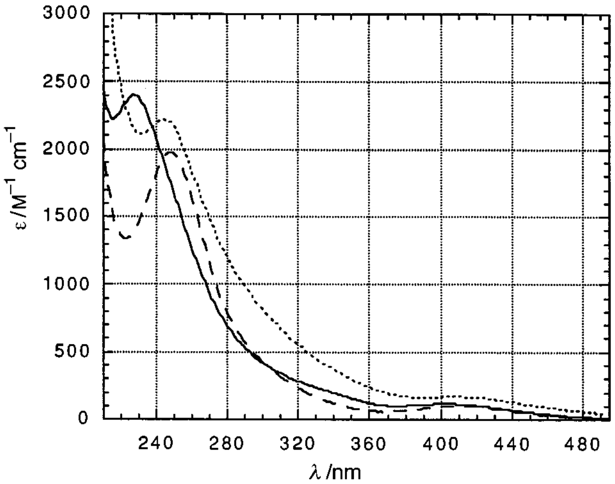


Fig. 1 The UV/VIS spectra of the three forms of the trinuclear rhodium(III) aqua ion, **3** (——), **4** (– – –) and **5** (------). The spectra of **3** and **4** were measured in 1 M perchloric acid while that of **5** was measured at pH ≈ 3 in sodium perchlorate medium. Note that **3** is converted into **5** at pH ≈ 3 (see text)

were extracted at various wavelengths and analysed as described below. The observed rate constants, k_{obs}, were found to be independent of λ and [**4**]. Consequently, the reaction was followed at 250 nm where increases in absorbance, of *ca.* 0.1–0.4 units, were observed for the range of [**4**] used. Data were collected over at least 5 half-lives and the absorbance *vs.* time data fitted by the expression $A_t = A_\infty - (A_0 - A_\infty)e^{-k_{obs}t}$, using a least-squares procedure. In all cases, A_0, A_∞ and k_{obs} were determined from the analysis and excellent fits of the data were obtained.

Results and Discussion

Analytical data for the forms of the trinuclear rhodium(III) aqua ion

The triangular form of the trinuclear aqua ion, **4**, is conveniently isolated from rhodium(III) oligomer mixtures by cation-exchange chromatography. The ^{103}Rh NMR spectrum recorded in 1 M $HClO_4$ was identical to that obtained by Glaser and co-workers[2] with two peaks at δ 10 000 and 9964 in the ratio 1 : 2 and confirms that the oligomer is that characterized previously. No change in NMR spectrum attributable to the presence of another form of the trinuclear aqua ion, with possibly a different degree of deprotonation, was observed in the [H^+] range 0.1–2 M. The UV/VIS spectrum of **4** (Fig. 1, Table 1) is similar to that of the rhodium(III) dimer[1] but is clearly different to that of $[Rh(H_2O)_6]^{3+}$.[11] As for the rhodium(III) dimer, the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition is observed at lower energy (408 nm) than for $[Rh(H_2O)_6]^{3+}$. The other d–d transition expected at *ca.* 300 nm is masked by a more intense band at 248 nm, assigned to an OH→M charge transfer.[1]

A comparison of the elution behaviour of compound **4** with that of known chromium(III) oligomers suggests a charge of 5+. When combined with a charge per Rh of 1.85 ± 0.08 a nuclearity of 2.75 ± 0.12 is obtained indicating that the oligomer is trinuclear. On the other hand, a charge of 5.55 ± 0.24 is obtained if a trinuclear species is assumed. Such measurements provide a guide to the charge and/or nuclearity but they can be influenced by deprotonation processes if these occur at low pH (⩽2). The reproducible and higher than expected charge per Rh (expected 1.67), together with the fact that **4** is converted into other trinuclear forms, suggests that this could be the case here. Although there is no spectral change in the range pH 0–2 which would suggest deprotonation is occurring, this does not discount the possibility that this species exists in the monodeprotonated form in this pH range and thus would elute with other 5+ ions. Above pH 2 three deprotonation processes are observed for **4**, *viz.* 3.09 ± 0.05, 4.48 ± 0.06 and 6.1 ± 0.1. The first two constants are significantly lower than those of the chromium(III) trimer, in keeping with the generally observed greater acidity of aqua ligands co-ordinated to Rh^{III} rather than Cr^{III},[12,13] while the third matches that of the chromium(III) trimer.[13]

For many chromium(III) oligomers additional evidence supporting their proposed structures was gained from acid-cleavage studies and the analysis of the products of such reactions.[13,14] The attempted cleavage of compound **4** was carried out in 1 M $HClO_4$ at 353 K and gave a single product, **3**, with a UV/VIS spectrum that is different to that of **4**, the dimer and $[Rh(HO_2)_6]^{3+}$. The two absorption maxima have shifted to higher energy relative to **4** (Fig. 1, Table 1). Ion-exchange chromatography showed that neither the rhodium(III) dimer nor $[Rh(H_2O)_6]^{3+}$ formed during any of these experiments (these are the expected products of cleavage regardless of the structure of the trinuclear ion). Indeed, small amounts of dimer and $[Rh(H_2O)_6]^{3+}$ (<10% of total Rh) were found only after heating of the solution at 353 K for prolonged periods (⩾1 week). This means that the trinuclear ion is undergoing a rearrangement that is much faster than cleavage. In addition, the rate of conversion of **4** into **3** or **5** increases with pH (see below), typical of intramolecular bridge formation and not bridge-cleavage processes.[15]

Pure solutions of the new form of the trinuclear rhodium(III) aqua ion, **3**, were obtained by heating solutions of the 'active' hydroxide of **4** in 1 M $HClO_4$ followed by cation-exchange chromatography. The elution behaviour of **3** suggests that it has a charge of 5+. When coupled with a charge per Rh of 1.63 ± 0.08 a nuclearity of 3.1 ± 0.2 is obtained, indicating that this new aqua ion is also trinuclear. In the UV/VIS spectrum of **3** the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition is found at 404 nm and is of similar intensity to that for **4**. A more striking difference is observed in the UV region where the band observed at 248 nm for **4** has shifted to 228 nm for **3**. The intensity of the spectrum of **3** is pH dependent showing a significant drop in ε value with little change in absorption maxima in the range pH 0–1.5. This indicates that **3** is undergoing deprotonation and, therefore, is a moderately strong acid. Indeed pK_{a1} for **3**, determined from the changes in the spectrum with pH, was found to be 0.5 ± 0.1.

The ^{103}Rh NMR spectrum of a pure solution of compound **3** is shown in Fig. 2 along with that of **4** and **5**. The spectrum of **3** exhibits two peaks at δ 9671 and 9841 in a ratio of 1 : 2 {*vs.* $[Rh(H_2O)_6]^{3+}$ at δ 9913}, which indicates that this form of the

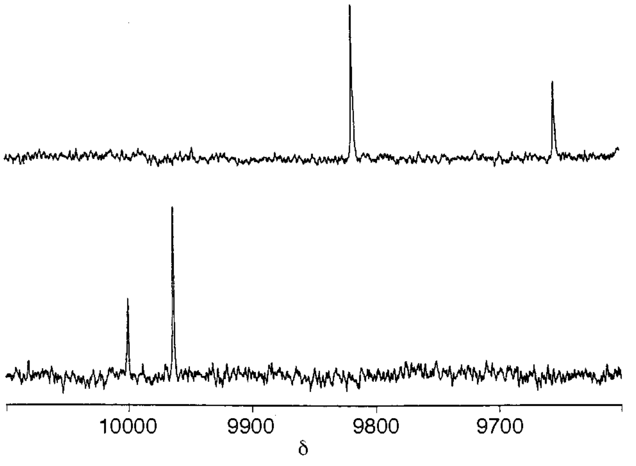


Fig. 2 The ^{103}Rh NMR spectra of pure solutions of compounds **3** (top) and **4** (bottom) measured in 1 M perchloric acid

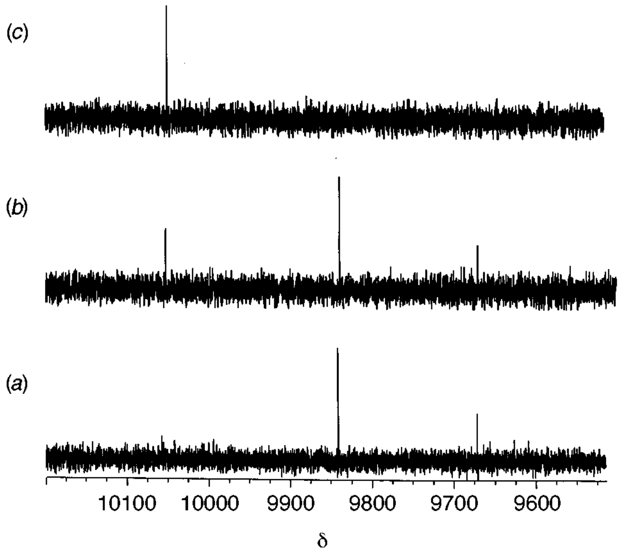
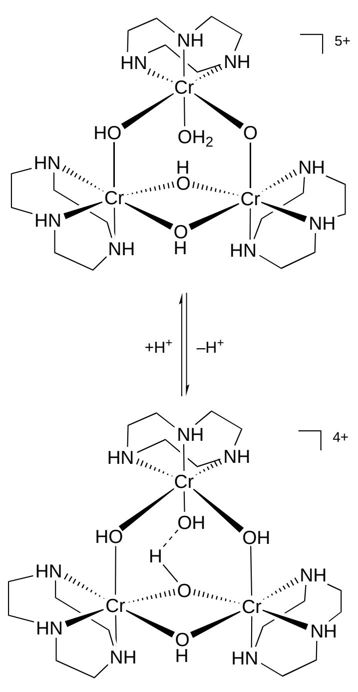


Fig. 3 pH Dependence of the ^{103}Rh NMR spectrum of a pure solution of compound **3** measured in 1 M perchlorate media: (*a*) at pH ≈ 0, only **3** is observed; (*b*) at pH ≈ 2, both **3** and **5** are observed; (*c*) at pH ≈ 3, only **5** is observed

trinuclear aqua ion also has two different rhodium chemical environments. A spectrum of a more concentrated solution, prepared by dissolving the 'active' hydroxide of **4** in 1 M $HClO_4$ and heating at 343 K for 24 h, exhibits these same signals. The pH dependence of the ^{103}Rh NMR spectrum of **3** shown in Fig. 3 provided additional information about the structures of the various forms of the ion. The spectrum run at pH ≈ 2 exhibits signals at δ 9670, 9839 and a weak signal at 10 052 and is consistent with the presence of the initial form of **3** as well as a new form **5**. At pH > 3 the signal at δ 10 049 dominates the spectrum and the other two signals have almost disappeared. Notably, the UV/VIS spectrum of **5** is different from that of the other forms of the aqua ion, showing a strong band at 244 nm ($\varepsilon = 2200\ \text{M}^{-1}\ \text{cm}^{-1}$) rather than at 228 and 248 nm as observed for **3** and **4**, respectively. The rationalization of the analytical data in terms of a triangular, and not linear, arrangement of rhodium(III) centres is detailed below.

Structural forms of the trinuclear rhodium(III) aqua ion 3–5

The analytical and spectroscopic data for the various forms of trinuclear rhodium(III) aqua ion can be interpreted in terms of the structures shown in Scheme 1. We propose that the form of the ion isolated from aged solutions of Rh^{3+} has the three rhodium(III) centres, each linked to the other two by a single μ-OH bridge (**4**). It is the least condensed form of the ion which has a total of three OH bridges linking the three rhodium(III) centres. Two arrangements of this ion are possible, one having the three Rh^{III} equivalent (**4a**) while in the other one Rh^{III} sits directly above the OH bridge linking the other two centres (**4b**) giving rise to two different rhodium(III) environments in a 1 : 2 ratio, as observed in the ^{103}Rh NMR spectrum at δ 10 000 and 9964. Stabilization of **4b** over the more symmetric structure (**4a**) can be rationalized by proposing the formation of a strong hydrogen bond between the OH group linking the two identical rhodium(III) centres and a water ligand on the third, dissimilar centre. A second possibility is the formation of a strong hydrogen bond between a terminal OH group, formed by deprotonation of a water ligand on the dissimilar centre, and the OH group bridging the other two centres (**4c**). Although there is no evidence for deprotonation at pH > 0, a combination of the high charge (6+) coupled with strong hydrogen bonding could cause deprotonation to occur below this pH. Such hydrogen bond stabilization finds precedent in the trinuclear chromium(III) complex, $[Cr_3(tacn)_3(OH)_4(H_2O)]^{5+}$, where tacn = 1,4,7-triazacyclonane.[16] The sole aqua ligand in this complex deprotonates at low pH (<3 when pK_{a1} for similar ions is typically 4–5) and crystallizes as $[Cr_3(tacn)_3(OH)_5]^{4+}$, a complex with a very strong hydrogen bond between the terminal OH group and a bridging OH group (Scheme 2), as is evident from the short O · · · O distance.



Scheme 2 Hydrogen-bond stabilization of $[Cr_3(tacn)_3(OH)_5]^{4+}$

Heating converts compound **4** into a more condensed form, **3**, which also has two rhodium environments, observed in the ^{103}Rh NMR spectrum at δ 9671 and 9841. The extremely slow cleavage of the trinuclear ion to dimer and Rh^{3+} coupled with the retention of nuclearity that accompanies the quantitative conversion of **4** into **3** or **5** indicates that an intramolecular rearrangement is occurring rather than oligomer cleavage or formation. Studies carried out on the chromium(III) system have shown that oligomer formation reactions always produce a mixture of oligomers an not a single product.[17] Furthermore, the fact that the rate of conversion of **4** into **3** or **5** increases with pH (see below) is typical of intramolecular bridge formation and not a bridge-cleavage process.[15] The data are consistent with this form of the ion having structure **3**, in which there is a triangular arrangement of Rh atoms in two environments, and not the previously proposed linear structure (**1**).[2] Thus, the pH-dependent conversion of **4** can be rationalized in terms of the addition of a μ-OH bridge between two of the three Rh

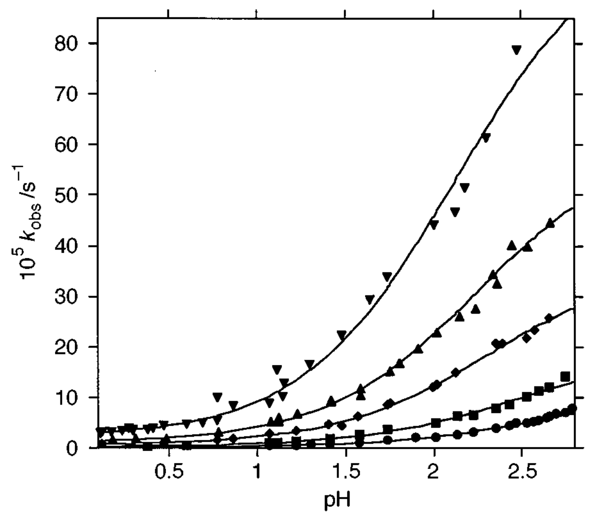


Fig. 4 The pH temperature dependence of k_{obs} for the conversion of compound **4** into **3** studied at I = 1.0 M (perchlorate media): ●, 328.2; ■, 333.2; ◆, 338.3; ▲, 353.2; ▼, 358.2 K; solid lines represent the fitted curves (see text for details)

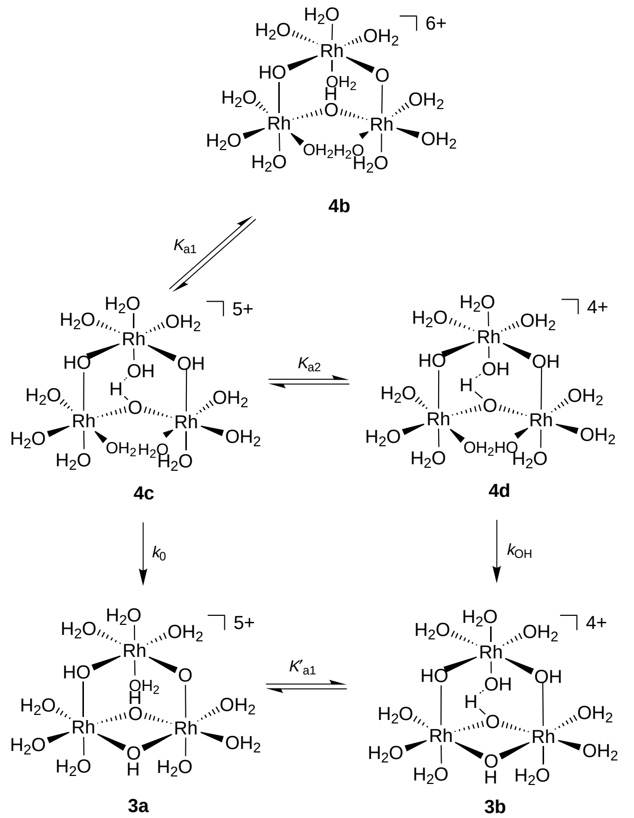
atoms. The remarkably low pK_{a1} of **3** can be attributed to a strong H-bonding interaction analogous to that observed in $[Cr_3(tacn)_3(OH)_5]^{4+}$ (Scheme 2).[16] The low pK_{a1} of **3** lends further support to the proposal that **4**, with a charge of 6+, is a strong acid deprotonating below pH 0. Above pH 2 the conversion of **3** into a species with a single ^{103}Rh NMR signal at δ 10 049, and a different UV/VIS spectrum, is consistent with the formation of a new ion, **5**, with three identical rhodium(III) centres. The proposed structure is the same as that postulated for the chromium(III) trimer.[13,14]

It is interesting that, in acidic solution, reaction at elevated temperatures is necessary to convert compound **4** into **3**, a reflection of the greater inertness of Rh^{III} compared to Cr^{III}.[18–20] At room temperature in alkaline solution this rearrangement must be sufficiently slow to enable isolation of the thermodynamically unstable form, **4**. In fact, exposure of Rh^{3+} solutions to much longer reaction times in base does produce a mixture of **3** and **4** (when the spectrum is measured in 1 M perchloric acid following chromatographic separation), indicating that the conversion can be achieved in base at room temperature but is slower under acidic conditions. Further evidence that **4** is not the thermodynamically stable form of the trinuclear rhodium(III) aqua ion, over the range of conditions examined, comes from the ^{103}Rh NMR spectrum taken at the completion of the reaction converting **4** into **3** in relatively strong acid (≈1 M) which showed no evidence for the presence of **4**.

The interconversion between compounds **3** and **5** is reversible in that **3** is the favored form at low pH (<2) while **5** is favoured at pH > 3. The relative rapidity of this process is, at first sight, surprising but it should be pointed out that similar processes on the chromium(III) tetramer occur on the stopped-flow timescale[15b] and that the accelerations afforded by deprotonation could render these reactions quite rapid.

Kinetics of conversion of compound 4 into 3

The conversion of compound **4** into **3** or **5** has been studied in the range pH 0–3 and at 328.2–348.2 K. Chromatographic analysis of several reaction mixtures after the reaction had proceeded for over 10 half-lives at pH ⩽ 2 and various temperatures gave only one band with the properties of **3** (*e.g.* two ^{103}Rh NMR signals). Thus, the reaction was irreversible under the conditions of study. However, at the higher pH values (>2.2) and temperatures (⩾338 K) traces of higher oligomers were observed indicating that polymerization of the trimer was beginning to occur. In these cases the absorbance continued to increase, albeit extremely slowly, after completion of the reaction. Nevertheless, analysis of the data showed no deviation from a first-order process in [aqua ion] over at least 5 half-lives of reaction.



Scheme 3 Pathways for conversion of compounds **4** into **3**

The increase in k_{obs} with pH (Fig. 4) is typical of a ring-closure reaction whose overall rate generally increase with increasing pH.[15] This has been confirmed to be the case in extensive kinetic studies of chromium(III) oligomers[15] and related binuclear complexes, $[A_4M(\mu\text{-OH})_2MA_4]^{5+}$, where $A_4 = (NH_3)_4$ or (en)$_2$ (en = ethane-1,2-diamine) and M = Cr, Rh or Ir.[20] The conversion of **4** into **3** can be interpreted in terms of the reaction pathways described in Scheme 3, which assumes the first deprotonation of **4** occurs below pH 0 and thus that the form of the aqua ion reacting initially is **4c** (a valid analogous scheme could be formulated assuming monodeprotonation does not occur below this pH). Note that room-temperature NMR studies indicate that the conversion of **3** into **5** is faster than that of **4** into **3** and cannot be rate determining at the temperatures of the kinetic study. The reaction is, therefore, proposed to occur *via* both the mono- (k_0 pathway) and doubly deprotonated (k_{OH}) forms of **4**. The site of deprotonation of **4c** has been assigned to a water ligand on one of the two equivalent rhodium(III) centres, since they have no terminal hydroxo groups. This deprotonation is further proposed to occur at a water ligand that is *trans* to another water ligand, since such water molecules would be expected to be bound more tightly than those *trans* to OH groups. The condensation of **4c** is proposed to involve nucleophilic attack by the terminal OH group at one of the two identical rhodium(III) centres coupled with the release of a co-ordinated water molecule. The major increase in rate with pH has been attributed to the deprotonation of **4c** to give **4d** which then undergoes faster conversion into the closed form. A terminal OH group on one rhodium(III) centre would then preferentially attack the second centre with a terminal OH group since this centre would be expected to be more labile. This proposal is in keeping with previous studies which have shown that deprotonation of co-ordinated water causes substantial accelerations in the rates of: (*i*) water exchange on Cr^{3+}, Rh^{3+}, chromium(III) dimer[7] and rhodium(III) dimer;[21] (*ii*) intramolecular ring-closure reactions of chromium(III) oligomers[15] and closely related systems.[19]

Table 2 Values of k_0, k_{OH}, and K_{a2} for the conversion of compound **4** into **3**

T/K	$10^5\ k_0$/s^{-1}	$10^5\ k_{OH}$/s^{-1}	$10^3\ K_{a2}$/M
298.2			0.81 ± 0.1 *
328.1	0.23 ± 0.02	12.6 ± 0.3	1.93 ± 0.06
333.1	0.03 ± 0.04	19.2 ± 0.7	3.35 ± 0.19
338.2	0.59 ± 0.06	36.8 ± 1.6	4.81 ± 0.31
343.1	1.00 ± 0.04	61.1 ± 6.1	5.60 ± 0.73
348.1	2.1 ± 0.12	104 ± 11	7.5 ± 1.1

* Determined from potentiometric titration and used in the calculation of the thermodynamic parameters shown in Table 3.

Table 3 Activation parameters and rate constants for the conversion of compound **4** into **3** at 298 K

Parameter	k/K_a	$\Delta H^{\ddagger\circ}$/kJ mol^{-1}	$\Delta S^{\ddagger\circ}$/J K^{-1} mol^{-1}
k_0/s^{-1}	3.5×10^{-8}	106 ± 11	−33 ± 34
k_{OH}/s^{-1}	3.5×10^{-6}	94 ± 6	−34 ± 18
K_{a2}/M	8×10^{-4}	28 ± 4	33 ± 12
Water-exchange rates			
$k_{Rh^{3+}}$/s^{-1}	5.6×10^{-9}[a]	134[a]	47[a]
	2.2×10^{-9}[b]	131 ± 23[b]	29 ± 69[b]
$k_{Rh(OH)^{2+}}$/s^{-1}	3.9×10^{-6}[a]		
	4.2×10^{-5}[b]	103[b,c]	
k_{fast} (dimer)/s^{-1}	1.3×10^{-8}[d]	119 ± 4[d]	41 ± 12[d]
k_{fast} (dimer − H)/s^{-1}	3.4×10^{-8}[d]	146 ± 4[d]	140 ± 11[d]
k_{slow} (dimer)/s^{-1}	4.9×10^{-9}[d]	64 ± 9[d]	−150 ± 30[d]
k_{slow} (dimer − H)/s^{-1}	2.7×10^{-8}[d]	102 ± 3[d]	−9 ± 11[d]

[a] Data taken from ref. 13. [b] Data taken from ref. 19. [c] Estimated. [d] Data taken from ref. 21.

The rate law for the conversion of compound **4** into **3** is given by equation (1) where $[\mathbf{4}]_T$ is the sum of the concentrations of

$$-\frac{d[\mathbf{4}]_T}{dt} = k_{obs}[\mathbf{4}]_T; \quad k_{obs} = \frac{k_0 + k_{OH}K_{a2}[H^+]^{-1}}{([H^+]/K_{a1}) + 1 + K_{a2}[H^+]^{-1}} \qquad (1)$$

the aqua ions **4b**, **4c** and **4d** at time t, k_0 the rate constant for conversion of **4c** into **3a**, k_{OH} the rate constant for conversion of **4d** into **3b** and K_{a2} the second acid-dissociation constant of **4**. In analysing the $[H^+]$ dependence of k_{obs}, using weighted least-squares procedures, the data could be fitted extremely well by assuming the first deprotonation occurs well outside the range of $[H^+]$ used. That is, the $[H^+]/K_{a1}$ term is small and the expression for k_{obs} becomes (2). The good fit to the data also

$$k_{obs} = \frac{k_0 + k_{OH}K_{a2}[H^+]^{-1}}{1 + K_{a2}[H^+]^{-1}} \qquad (2)$$

indicates that the conversion of very small amounts of the triply deprotonated form of **4** ($K_{a3} = 3.31 \times 10^{-5}$ M at 298 K), which will be present in the reaction mixtures at the higher pH values used in this study, makes no detectable contribution to the overall reaction rate. The values of k_0, k_{OH} and K_{a2} are listed in Table 2 while the corresponding activation and thermodynamic parameters are listed in Table 3, together with calculated values at 298 K. Thermodynamic constants of this type are scarce for hydrolytic oligomers but the data for **4**, $\Delta H^\circ = 28 \pm 4$ kJ mol^{-1} and $\Delta S^\circ = 33 \pm 12$ J K^{-1} mol^{-1}, are surprisingly similar to those for the chromium(III) dimer ($\Delta H^\circ = 31 \pm 2$ kJ mol^{-1} and $\Delta S^\circ = 35 \pm 5$ J K^{-1} mol^{-1}),[6] while ΔS° for pK_{a1} of the rhodium(III) dimer is significantly different ($\Delta H^\circ = 31.7 \pm 0.5$ kJ mol^{-1} and $\Delta S^\circ = 76 \pm 2$ J K^{-1} mol^{-1}).

The rates of conversion of compound **4** into **3** are slower than all previously studied intramolecular condensation processes involving chromium(III) oligomers,[15] and reflect the relative lability of these metal centres. The increase in rate of almost 100 fold observed for the reaction of **4d** when compared with **4c** indicates that deprotonation significantly enhances the reaction. This rate increase can be attributed either to the provision of a better nucleophile for attacking a second rhodium(III) centre, although such a group is present in **4c** it is likely to be involved in hydrogen bonding, or to labilization of the rhodium(III) co-ordination sphere at which deprotonation occurs. Either of these factors would lead to significant rate enhancements. It might be anticipated that H_2O ligands *trans* to H_2O ligands would be more likely to deprotonate since they are expected to co-ordinate more strongly than those *trans* to OH groups. This argument has been applied previously to rationalize the pK_a values of some chromium(III) oligomers.[13] Moreover, a weak *trans* influence of this type has been observed in the structure of the rhodium(III) dimer.[1]

The rate enhancement resulting from deprotonation of compound **4**, of 100 fold, is similar to those observed for chromium(III) oligomers, where rate enhancements of 50–200 fold have been observed for intramolecular ring-closure reactions and oligomer formation processes.[15] These increases are believed to result from labilization at one metal which facilitates nucleophilic attack of the OH^- on another metal centre. While this is a well established phenomenon on the case of chromium(III) oligomers, where a clear relationship exists between the OH : Cr ratio of the oligomer and the rate of substitution reactions,[7] reports relating to rhodium(III) aqua ions are few. Plumb and Harris,[12] and subsequently Merbach and co-workers,[19] found that water exchange on $[Rh(H_2O)_5(OH)]^{2+}$ is *ca.* 19 000 times faster than on $[Rh(H_2O)_6]^{3+}$. In contrast, deprotonation has been bound to cause smaller accelerations in the water-exchange rates of the rhodium(III) dimer and in the current study. Thus, the effect of the degree of deprotonation of rhodium(III) aqua ions on the rate of hydrolytic processes seems to vary substantially from system to system.

Previous work on chromium(III) oligomers indicates that deprotonation results in a more dissociative mechanism of substitution.[15] The uncertainties in $\Delta S^\ddagger$ for the two pathways for conversion of **4** into **3** make the elucidation of changes in mechanism difficult although it is clear that $\Delta H^\ddagger$ for both pathways is significantly reduced from that found for water exchange on $[Rh(H_2O)_6]^{3+}$.[12,19] Activation parameters for water-exchange studies on Rh^{3+} (in particular the more positive $\Delta V^\ddagger$ values) and the rhodium(III) dimer indicate that the mechanism of substitution becomes more dissociative on deprotonation.[19,21] Surprisingly, the $\Delta S^\ddagger$ values for conversion of **4** into **3** seems to indicate little change in mechanism, although the uncertainties in these values makes it difficult for firm conclusions to be drawn.

Conclusion

Solution studies have shown that the trinuclear rhodium(III) aqua ions can exist in three forms **3**–**5** (Scheme 1) and that, depending on pH, **4** can be converted into either **3** or **5**. Thus, the three forms of the ion have a compact, triangular arrangement of rhodium(III) centres similar to that proposed for the chromium(III) analogue.[13] The greater inertness of Rh^{III}, compared with Cr^{III}, enables the trapping and study of metastable intermediates formed during polymerization and therefore provides additional opportunities in the study of metal-ion polymerization processes. Deprotonation of **4** results in a substantial enhancement in the rate of intramolecular condensation similar to those observed in the reactions of chromium(III) oligomers.[15]

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