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Synthesis and characterization of rhodium(III)–chromium(III) heterotrinuclear aqua ions

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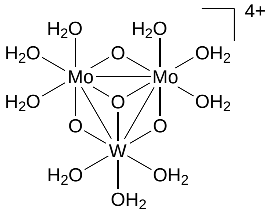
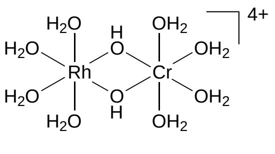
Two new heterotrinuclear aqua ions, $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ and $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$, have been prepared by treating chromium(III) dimer with Rh^{3+} and Cr^{3+} with rhodium(III) dimer in alkaline solution and isolated as pure solutions by ion-exchange chromatography. Formation of the heterometallic aqua ions has been confirmed through various solution characterization studies and analyses of the 'active' hydroxides derived from them. These heterotrinuclear aqua ions are proposed to be generated through nucleophilic attack by OH groups attached to the rhodium(III) aqua ion, formed by deprotonation of terminal aqua ligands, at the more labile chromium(III) centres. Acid cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ gave the parent mononuclear aqua ions Rh^{3+} and Cr^{3+} in a 1:2 ratio by a process which is first order in both [aqua ion] and $[H^+]$. The acid dependence of the reaction rate reflects the existence of acid-independent [$k_{uc} = 2.4 \times 10^9\ s^{-1}$, $\Delta H^‡ = 132(3)\ kJ\ mol^{-1}$; $\Delta S^‡ = +32(7)\ J\ K^{-1}\ mol^{-1}$] and -dependent [$k_c = 2.8 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$, $\Delta H^‡ = 150(1)\ kJ\ mol^{-1}$; $\Delta S^‡ = +93(4)\ J\ K^{-1}\ mol^{-1}$] cleavage pathways. The activation parameters for the acid-independent process indicate an I_d mechanism which becomes more associative on protonation of the aqua ion.

Heterometallic aqua ions, in which the metal centres are linked by hydroxo and oxo bridging groups and the remaining co-ordination sites are occupied by water molecules, are rare compared with complexes which have other ligands co-ordinated to the metal centres. This is true of heterotrinuclear ions where the $[WMo_2(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ ion, formed by treating $K_2[MoCl_6]$ with $K_2[WCl_6]$ in a 2:1 ratio, is one of few examples.[1,2] X-Ray structural analysis of the thiocyanato derivative $[NMe_4]_5[WMo_2O_4(NCS)_9]\cdot C_6H_5Me$ was consistent with the aqua ion structure **1** proposed from solution studies.[1,2] Work on metal–sulfur clusters has been more successful in this regard and has led to the synthesis of many related sulfido-bridged aqua ions. Two W^{IV}–Mo^{IV} trinuclear aqua ions, $[M_2M'S_4(H_2O)_9]^{4+}$,[3–5] and several higher-nuclearity ions, usually produced by treating $[M_3S_4(H_2O)_9]^{4+}$ with various metal ions, have been reported.[6–12]

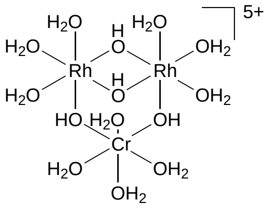
Our interest in the polymerization of the inert metal ions, $[Cr(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$,[13–22] has led to the study of heterometallic polynuclear aqua ions containing both Rh^{III} and Cr^{III}. Thus far a binuclear ion, $[(H_2O)_4Rh(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$, has been isolated and characterized. X-Ray structural analysis of its mesitylate salt confirmed the structure **2** was that proposed from solution studies.[23] Kinetic and thermodynamic studies on the interconversion between $[(H_2O)_4Rh(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ and $[(H_2O)_5Rh(\mu\text{-}OH)Cr(H_2O)_5]^{5+}$ and acid-catalysed cleavage of this binuclear ion to $[Cr(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$ have revealed that cleavage is much slower than interconversion, allowing identification of the singly bridged form $[(H_2O)_5Rh(\mu\text{-}OH)Cr(H_2O)_5]^{5+}$.[24] Described here are the synthesis and solution characterization of two heterometallic trinuclear aqua ions, $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ and $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$, and the acid-catalysed cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ to the parent mononuclear aqua ions.



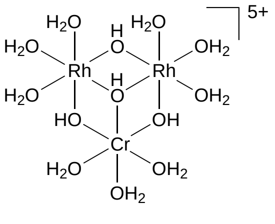
$[WMo_2O_4(H_2O)_9]^{4+}$



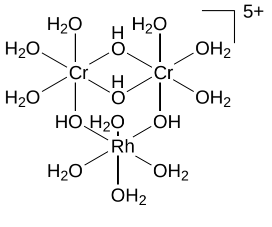
$[RhCr(OH)_2(H_2O)_8]^{4+}$ **1**



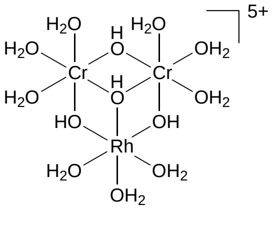
$[Rh_2Cr(OH)_4(H_2O)_{10}]^{5+}$ **2a**



$[Rh_2Cr(OH)_4(H_2O)_9]^{5+}$ **2b**



$[RhCr_2(OH)_4(H_2O)_{10}]^{5+}$ **3a**



$[RhCr_2(OH)_4(H_2O)_9]^{5+}$ **3b**

Experimental

Materials

The compound $RhCl_3\cdot xH_2O$ was prepared from rhodium metal by the electrochemical method of Dickson[25] and converted into $[Rh(H_2O)_6][ClO_4]_3\cdot 3H_2O$ using the method of Ayres and Forrester.[26] Solutions and sulfonate salts of the chromium(III) dimer $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$[27] were also prepared by literature methods. All other reagents were of LR grade or better and used as received, although for quantitative measurements AR reagents were used. Cation-exchange chromatography was carried out on Sephadex SP C25 resin (Pharmacia). Aqueous solutions were prepared with distilled water and filtered through Millipore filters (GSWP, 0.22 μm) prior to use. Standard solutions of $NaClO_4$ were made by neutralizing standard solutions of NaOH with $HClO_4$.

Instruments and methods

A Cary 3 spectrophotometer was used to record UV/VIS spectra and to carry out kinetic studies.[24] The pH was measured using equipment described earlier.[19] Electron microprobe analyses were made as described previously and Rh : Cr ratios established by comparison with the electron microprobe of $[(H_2O)_4Rh(\mu\text{-}OH)_2Cr(H_2O)_4][dmtos]_4{\cdot}4H_2O$ which has a Rh : Cr ratio of 1 : 1.[23]

Rhodium was determined by the $SnCl_2$–HCl method[28] for rhodium(III) aqua ions and by the hypochlorite method[29] for solutions containing both rhodium(III) and chromium(III) ions, since Cr^{III} was found to interfere with the analysis of rhodium by the first method. Calibration curves were constructed using rhodium(III) standards which contained appropriate amounts of Cr^{III}. Chromium was determined by the chromate method.[13,30] The charge on new polynuclear aqua ions was estimated by comparing their chromatographic elution behaviour with that of aqua ions of known charge.[21] Charge per Rh values were determined as follows: (i) titration of aliquots of the new aqua ions of known [Rh] with base to the point of total precipitation of the 'active' hydroxide gave the moles of base needed to neutralize the charge on the complex; (ii) division of this value by the moles of Rh in the samples gave the charge per Rh value.[21,22]

Synthesis of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ and $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$

The synthesis of these ions follows the method used for $[(H_2O)_4Rh(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$.[23] In a typical synthesis of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ a solution of $[Rh(H_2O)_6]^{3+}$ (5.4 cm^3, [Rh] = 0.028 mol dm^{-3}) was adjusted to pH > 12 with 1 mol dm^{-3} NaOH, placed in an ice–salt bath and vigorously stirred. A solution of $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ (20 cm^3, $[Cr_2]$ = 0.0076 mol dm^{-3}) at pH ≈ 2 was added dropwise over 15 min (final pH > 12). Reaction was immediately quenched by adjusting the pH to 1.5 with 1 mol dm^{-3} $HClO_4$ and the resultant solution subjected to cation-exchange chromatography.

The same synthetic procedure was used to prepare $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ with the exception that in this case a $[Cr(H_2O)_6]^{3+}$ solution (3.7 cm^3, [Cr] = 0.016 mol dm^{-3}) at pH ≈ 2 was added to an alkaline solution (pH > 12) of $[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ (20 cm^3, [Rh] = 0.003 mol dm^{-3}).

Separation and purification of the heterotrinuclear aqua ions

Mixtures of the polynuclear aqua ions were diluted with 0.02 mol dm^{-3} $HClO_4$, absorbed onto Sephadex SP C25 cation-exchange columns (H^+ form, 15 × 2 cm) and the columns washed thoroughly with water prior to elution. As for the homonuclear chromium(III) and rhodium(III) aqua ions,[13,21] the electrolytes ($[NaClO_4]$ = 0.5–4 mol dm^{-3}) were acidified (0.02 mol dm^{-3} $HClO_4$) to minimize further polymerization or acid cleavage during elution and storage.

In the case of the reaction of $[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ with $[Cr(H_2O)_6]^{3+}$, elution with 0.5 mol dm^{-3} $NaClO_4$ separated a yellow band from a green band at the top of the column. Continued elution with 1 mol dm^{-3} $NaClO_4$ led to the removal of the yellow band, consisting of $[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$, and also caused a second green fraction containing $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ to separate from the remaining species. This fraction was completely eluted with 2 mol dm^{-3} $NaClO_4$ leaving small amounts of green species bound to the column. In the case of the reaction of $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ with $[Rh(H_2O)_6]^{3+}$, a yellow band consisting of $[Rh(H_2O)_6]^{3+}$ was eluted with 0.5 mol dm^{-3} $NaClO_4$ and a blue fraction of $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ with 1 mol dm^{-3} $NaClO_4$. Addition of 2 mol dm^{-3} $NaClO_4$ eluted a third, green fraction containing $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ again leaving behind small amounts of green species. Solutions of both aqua ions were further purified and concentrated by chromatography prior to solution characterization. Typical yields of the two ions were 25%.

'Active' hydroxides of the two new heterotrinuclear aqua ions were prepared by a literature method.[14–16] Electron microprobe analyses on these hydroxides (see under Instruments and Methods) were used to establish Cr : Rh ratios for these ions.

Kinetic experiments

The acid cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ was studied in the 348–363 K temperature range. Solutions for each kinetic run were prepared by allowing a solution (2.5 cm^3) containing varying proportions of $HClO_4$ and $NaClO_4$ (I = 1.0 mol dm^{-3}) to come to thermal equilibrium at the desired temperature in the spectrophotometer cell block and then adding $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ stock solution (0.25 cm^3). The final reaction conditions were $[RhCr_2] = 1.93 \times 10^{-3}$, $[HClO_4]$ = 0.04–1.0 and I = 1.0 mol dm^{-3}. The acid concentrations were corrected for the temperature-dependent expansion of the solvent in the final analysis of kinetic data.

The reaction was monitored by spectrophotometry in the UV region (<300 nm) where the absorbance was found to decrease as the trinuclear ion is converted into Cr^{3+} and Rh^{3+}. The data were analysed at 250 nm where this decrease was between 1.0 and 1.2 absorbance units. Pseudo-first-order rate constants, k_{obs}, were calculated at this wavelength from the change in absorbance, A_t, with time, t, by non-linear least-squares fitting of the data by the expression $A_t = (A_0 - A_\infty)\exp(-k_{obs}t) + A_\infty$. The suitability of this method was checked by using the experimentally measured A_∞ in the calculation of k_{obs}. The values of k_{obs} obtained from the two treatments were in excellent agreement as were the experimental and fitted A_∞ values. The values of k_{obs} did not vary with wavelength.

Product analyses

Product distributions for the acid cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_x]^{5+}$ were determined under conditions similar to those used in the kinetic study. Aliquots of 5 cm^3 were taken at regular time intervals from a bulk solution consisting of $[RhCr_2] = 5.45 \times 10^{-3}$ mol dm^{-3}, $[H^+]$ = 1.01 mol dm^{-3} at 363 K. These aliquots were chilled at 273 K to quench the cleavage reaction prior to analysis. The mononuclear products present in the reaction mixtures were separated from $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ by cation-exchange chromatography. The presence of $[Cr(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$ was established by comparing the UV/VIS spectrum with that reported for the aqua ions.[13,21] The spectrophotometric methods detailed under Instruments and Methods were used to determine the number of moles of each ion present in each aliquot and their variation with time.

Results and Discussion

Synthesis of heterotrinuclear aqua ions

Dropwise addition of $[Cr(H_2O)_6]^{3+}$ solutions to alkaline solutions of rhodium(III) dimer and chromium(III) dimer to alkaline solutions of $[Rh(H_2O)_6]^{3+}$ results in the formation of heterometallic aqua ions. The reactions have been carried out over a short period of time (≈15 min) and at 273 K to minimise polymerization to large polynuclear species.

The choice of reaction conditions was important in order to minimize the formation of the homopolynuclear chromium(III) and rhodium(III) oligomers. Cervini *et al.*[21] have reported that, at room temperature (292–298 K), the polymerization of $[Rh(H_2O)_6]^{3+}$ is slow even at pH >12. Indeed, mononuclear rhodium(III) species were still present in solutions of $[Rh(H_2O)_6]^{3+}$ which had been left at room temperature and pH >12 for 90 min. Considering the short synthesis time and lower temperature used here, formation of rhodium(III) oligomers is very unlikely. Conversely, under the same conditions the polymerization of $[Cr(H_2O)_6]^{3+}$ is rapid. Previous studies indicate that, even if solutions of $[Cr(H_2O)_6]^{3+}$ are acidified immediately after addition of an excess of base, extensive

Table 1 The UV/VIS data for homo- and hetero-polynuclear aqua ions of Rh^{III} and Cr^{III}[a]

Complex	λ_1/nm	ε_1/dm^3 mol^{-1} cm^{-1}	λ_2/nm	ε_2/dm^3 mol^{-1} cm^{-1}	λ_3/nm	ε_3/dm^3 mol^{-1} cm^{-1})	Ref.
$[RhCr(\mu\text{-}OH)_2(H_2O)_8]^{4+}$	580	22.1 (22.1)[b]	410	85.4 (85.4)[c]	225[d]	1600 (1600)[c]	This work
$[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$	563	21.3 (21.3)[b]	410	210 (105)[c]	230[d]	3780 (1890)[c]	This work
$[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$	577	31.8 (15.9)[b]	411	124 (124)[c]			This work
$[Cr(H_2O)_6]^{3+}$	575	13.2 (13.2)[b]	408	15.5 (15.5)[b]			13
$[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$	582	34.8 (17.4)[b]	417	40.8 (20.4)[b]			13
$[Cr_3(\mu\text{-}OH)_4(H_2O)_9]^{5+}$	584	57.6 (19.2)[b]	425	91.5 (30.5)[b]			13
$[Rh(H_2O)_6]^{3+}$			396	62 (62)[c]	310	66 (66)[c]	21
$[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$			408	192 (96)[c]	242	3500 (1750)[c]	21

[a] Recorded at 25 °C. [b] Molar absorption coefficient per chromium(III) centre. [c] Molar absorption coefficient per rhodium(III) centre. [d] Shoulder.

polymerization has already occurred.[16] Thus, in attempting to prepare heteropolynuclear aqua ions, exposure of $[Cr(H_2O)_6]^{3+}$ and chromium(III) dimer solutions to highly alkaline conditions must be minimized. Therefore, these solutions were kept at pH $\approx$ 2 and 273 K (they polymerize slowly under these conditions[13–15]) and added to alkaline solutions of either $[Rh(H_2O)_6]^{3+}$ or rhodium(III) dimer. Throughout the addition, the chromium(III) aqua ion concentration is such that self-condensation to chromium(III) oligomers is minimized but sufficiently high to allow condensation with the more concentrated rhodium(III) species.

Under the reaction conditions both the chromium(III) and rhodium(III) reactants will be deprotonated. This means that co-ordinated hydroxo groups are present on both the chromium(III) and rhodium(III) centres. However, since substitution is faster at Cr^{III} than Rh^{III}, polynuclear species will most likely form by attack at a chromium(III) centre by a hydroxo group co-ordinated to Rh^{III} rather than the reverse. Previous kinetic data on many substitution reactions of $[Cr(H_2O)_6]^{3+}$ and chromium(III) oligomers have shown that labilization of the chromium(III) co-ordination sphere through deprotonation has a greater effect on reaction rates than any other single factor.[14,18–20,31] These studies indicate that the rate of formation of the heterometallic aqua ions will depend on the degree of deprotonation of the chromium(III) reactant.

Cation-exchange chromatography of the $[Rh(H_2O)_6]^{3+}$ and chromium(III) dimer reaction mixture gave three fractions corresponding to the unchanged starting materials, $[Rh(H_2O)_6]^{3+}$ and chromium(III) dimer, and a new trinuclear aqua ion shown to have the composition $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$. The reaction of $[Cr(H_2O)_6]^{3+}$ with rhodium(III) dimer gave two fractions consisting of unchanged dimer and $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$. The yields of trinuclear aqua ions of *ca.* 25% are typical for such complex polymerization processes.

Characterization studies

Solution and solid-state techniques were used to probe the structure of the new aqua ions. Comparisons of the elution behaviour of both the green and yellow-green reaction products with that of chromium(III) trimer indicated both ions have a 5+ charge. The product of the reaction of $[Rh(H_2O)_6]^{3+}$ with chromium(III) dimer was found to have a charge per Rh value of 2.6 ± 0.1, determined by applying the method used in the case of rhodium(III) oligomers.[21] This result together with electron microprobe analyses on the active hydroxide (Rh : Cr = 1 : 2) led to the conclusion that this new green aqua ion is trinuclear with a $[RhCr_2(\mu\text{-}OH)_4]^{5+}$ core. Cleavage of this ion gave a mixture of $[Cr(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$ whose UV/VIS spectrum indicated a Cr : Rh ratio of 1 : 2 when it was compared with those of the pure mononuclear aqua ions, supporting the proposed structural core. By comparison the well characterized binuclear ion $[RhCr(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ gives an equimolar mixture of $[Cr(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$ on cleavage.[24] The product of the reaction of $[Cr(H_2O)_6]^{3+}$ with rhodium(III) dimer has a charge per Rh value of 4.5 ± 0.2 and Rh : Cr ratio of 2 : 1 indicating that the new yellow-green aqua ion is also trinuclear with a $[Rh_2Cr(\mu\text{-}OH)_4]^{5+}$ core. This proposal is strongly supported by the products of acid cleavage ($\approx$1 mol dm^{-3} $HClO_4$) which were present in solutions of these ions after cleavage for over 1 week at 353 K, *viz.* $[Cr(H_2O)_6]^{3+}$ and $[Rh_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ separated by ion-exchange chromatography. Chromium and rhodium analyses of these bands gave a Rh : Cr ratio of 1.97 ± 0.08 : 1 indicating that equimolar amounts of the two products had formed and thus confirming the trinuclear nature of the new ion.

The UV/VIS spectra of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$, $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ and $[RhCr(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ are different to those of $[Cr(H_2O)_6]^{3+}$, $[Rh(H_2O)_6]^{3+}$, any of the known homometallic chromium(III) or rhodium(III) aqua ions and mixtures of these ions (see Fig.1 and Table 1) and provide further support for conclusions reached from other studies. Each ion has a band at *ca.* 580 nm which is a feature of homopolynuclear chromium(III) aqua ions[13] and is due to the chromium(III) d–d transition $^4A_{2g}(F) \longrightarrow {}^4T_{2g}(F)$. A second band is observed at *ca.* 410 nm in the spectra of all heteronuclear aqua ions. The variation in the intensity of this band indicates that it is a combination of the chromium(III) $^4A_{2g}(F) \longrightarrow {}^4T_{1g}(F)$ transition and the first rhodium(III) d–d transition, $^1A_{1g} \longrightarrow {}^3T_{1g}$.[13,21] The ε values for this band confirm the trimetallic nature and proposed metal stoichiometry of the new aqua ions. In particular, the ε values for $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ and $[RhCr(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ are about half that for $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$, indicating that the latter contains twice as many rhodium(III) centres per ion. This is borne out by the ε values per Rh^{III} which are *ca.* 100 dm^3 mol^{-1} cm^{-1} for the three ions [this comparison is appropriate because the first rhodium(III) d–d transition is *ca.* 3–4 times more intense than the second chromium(III) transition]. As was the case for the rhodium(III) oligomers,[21,22] the second rhodium(III) d–d transition ($^1A_{1g} \longrightarrow {}^1T_{2g}$), expected at about 300 nm, is obscured by a more intense band, probably an $OH^- \rightarrow Rh^{III}$ charge-transfer (CT) transition, which results in a shoulder at *ca.* 225 nm.

Although the conclusive assignment of structure of these trinuclear aqua ions is not possible on the basis of the available data, similarities in behaviour to the previously characterized

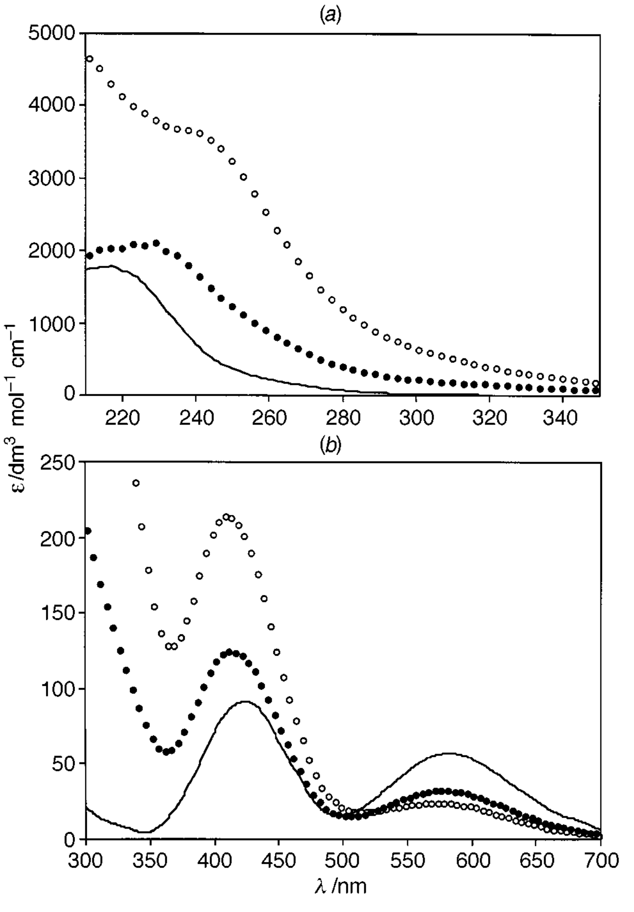


Fig. 1 The UV/VIS spectra of $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ (○), $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ (●) and chromium(III) trimer (—) recorded at 298 K (*a*) between 200 and 350, (*b*) between 300 and 700 nm

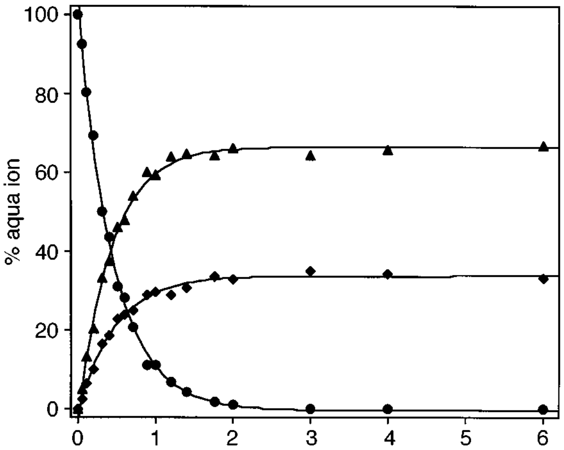


Fig. 2 Aqua ion distribution curve for the acid cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ in 1.01 mol dm^{-3} H^+ at 363 K determined by cation-exchange chromatography. ●, $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$; ▲, $[Cr(H_2O)_6]^{3+}$; ◆, $[Rh(H_2O)_6]^{3+}$. Full lines were obtained by fitting the data using a first-order process

Table 2 Rate constants for the acid cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$

T/K	$10^5\,k_{uc}/s^{-1}$	$10^5\,k_c/dm^3\,mol^{-1}\,s^{-1}$
348.2	0.575 (0.010)	1.882 (0.022)
353.2	1.124 (0.045)	4.206 (0.086)
358.2	2.136 (0.072)	8.38 (0.14)
363.2	3.90 (0.15)	16.49 (0.30)

chromium(III) and rhodium(III) homotrinuclear aqua ions suggest that these ions have the same compact configurations, as shown (for simplicity we refer to the most condensed forms throughout this paper). Note, however, that it is possible that in acidic solution these ions could exist in either the fully condensed forms (**2b** or **3b**) or the more open forms (**2a** and **3a**). In this regard it is worth pointing out that preliminary kinetic studies on $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ indicate that this ion is actually isolated in form **2a** from ion-exchange chromatography and undergoes a ring closure to the more condensed form **2b** in the range pH 0–3. This behaviour parallels that of rhodium(III) trimer, whose interconversion between various compact structural configurations have been elucidated recently *via* detailed kinetic and ^{103}Rh NMR studies.[22]

Kinetic studies

Initial studies showed that $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ undergoes an acid-cleavage process at elevated temperature (>350 K) which results in significant formation of $[Cr(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$ in a 2:1 molar ratio over a 24 h period. In contrast, little or no cleavage of $[Rh_2Cr(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ occurred over the same period of time. The reaction stoichiometry for cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ was established through a large-scale kinetic run carried out at 363 K and $[H^+] = 1.01$ mol dm^{-3}. The data, summarized in Fig. 2, clearly show that cleavage of the trinuclear aqua ion produces only the mononuclear cations. Anticipated intermediates such as $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ and $[RhCr(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ are not observed at any stage during the process. Since the trinuclear aqua ion is generated by reaction of chromium(III) dimer and $[Rh(H_2O)_6]^{3+}$ and cleavage of the dimer is not likely under the reaction conditions either it or the $Rh^{III}Cr^{III}$ binuclear ion must be an intermediate in the cleavage process (the latter is more likely since substitution at Cr^{III} would be expected to be faster than at Rh^{III}). The fact that neither of these species could be detected during the reaction indicates that they cleave more rapidly than does the starting trinuclear ion. In keeping with this the rate of cleavage of the trinuclear ion is slower than cleavage of chromium(III) dimer or the $Rh^{III}Cr^{III}$ binuclear ion. In contrast, chromium(III) dimer was an intermediate in the acid cleavage of chromium(III) trimer and, at the temperatures of that kinetic study, its cleavage to $[Cr(H_2O)_6]^{3+}$ was rate determining.[20]

The kinetics of acid cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ have been studied as a function of $[H^+]$ and temperature using UV/VIS spectrophotometry. Pseudo-first-order rate constants were determined as described in the Experimental section. At 363 K rate constants were also determined from the chromatographic data shown in Fig. 2 by fitting a first-order expression to the variations in concentration of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$, $[Cr(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$ with time. The corresponding rate constants were $(2.24 \pm 0.05) \times 10^{-4}$, $(2.30 \pm 0.09) \times 10^{-4}$ and $(2.07 \pm 0.10) \times 10^{-4}\ s^{-1}$. In addition to being self-consistent these data were in good agreement with the value of $1.92 \times 10^{-4}\ s^{-1}$ obtained from spectrophotometric data at the slightly lower $[H^+]$ of 0.93 mol dm^{-3}.

Fig. 3 shows that the rate constants vary linearly with $[H^+]$. The fact that the data pass through a non-zero intercept indicates that cleavage of the trinuclear aqua ion occurs *via* both acid-dependent and -independent pathways. The data were fitted using expression (1) where k_{uc} and k_c correspond to the

$$k_{obs} = k_{uc} + k_c[H^+] \qquad (1)$$

rate constants for the acid-independent and -dependent pathways, respectively. Values of k_{uc} and k_c were obtained at each temperature of study from which activation parameters were determined and are summarized in Table 2. The rates of cleavage for this ion are clearly slower than for any other previously studied homo- and hetero-metallic aqua ions of Cr^{III} and Rh^{III}.

Table 3 Activation parameters and calculated rate constants for the acid-dependent and -independent cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ and related polynuclear aqua ions

Parameter	$10^8 k^a$ (298 K)	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
$[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+\,b}$			
k_{uc}/s^{-1}	0.24	132(3)	+32(7)
k_c/dm^3 mol^{-1} s^{-1}	0.28	150(1)	+93(4)
$[RhCr(\mu\text{-}OH)_2(H_2O)_8]^{4+\,c}$			
k_{uc}/s^{-1}	1.0	112(4)	+38(13)
k_c/dm^3 mol^{-1} s^{-1}	17	95(3)	0(9)
$[Cr_3(\mu\text{-}OH)_4(H_2O)_9]^{5+\,d}$			
k_{uc1}/s$^{-1\,e}$			
k_{c1}/dm^3 mol^{-1} s^{-1}	8.0	138(9)	+82(25)
k_{uc2}/s^{-1}	1.1	125(11)	+23(32)
k_{c2}/dm^3 mol^{-1} s^{-1}	88	77(4)	−104(11)
$[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+\,f}$			
k_{uc}/s^{-1}	3.8	109(1)	+35(2)
k_c/dm^3 mol^{-1} s^{-1}	150	83(1)	−22(2)

[a] Values calculated from activation parameters. [b] This work. [c] Ref. 24. [d] Ref. 20. [e] Not observed. [f] Ref. 18.

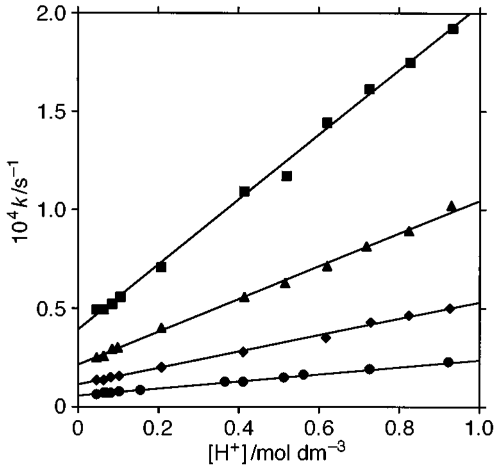


Fig. 3 Temperature- and acid-concentration dependence of the rate of acid cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$. (●) 348, (◆) 353, (▲) 358, (■) 363 K. Full lines were obtained by linear least-squares analysis of the data

The slower rates may result from changes in the position of the equilibrium established prior to rate-determining cleavage to the mononuclear aqua ions (*e.g.* $RhCr_2 \longrightarrow Cr + RhCr$) or inductive effects which reduce the lability of the chromium(III) co-ordination sphere, at which cleavage is almost certainly occurring.

A comparison of the activation parameters for acid cleavage of $[RhCr_2(\mu\text{-}OH)_4(H_2O)_9]^{5+}$ with those for various chromium(III) and $Rh^{III}Cr^{III}$ aqua ions reveals some striking similarities (Table 3). The $\Delta S^\ddagger$ values for the acid-independent pathways are identical again indicating that the site of substitution must be a chromium(III) centre in all cases and, moreover, that this process occurs *via* some sort of dissociative mechanism, most likely I_d. The variation in the rate constants for this pathway over all systems studied so far, although small (*ca.* 20 fold), results in significant changes in $\Delta H^\ddagger$ which reflect some variation in Cr–O bond strength. Comparison of the data for the acid-catalysed pathways is more difficult since the thermodynamic parameters for the protonation of the trinuclear ion are unknown. Assuming $\Delta H° \approx -45$ kJ mol^{-1} and $\Delta S° \approx -130$ J K^{-1} mol^{-1} for such a protonation process,[24] the activation parameters for the acid-catalysed pathway (k_c in Table 3) convert into $\Delta H^\ddagger \approx 105$ kJ mol^{-1} and $\Delta S^\ddagger \approx -37$ J K^{-1} mol^{-1}. The smaller predicted value of $\Delta H^\ddagger$ would be reflecting an increase in the ease of cleavage of the Cr–O bond on protonation, assuming protonation occurs at a bridging group. Regardless of the site of protonation, the labilization effect of the OH group on the metal co-ordination sphere will be removed on protonation thereby increasing the strength of bonding to the terminal water ligands. This in turn would lead to a more associative substitution process, as indicated by the estimated value of $\Delta S^\ddagger$.

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