Reactivity of the Tri-μ-hydroxo-bis[triamminecobalt(III)] Ion in Halide Media

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The kinetics of acid hydrolysis of *trans*-$[(H_2O)(NH_3)_3Co(\mu\text{-}OH)_2Co(NH_3)_3(H_2O)]^{4+}$ in acidic chloride and bromide solutions was studied using stopped-flow and conventional spectrophotometric techniques, at an ionic strength of 1.0 mol dm^{-3} and over the ranges $0.10 \leqslant [H^+] \leqslant 0.50$ mol dm^{-3}, $0.10 \leqslant [X^-] \leqslant 0.50$ mol dm^{-3}, $25 \leqslant T \leqslant 35$ °C and in binary aqueous cosolvent mixtures containing up to 40% methanol by volume. The rate equation observed was of the form $k_{obs} = (k_c[H^+] + k'_c)[X^-]$. At 25 °C the rate constants k_c were 1.10×10^{-2} and 1.22×10^{-3} dm^6 mol^{-2} s^{-1} in chloride and bromide solutions respectively for the $[H^+]$-dependent term. The corresponding values for the $[H^+]$-independent pathway, k'_c, were 4.5×10^{-4} and 0.7×10^{-4} dm^3 mol^{-1} s^{-1}. The activation parameters in chloride solution were $\Delta H^\ddagger(k_c) = 51 \pm 14$ kJ mol^{-1}, $\Delta S^\ddagger(k_c) = -110 \pm 48$ J K^{-1} mol^{-1}; $\Delta H^\ddagger(k'_c) = 132 \pm 32$ kJ mol^{-1} and $\Delta S^\ddagger(k'_c) = 136 \pm 105$ J K^{-1} mol^{-1}. At constant $[H^+]$ (0.5 mol dm^{-3}) the reaction was first order with respect to $[Cl^-]$ and $[Br^-]$ and the rate constants, k_d, were 4.5×10^{-3} and 3.3×10^{-3} dm^3 mol^{-1} s^{-1} respectively.

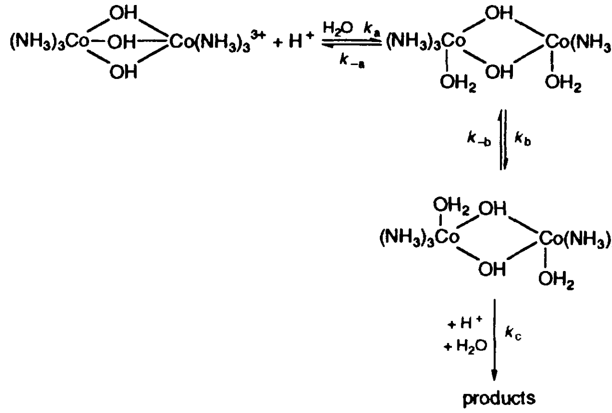
The stability of dinuclear hydroxo-bridged cobalt(III) complexes and the mechanistic details of their hydrolysis to mononuclear species in both acidic and basic media have been an area of interest for the past forty years.[1–4] The kinetics of acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ has been reported by various authors,[5–8] as well as similar studies involving the analogous diethylenetriamine, *cis,cis*-1,3,5-triaminocyclohexane and 1,4,7-triazacyclononane complexes.[6] In acidic perchlorate the mechanism for the hydrolysis of the ammine complex is as shown in Scheme 1.[8] This involves a fast (stopped-flow) acid-catalysed bridge-cleavage and bridge-formation reaction, followed by a slower, but still fast (stopped-flow), isomerisation reaction. Slow (conventional spectrophotometry) bridge cleavage of *trans*-$[(H_2O)(NH_3)_3Co(\mu\text{-}OH)_2Co(NH_3)_3(H_2O)]^{4+}$ affords the mononuclear product, *fac*-$[Co(NH_3)_3(H_2O)_3]^+$. A study of the reaction in an acidic chloride medium reported similar results for the first two steps.[6] It was proposed, however, that the kinetics of the third stage was complicated by what was assumed to be chloride substitution into the dihydroxo-bridged intermediate. Our studies have shown that the kinetics of the last stage is significantly enhanced in halide solution. An analysis of the products from the reaction showed that $[CoCl_2(NH_3)_3(H_2O)]^+$ and $[Co(NH_3)_3(H_2O)_3]^{3+}$ were formed.

We report here the kinetics of the reactions of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in acidic chloride and bromide solutions. The effect of the methanol content of the solvent on the kinetics was also studied and the variation of the rate with solvent composition is discussed with respect to the mechanism involved.

Experimental

Materials.—All chemicals used were either Reagent or Analar grade. Distilled water was obtained from a Corning all-glass distillation unit. Deionised water, obtained by passing distilled water through a Milli-Q water-purification unit (Millipore, Milford, MA), was used to make up solutions for all physical measurements.

Preparation of Complexes.—Tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate dihydrate was prepared as previously described.[9] Its purity was determined by comparing the UV/VIS spectrum with that in the literature[9] and elemental analysis (Butterworth Laboratories Ltd.) {Found: H, 3.20; Cl, 17.55; Co, 19.05; N, 13.50. Calc. for $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3][ClO_4]_3 \cdot 2H_2O$: H, 4.15; Cl, 17.55; Co, 19.45; N, 13.09%}.



Scheme 1

Kinetic Measurements.—The kinetics of the acid hydrolysis was studied using stopped-flow and conventional spectrophotometry at 544 nm as a function of the decrease in absorbance with time. The complex and acid solutions were prepared separately. All runs were done under pseudo-first-order conditions at an ionic strength of 1.0 mol dm^{-3} which was maintained with sodium chloride or sodium bromide. The solutions were equilibrated at the reaction temperature for about 10 min prior to each run. For the reactions in mixed-solvent media the non-aqueous solvent was present in the same ratio in both the solutions so that no temperature change would occur on mixing. The error in each reported k_{obs} value is less than 5%.

Separation of Reaction Products.—Separation of the products from the acid hydrolysis in chloride solution was achieved by using a 25 × 2 cm column containing the sodium form of Dowex 50W-X12 cation-exchange resin (100–200 mesh). The components were successively eluted using acidic sodium perchlorate solutions of increasing concentration. The products were characterised by their UV/VIS spectra.

Results and Discussion

Preliminary Studies.—The spectral changes for the third stage of the hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in acidic chloride solution are shown in Fig. 1, where (*a*) and (*b*) are the spectra of $[(H_2O)(NH_3)_3Co(\mu\text{-}OH)_2Co(NH_3)_3(H_2O)]^{4+}$ and the products respectively. Fig. 2 shows the corresponding UV spectra as well as that of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ (*c*). The UV spectrum of the products shows that no dinuclear species are present since a chloride-substituted product would still have a characteristic peak at 295 nm, as observed in the spectrum of $[(NH_3)_3FCo(\mu\text{-}OH)_2CoF(NH_3)_3]^{2+}$ by Linhard and Siebert.[1] Spectrum (*b*) does not correspond to $[Co(NH_3)_3(H_2O)_3]^{3+}$. The products of the reaction of 0.301 g of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in 10 cm³ of 1.0 mol dm^{-3} HCl were separated following the procedure described in the Experimental section. Two fractions resulted, with spectra corresponding to $[Co(NH_3)_3(H_2O)_3]^{3+}$ and $[CoCl_2(NH_3)_3(H_2O)]^{+}$. The absorption coefficients indicated that the concentration of each mononuclear species represents half the total cobalt from the (μ-OH)$_3$ complex. Spectrum (*b*) corresponds to that of a synthetic mixture containing 1.0 × 10^{-3} mol dm^{-3} each of $[Co(NH_3)_3(H_2O)_3][ClO_4]_3$ and $[CoCl_2(NH_3)_3(H_2O)]Cl$.

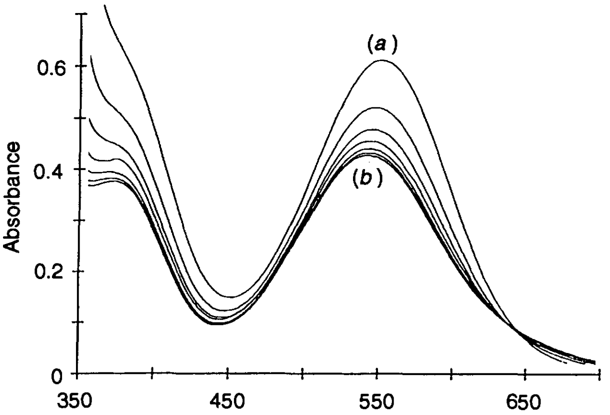


Fig. 1 Spectral changes for the third stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3(NH_3)_3]^{3+}$ in a chloride medium: (*a*) $[(H_2O)(NH_3)_3Co(\mu\text{-}OH)_2Co(NH_3)_3(H_2O)]^{4+}$, (*b*) reaction products

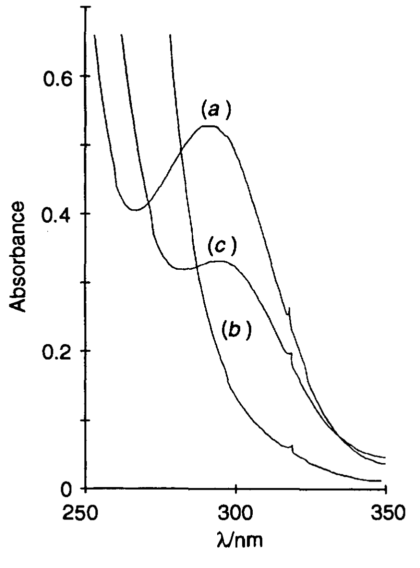


Fig. 2 The UV spectra of the various species for the third stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in a chloride medium: (*a*) and (*b*) as in Fig. 1, (*c*) $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$

Kinetics of the Reaction in a Halide Medium.—The kinetic results for the first two stages of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in chloride solution are listed in Tables 1 and 2 respectively. The rate parameters based on the derived rate expressions[8] (1) for the first stage and (2) for

$$k_{obs} = k_a[H^+] + k_{-a} \tag{1}$$

$$k_{obs} = \frac{k_b K_a[H^+]}{1 + K_a[H^+]} + k_{-b} \tag{2}$$

the second stage, where $K_a = k_a/k_{-a}$, are shown in Table 3 along with the activation parameters. Under our reaction conditions the term k_{-b} was either negligible or is comparable to the magnitude of the error associated with the pseudo-first-order rate constants. Thus, the data in Table 2 fit the modified expression (3). The results in Table 3 are comparable with the

$$k_{obs} = \frac{k_b K_a[H^+]}{1 + K_a[H^+]} \tag{3}$$

previously reported rate and activation parameters for the first and second steps of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in chloride[6] and perchlorate media.[8] These values are also included in Table 3.

The third stage of the reaction, detailed in Scheme 2, shows a first-order dependence of the form (4). The kinetic results are

$$k_{obs} = k_c[H^+] + k'_c \tag{4}$$

shown in Table 4. The rate parameters from a linear regression analysis of the data (Fig. 3) and the derived activation parameters for the reactions in 1.0 mol dm^{-3} halide solution are

Table 1 Pseudo-first-order rate constants for the first stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in chloride solution. Initial [complex] = 1.0 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} (NaCl)

	k_{obs}/s^{-1}		
[H$^+$]/mol dm^{-3}	25.1	30.1	35.2 °C
0.10	2.52	4.65	7.46
0.20	3.28	5.60	8.47
0.30	4.10	7.36	10.45
0.40	5.42	8.19	12.27
0.50	6.36	9.71	14.84

Table 2 Pseudo-first-order rate constants for the second stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in chloride solution. Initial [complex] = 1.0 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} (NaCl)

	10^2 k_{obs}/s^{-1}		
[H$^+$]/mol dm^{-3}	25.1	30.1	35.2 °C
0.010	1.80	3.18	4.89
0.020	2.15	4.33	7.34
0.030	2.95	5.51	9.78
0.040	3.48	6.31	11.86
0.050	4.23	7.61	13.77
0.060	4.86	8.86	15.85
0.070	5.42	10.30	16.27
0.080	6.09	11.11	18.25
0.090	6.67	11.65	19.99
0.100	6.82	12.11	22.62

Table 3 Summary of rate and activation parameters for the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$, I = 1.0 mol dm^{-3}

Rate constant	T/°C 25	30	35	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	Ref.
k_a/dm^3 mol^{-1} s^{-1}	9.83	12.71	18.57	46 ± 6	−72 ± 19	This work
k_{-a}/s^{-1}	1.39	3.29	5.13	98 ± 17	86 ± 58	This work
k_b/s^{-1}	0.16	0.25	0.44	76 ± 22	−6 ± 4	This work
k_a/dm^3 mol^{-1} s^{-1}	8.2^a	—	—	—	—	6
k_{-a}/s^{-1}	1.3^a	—	—	—	—	6
k_b/s^{-1}	0.15^a	—	—	—	—	6
k_a/dm^3 mol^{-1} s^{-1}	4.22^b	—	—	47 ± 8	−77 ± 28	8
k_{-a}/s^{-1}	1.80^b	—	—	73 ± 7	3 ± 20	8
k_b/s^{-1}	0.18^b	—	—	99	70	8

^{a} Chloride medium, 20 °C. ^{b} Perchlorate medium.

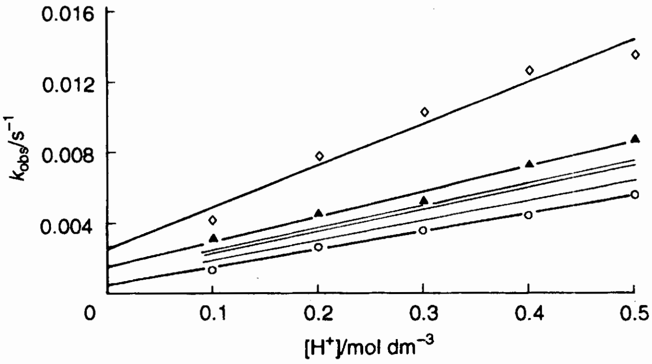


Fig. 3 Plots of k_{obs} *vs.* [H$^+$] for the third stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in a chloride medium at 25 (○), 30 (▲) and 35 °C (◇). The lines between 25 and 30 °C represent data in 10, 20 and 30% methanol at 25 °C

Table 4 Pseudo-first-order rate constants for the third stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in halide solution. Initial [complex] = 1.0 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3}

[H$^+$]/mol dm^{-3}	10^3 k_{obs}/s^{-1} 25.1^a	25.1^b	30.1^b	35.2 °C^b
0.10	0.19	1.33	3.05	4.12
0.20	0.31	2.67	4.58	7.70
0.30	0.44	3.57	5.21	10.34
0.40	0.56	4.35	7.25	12.61
0.50	0.67	5.56	8.81	13.54

^{a} Bromide medium. ^{b} Chloride medium.

listed in Table 5. At 25 °C the values of k_c and k'_c are 1.10 × 10^{-2} dm^6 mol^{-2} s^{-1} and 4.4 × 10^{-4} dm^3 mol^{-1} s^{-1} (X^- = Cl^-) and 1.22 × 10^{-3} dm^6 mol^{-2} s^{-1} and 0.7 × 10^{-4} dm^3 mol^{-1} s^{-1} (X^- = Br^-). The corresponding values in perchlorate solution are 6.07 × 10^{-5} dm^3 mol^{-1} s^{-1} and 9.5 × 10^{-7} s^{-1} (where the participation of perchlorate was not considered).[8] This disparity in rate constants implies that the halide ions are participating in the rate-determining step of the reaction and is supported by the fact that between 47 and 50% of the products from the reaction in chloride solution is $[CoCl_2(NH_3)_3(H_2O)]^+$.

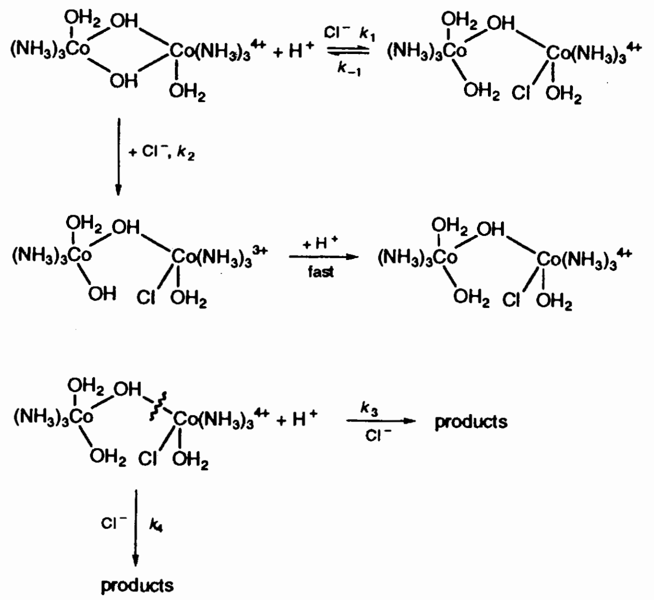
Table 6 contains the pseudo-first-order rate constants for the third stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ as a function of [Cl^-] and [Br^-] at constant [H$^+$]. The right-hand column shows that the rate of the reaction is first order with respect to [X^-], equation (5).

$$k_{obs} = k_d[X^-] \qquad (5)$$

A linear regression analysis of the data yields the values of k_d as 4.5 × 10^{-3} (Cl^- at 25 °C) and 3.3 × 10^{-3} dm^3 mol^{-1} s^{-1} (Br^- at 35 °C). This indicates that equation (4) should be correctly written as in (6).

$$k_{obs} = (k_c[H^+] + k'_c)[X^-] \qquad (6)$$

Based on these results we can propose the mechanism shown in Scheme 2 for the third step of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in chloride media. This mechanism shows that the reaction involves two pathways,



Scheme 2

Table 5 Kinetic and activation parameters for the third stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in a chloride medium. Initial [complex] = 1.0 × 10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3}

T/°C	10^2 k_c/ dm^6 mol^{-2} s^{-1}	10^3 k'_c/ dm^3 mol^{-1} s^{-1}
25	0.12*	0.07*
25	1.10	0.45
30	1.42	1.53
35	2.37	2.54

$\Delta H^‡(k_c)$ = 51 ± 14 kJ mol^{-1}, $\Delta S^‡(k_c)$ = −110 ± 48 J K^{-1} mol^{-1}; $\Delta H^‡(k'_c)$ = 132 ± 30 kJ mol^{-1}, $\Delta S^‡(k'_c)$ = 136 ± 105 J K^{-1} mol^{-1}

* In bromide medium.

Table 6 Pseudo-first-order rate constants for the third stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in halide media, $[H^+] = 0.5$ mol dm^{-3}

	$10^3\ k_{obs}$/s^{-1}		$10^2\ k_{obs}[X^-]^{-1}$/dm^3 mol^{-1} s^{-1}	
$[X^-]$/mol dm^{-3}	$Cl^{-\,a}$	$Br^{-\,b}$	$Cl^{-\,a}$	$Br^{-\,b}$
0.1	0.44	0.31	0.44	0.31
0.2	0.89	0.72	0.44	0.36
0.3	1.36	0.98	0.45	0.33
0.4	1.79	1.41	0.45	0.35
0.5	2.24	1.62	0.45	0.32

^{a} 25 °C. ^{b} 35 °C.

both involving Cl^- (or Br^-) attack in the rate-determining steps (k_1 and k_2) and forming the monohydroxo-bridged species $[(H_2O)_2(NH_3)_3Co(\mu\text{-}OH)CoCl(NH_3)_3(H_2O)]^{4+}$ as a common intermediate. Assuming steady-state conditions for this intermediate gives the rate equation (7) from which we

$$k_{obs} = \frac{k_2k_4 + (k_1k_4 + k_2k_3)[H^+] + k_1k_3[H^+]^2}{k_{-1} + k_4 + k_3[H^+]}[X^-] \quad (7)$$

can deduce that the k'_c term in equation (6) is equivalent to $k_2k_4/(k_{-1} + k_4 + k_3[H^+])$ while k_c is equivalent to $(k_1k_4 + k_2k_3)/(k_{-1} + k_4 + k_3[H^+])$ with $k_3[H^+] \ll k_{-1} + k_4$. The linear plots of k_{obs} *versus* $[H^+]$ (Fig. 3) indicate that the contribution from the term $k_1k_3[H^+]^2$ is negligible. The bond which undergoes cleavage to give the mononuclear species is indicated in Scheme 2. This cleavage in steps k_3 and k_4 is expected to be facilitated by the *cis*-chloro group.[10] The five-co-ordinate intermediate generated is expected preferentially to pick up a halide ion to complete its octahedral co-ordination shell.

A similar mechanism has been proposed for the acid hydrolysis of the closely related $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]^{4+}$ complex in chloride and bromide media.[11] The rate parameters corresponding to k_c and k'_c at 25 °C were reported to be 9.6×10^{-4} dm^6 mol^{-2} s^{-1} and 1.2×10^{-4} dm^3 mol^{-1} s^{-1} respectively in chloride solution and 4.33×10^{-4} dm^6 mol^{-2} s^{-1} and 1.4×10^{-4} dm^3 mol^{-1} s^{-1} respectively in bromide solution. In a perchlorate medium[12] the reported values at 35 °C are $k_c = 1.6 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} and $k'_c \approx 4.5 \times 10^{-5}$ s^{-1}. From the temperature dependence of the rate in chloride solution the activation parameters are $\Delta H^‡(k_c) = 68 \pm 2$ kJ mol^{-1}, $\Delta S^‡(k_c) = -76 \pm 8$ J K^{-1} mol^{-1} and $\Delta H^‡(k'_c) = 105 \pm 16$ kJ mol^{-1}, $\Delta S^‡(k'_c) = 31 \pm 54$ J K^{-1} mol^{-1}. If these values are compared with those for the third stage of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in halide and perchlorate media we can conclude that the same mechanism is operating in all cases. The much lower values for the rate constants in perchlorate solution are possibly a reflection of the low propensity for the ClO_4^- ion to act as a nucleophile and its greater steric bulk relative to Cl^- and Br^-.

Similar studies for the reaction of $[(en)_2Co(\mu\text{-}OH)_2Co(en)_2]^{4+}$ (en = ethane-1,2-diamine) in $HClO_4$, HNO_3, HCl and H_2SO_4 solutions[13] support the generalisation of the effects of nucleophiles in catalysing the hydrolysis of dinuclear hydroxo-bridged cobalt(III) complexes. Isolation of substituted products such as *cis*-$[Co(en)_2(SO_4)]^+$, *cis*-$[Co(en)_2Cl(H_2O)]^{2+}$ and *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ from the reactions also support the mechanism.

Effect of the Methanol Content of the Solvent.—The rate parameters derived from the pseudo-first-order rate constants for the three steps of the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in aqueous methanol indicate that only the third step shows a significant rate dependence on the methanol content of the solvent. The results are summarised in Table 7 and Fig. 3 includes the variation of rate as a function of $[H^+]$ and methanol content. The increase in rate with increasing methanol content of the solvent is mainly due to an increase in the k'_c term, with a smaller contribution from the k_c term. Unfortunately it is impossible to quantify these solvent effects in terms of an initial state–transition state analysis,[14] since both k_c and k'_c are composite and it would be very difficult to obtain transfer chemical potential data for the di-μ-hydroxy-diaqua complex at the start of the Scheme 2 sequence. However two contributions to the reactivity trend can be recognised in a qualitative way. (*i*) The transfer chemical potential of the entering chloride (bromide) becomes increasingly, albeit slightly, more positive with increasing methanol content.[15] This could contribute to the observed modest reactivity increase through slight destabilisation of the initial state. (*ii*) Practically all mono- and di-nuclear cobalt(III) complexes have positive transfer chemical potentials from water into methanol–water mixtures,[16] including $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ at the start of the reaction sequence of Scheme 1, for which the transfer chemical potential is +3 kJ mol^{-1} from water into 40% methanol.[17] This too would lead to slightly increased rate constants by increasing the chemical potential of the initial state.

Table 7 Summary of rate parameters for the effect of the methanol content of the solvent on the acid hydrolysis of $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ in chloride solution

	Methanol content (%)			
Rate constant	10	20	30	40
k_a/dm^3 mol^{-1} s^{-1}	10.08	11.23	10.88	10.08
k_{-a}/s^{-1}	1.38	1.15	1.23	1.51
k_b/s^{-1}	0.20	0.17	—	—
$10^2\ k_c$/dm^6 mol^{-2} s^{-1}	1.19	1.27	1.26	1.49
$10^3\ k'_c$/dm^3 mol^{-1} s^{-1}	0.33	0.78	1.12	1.05

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