Kinetics of Aquation of Penta-amminechlororuthenium(III) Dichloride and *cis*-Dichlorobis(ethylenediamine)ruthenium(III) Chloride Hydrate in Mixed Water–Organic Solvents

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Kinetic data are reported for the spontaneous aquations of $[Ru(NH_3)_5Cl]Cl_2$ and *cis*-$[Ru(en)_2Cl_2]Cl$ in a variety of mixed water–organic solvents. Plots of log k_{H_2O} against Grunwald–Winstein Y values are linear with gradients *ca.* 0.25, suggesting essentially S_N1 mechanisms. The Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl]^{2+}$ has also been studied in both aqueous solution and in a variety of mixed water–organic solvents. Kinetic data in aqueous solution are consistent with pre-equilibrium formation of a chloro-bridged intermediate, $[(NH_3)_5Ru–Cl–Hg]^{4+}$, followed by dissociation to release $[HgCl]^+$ and the rapid pick up of water. Plots of log $k_{Hg^{2+}}$ against Y values for the Hg^{2+}-catalysed aquation in mixed solvents are markedly non-linear. This unusual behaviour is discussed in terms of the pre-equilibrium mechanism.

FOLLOWING the success of mixed-solvent studies in elucidating the mechanisms of organic solvolysis reactions,[1] this approach has been recently extended to the reactions of co-ordination complexes.[2-8] In particular, it has been shown [3-5] that for aquation of octahedral cobalt(III) complexes in mixed aqueous solvents a linear relation generally exists between log k_{H_2O} (the aquation rate constant in any solvent mixture) and the Grunwald–Winstein Y values. The existence of this correlation and the magnitude of the gradient (m 0·23—0·36) were suggested to be characteristic of a dissociative S_N1 mechanism for these aquations. On the other hand, the observation of significantly lower gradients for iron(II) (m 0·1—0·2) [6,7] and chromium(III) (m 0·12) [8] complexes was attributed to appreciable associative character in their

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[1] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; A. H. Fainberg and S. Winstein, *ibid.*, 1956, **78**, 2770 and refs. therein; P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

[2] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.

[3] J. Burgess and M. G. Price, *J. Chem. Soc.* (*A*), 1971, 3108 and refs. therein.

[4] G. R. H. Jones, R. C. Edmondson, and J. H. Taylor, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1752.

[5] G. Thomas and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1974, 1688.

[6] J. Burgess, *J. Chem. Soc.* (*A*), 1969, 1899.

[7] J. Burgess, *J.C.S. Dalton*, 1972, 203.

[8] J. Burgess, *J.C.S. Dalton*, 1973, 825.

substitution reactions. However, apart from some limited studies of bromide attack on *trans*-$[Ir(en)_2Cl_2]^+$ (en = ethylenediamine) and the Hg^{2+}-catalysed aquation of $[Rh(NH_3)_5Cl]^{2+}$,[3] there is little information concerning the effect of solvent variation on the reactions of second- and third-row transition-metal octahedral complexes.

In this paper we extend such investigations to ruthenium(III) complexes, reporting kinetic data for aquation of $[Ru(NH_3)_5Cl]Cl_2$ and *cis*-$[Ru(en)_2Cl_2]Cl{\cdot}OH_2$ in a variety of mixed water–organic solvents. These reactions are of some interest in view of their suggested [9] S_N2 character, and it was hoped that the present studies might throw some further light on their detailed mechanisms. Also reported are mixed-solvent studies for the Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl]Cl_2$.

EXPERIMENTAL

Materials.—The complexes $[Ru(NH_3)_5Cl]Cl_2$ and *cis*-$[Ru(en)_2Cl_2]Cl{\cdot}OH_2$ were prepared by published methods.[10,11] The salt $[Ru(NH_3)_5Cl][BF_4]_2$ was prepared by dissolving the chloride in water and adding excess of $Na[BF_4]$. The purity of the complexes was checked by comparing their u.v.–visible spectra with reported data. Analytical grade methanol, ethanol, acetone, and glacial acetic acid were used without further purification. Solutions of Hg^{2+} for the catalysed-aquation studies were prepared by dissolving a weighed amount of mercury(II) oxide in aqueous perchloric acid (or toluene-*p*-sulphonic acid) and diluting with the appropriate organic solvent. Final Hg^{2+} concentration varied from $0{\cdot}10 \times 10^{-2}$ to $1{\cdot}50 \times 10^{-2}$M, but was maintained at $1{\cdot}21 \times 10^{-2}$M for the mixed-solvent study; * $[H^+]$ was kept at 0·01M for the spontaneous-aquation studies to prevent interference from base hydrolysis. In the Hg^{2+}-catalysed runs, 0·04M-$HClO_4$ was employed to stop hydrolysis of the mercury. The solvent ratios stated are those measured before mixing of the components.

Kinetic Studies.—Sufficient weighed samples of the ruthenium(III) complexes were dissolved in the appropriate mixed solvent (25 cm³) to give a final $[Ru^{3+}]$ of between $2{\cdot}5 \times 10^{-4}$ and 5×10^{-4}M. The volumetric reaction flask was then covered in aluminium foil and thermostatted in a water-bath at the desired temperature (±0·1 °C). After equilibration for 15 min samples were withdrawn periodically and their absorption spectra recorded between 360 and 280 nm using a Beckman DK2A spectrophotometer. The reactions were followed by observing the disappearance of the long-wavelength peaks of the original chloro-complexes at 328 $\{[Ru(NH_3)_5Cl]^{2+}\}$ and 355 nm {*cis*-$[Ru(en)_2Cl_2]^+$}. First-order rate constants were calculated from plots of log $(A_\infty - A_t)$ against time, using A_∞ values calculated from known [9] absorption coefficients of the products $[Ru(NH_3)_5(OH_2)]^{3+}$ and *cis*-$[Ru(en)_2Cl(OH_2)]^{2+}$ at the above wavelengths.

RESULTS

Aquation of $[Ru(NH_3)_5Cl]Cl_2$ in mixed solvents containing 0·01M-$HClO_4$ was generally followed for only the first 15% completion of reaction. Good first-order kinetics were obtained over this period. Although perchloric acid is known [12] to cause decomposition of amineruthenium(III) complexes, trial kinetic runs in water (between 36 and 64 °C) showed that the use of 0·01M-$HClO_4$ or 0·01M-*p*-$MeC_6H_4SO_3H$ gave identical aquation-rate plots until *ca*. 20—25% completion of reaction; *i.e.* decomposition by $[ClO_4]^-$ only becomes significant at this stage. The results in various mixed water–organic solvents for $[Ru(NH_3)_5Cl]Cl_2$ at 45·5 °C are summarised in Table 1, while temperature-dependence data are shown in Table 2. A good linear correlation was observed between log k_{H_2O} and the Grunwald–Winstein Y values (Figure 1) in all the solvents employed, with an average gradient of $+0{\cdot}23 \pm 0{\cdot}01$.

TABLE 1

Kinetic data for aquation of $[Ru(NH_3)_5Cl]Cl_2$ in mixed water–organic solvents at 45·5 °C and $[HClO_4]$ = 0·010M

Concentration of organic component/	Methanol *		Ethanol		Acetone	
% (v/v)	Y	$10^6k/s^{-1}$	Y	$10^6k/s^{-1}$	Y	$10^6k/s^{-1}$
0	3·49	10·6 (18·1)	3·49	10·6	3·49	10·6
10	3·28	9·25 (16·2)	3·31	9·51	3·23	9·08
20	3·03	8·19 (12·2)	3·05	8·39	2·91	7·51
30	2·75	7·11 (10·8)	2·72	7·15	2·48	5·96
40	2·39	5·74	2·20	5·57	1·98	4·56

* Values in parentheses are at 50·8 °C.

TABLE 2

Temperature dependence of aquation of $[Ru(NH_3)_5Cl]Cl_2$ in various water–ethanol mixtures at $[HClO_4]$ = 0·010M

Concentration of ethanol/% (v/v)	$10^6k/s^{-1}$ (45·5)	$10^6k/s^{-1}$ (59·9 °C)	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
0	10·6	41·7	20·1 *	−19
10	9·51	35·9	19·4	−21
20	8·39	27·6	17·4	−27
30	7·15	24·0	18·3	−25

* Agrees with the value of 20·0 kcal mol^{-1} reported (ref. 13) n 0·1M-*p*-$MeC_6H_4SO_3H$.

For the aquation of *cis*-$[Ru(en)_2Cl_2]Cl{\cdot}OH_2$ in mixed solvents containing 0·01M-*p*-$MeC_6H_4SO_3H$ (Table 3), first-order kinetics were observed for only 25% completion of reaction. The isosbestic points at 341 and 318 nm disappeared at this stage, indicating interference from the second-stage aquation step (2), as was previously observed [9] for aquation in water. A good linear log k_{H_2O} against Y plot was again obtained for each of the solvent mixtures (Figure 2). However, the gradient varied appreciably with the nature of the organic component, ranging from $m = 0{\cdot}33$ (methanol) to 0·16 (acetone) (Table 4).

$$[Ru(en)_2Cl_2]^+ + H_2O \longrightarrow [Ru(en)_2Cl(OH_2)]^{2+} + Cl^- \quad (1)$$

$$[Ru(en)_2Cl(OH_2)]^{2+} + H_2O \longrightarrow [Ru(en)_2(OH_2)_2]^{3+} + Cl^- \quad (2)$$

The corresponding data for the Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl]Cl_2$ in mixed solvents (0·04M-$HClO_4$) are

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* 1M = 1 mol dm^{-3}, 1 cal = 4·184 J.

[9] J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, 1968, **7**, 2519.

[10] A. D. Allen, F. Bottomley, P. O. Harris, V. P. Reinsalu, and C. V. Senoff, *Inorg. Synth.*, 1970, **12**, 2.

[11] J. A. Broomhead and L. Kane-Maguire, *J. Chem. Soc.* (*A*), 1967, 546.

[12] J. A. Broomhead and H. Taube, *J. Amer. Chem. Soc.*, 1969, **91**, 1261.

given in Table 6. The $k_{Hg^{2+}}$ (s^{-1}) values were calculated from the observed rate constants using equation (3) and k_{H_2O} data from Table 1. Reactions were generally only followed for one half-life, giving good first-order kinetics.

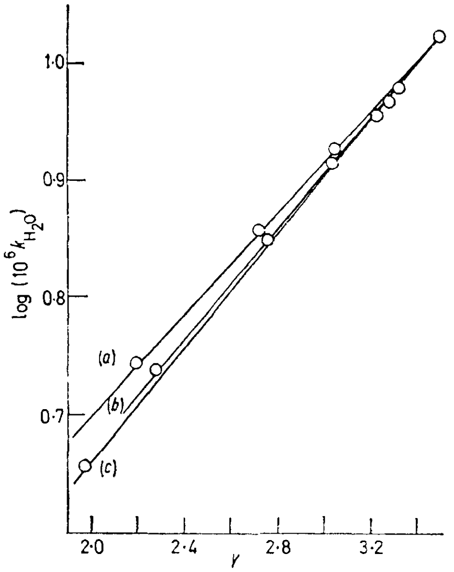

FIGURE 1 Variation of log k_{H_2O} with Y for aquation of $[Ru(NH_3)_5Cl]Cl_2$ in water–organic solvents: (a), ethanol; (b), methanol; (c), acetone

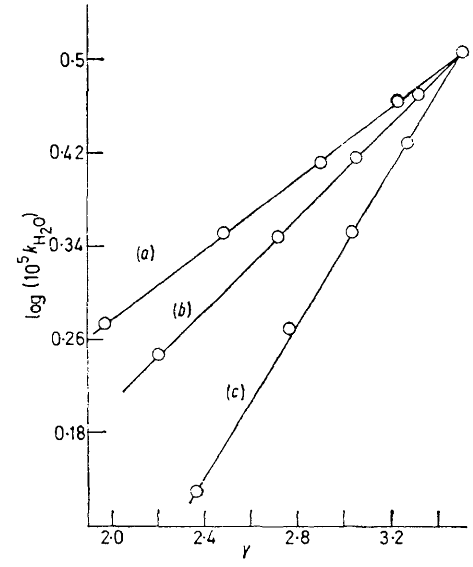

FIGURE 2 Variation of log k_{H_2O} with Y for aquation of *cis*-$[Ru(en)_2Cl_2]Cl$ in mixed water–organic solvents: (a), acetone; (b), ethanol; (c), methanol

Unlike the spontaneous aquations above, plots of log $k_{Hg^{2+}}$ against Y were distinctly non-linear (Figure 3).

$$k_{Hg^{2+}} = k_{obs.} - k_{H_2O} \qquad (3)$$

Rate constants for the Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl][BF_4]_2$ at various Hg^{2+} concentrations in 0·04M-$HClO_4$ are collected in Table 5. The $k_{Hg^{2+}}$ values were again calculated using equation (3). The corresponding $k_{Hg^{2+}}{}^0$ values at zero ionic strength were calculated using equation (4), which combines the Brønsted equation with the Debye–Huckel limiting law {Z_A, Z_B are the ionic charges on $[Ru(NH_3)_5Cl]^{2+}$ and Hg^{2+}, and I is the ionic strength of the solution}. The reactions were generally followed for one half-life, giving good pseudo-first-order kinetics. A plot of $k_{Hg^{2+}}{}^0$ against $[Hg^{2+}]$ was curved. However, a plot of $(k_{Hg^{2+}}{}^0)^{-1}$ against $[Hg^{2+}]^{-1}$ yielded a good linear relation (Figure 4).

$$\log k_{Hg^{2+}}{}^0 = \log k_{Hg^{2+}} - 1{\cdot}02\, Z_A Z_B\, I^{\frac{1}{2}} \qquad (4)$$

TABLE 3

Kinetic data for aquation of *cis*-$[Ru(en)_2Cl_2]Cl{\cdot}OH_2$ in mixed water–organic solvents at 25·0 °C and [p-$MeC_6H_4SO_3H$] = 0·010M

Concentration of organic component/	Methanol		Ethanol		Acetone	
% (v/v)	Y	$10^5k/s^{-1}$	Y	$10^5k/s^{-1}$	Y	$10^5k/s^{-1}$
0	3·49	3·23	3·49	3·23	3·49	3·23
10	3·28	2·66	3·31	2·94	3·23	2·88
20	3·03	2·24	3·05	2·58	2·91	2·53
30	2·75	1·87	2·72	2·22	2·48	2·25
40	2·39	1·34	2·20	1·72	1·98	1·86

Attempts to study aquation in water–acetic acid mixtures gave inconsistent results, probably due to concomitant substitution by acetate ions.

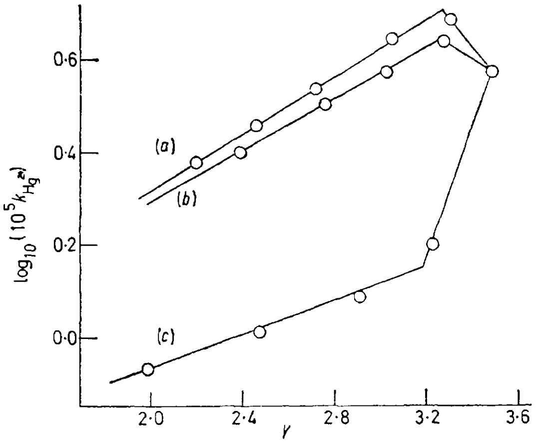

FIGURE 3 Variation of log $k_{Hg^{2+}}$ with Y for the Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl]Cl_2$ in mixed water–organic solvents: (a), ethanol; (b), methanol; (c), acetone

TABLE 4

Dependence of m values on the nature of the mixed-solvent pair for aquation of analogous cobalt(III) and ruthenium(III) complexes

Complex	$MeOH–H_2O$	$EtOH–H_2O$	$Me_2CO–H_2O$	Ref.
$[Ru(NH_3)_5Cl]^{2+}$	0·24	0·22	0·24	*a*
cis-$[Ru(en)_2Cl_2]^+$	0·33	0·22	0·16	*b*
$[Co(NH_3)_5Cl]^{2+}$	0·33	0·20	0·16	*c*
cis-$[Co(en)_2Cl_2]^+$	0·37	0·37	0·27	*c*

[a] This work, 45·5 °C. [b] This work, 25 °C. [c] Ref. 3, 35 °C.

DISCUSSION

Spontaneous Aquation.—Solvolysis of the complexes by the organic component does not occur in any of the sol-

TABLE 5

Kinetic data for Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl][BF_4]_2$ in 0·04M-$HClO_4$ at 45·5 °C

$10^2[Hg^{2+}]$/M	$10^4[Ru(NH_3)_5Cl^{2+}]$/M	$10^5k_{obs.}$/s^{-1}	$10^5k_{Hg^{2+}}$/s^{-1}	10^2I/M	$10^6k_{Hg^{2+}}^0$/s^{-1}
0·10	2·96	1·43	0·374	4·19	0·557
0·20	2·96	1·73	0·672	4·29	0·979
0·30	2·97	1·98	0·918	4·39	1·31
0·40	2·94	2·21	1·15	4·49	1·66
0·60	2·96	2·74	1·68	4·69	2·24
0·80	2·23	2·95	1·86	4·87	2·39
1·00	2·62	3·13	2·07	5·08	2·55
1·12	3·08	3·27	2·21	5·22	2·64
1·20	2·33	3·33	2·27	5·27	2·67
1·50	2·83	3·85	2·79	5·58	3·10

vent mixtures employed, since the same isosbestic points were always observed as were found for aquation [9,13] in water. Thus the rate constants reported refer only to aquation, possible interference from the reverse anation processes being eliminated by employing theoretical A_∞ values (see Experimental section).

TABLE 6

Kinetic data for Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl]Cl_2$ in mixed water–organic solvents at 45·5 °C, $[Hg^{2+}]$ = 0·0112M, and $[HClO_4]$ = 0·040M

Concentration of organic component/ % (v/v)	Methanol *		Ethanol		Acetone	
	Y	$10^5k_{Hg^{2+}}$/s^{-1}	Y	$10^5k_{Hg^{2+}}$/s^{-1}	Y	$10^5k_{Hg^{2+}}$/s^{-1}
0	3·49	3·74 (5·47)	3·49	3·74	3·49	3·74
10	3·28	4·34 (7·43)	3·31	4·83	3·23	1·58
20	3·03	3·74 (6·59)	3·05	4·39	2·91	1·21
30	2·75	3·15 (5·19)	2·72	3·42	2·48	1·02
35			2·46	2·88		
40	2·39	2·49	2·20	2·36	1·98	0·85

* Average of three separate determinations; average reproducibility 2—3%. Values in parentheses are at 50·8 °C.

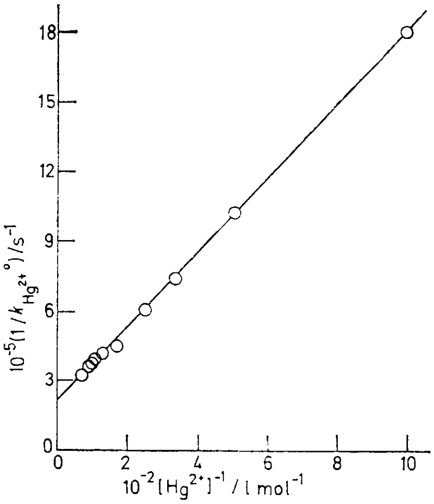

FIGURE 4 Dependence of $k_{Hg^{2+}}^0$ on $[Hg^{2+}]$ for the Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl][BF_4]_2$ in 0·04M-$HClO_4$

A striking feature of the spontaneous-aquation data is the good fit to the Grunwald–Winstein [1] relation (5),

$$\log (k/k_0) = mY \qquad (5)$$

where k is the aquation rate constant in any solvent, k_0 that in a standard solvent, Y a measure of the ionising power of the solvent, and m gives the sensitivity of the substrate to changes in the medium. Also interesting is the similarity of the m values (Table 4) to those previously observed for analogous cobalt(III) complexes.[3,4] Since the Co^{III} complexes are known to aquate *via* an essentially S_N1 dissociative mechanism,[14] a similar mechanism is therefore suggested for ruthenium(III). This observation contrasts with earlier evidence [9] (based on the effect of steric crowding and chelation) indicating an associative mechanism for aquation of these Ru^{III} complexes.

However, m values are known from organic studies [15] to depend not only on the mechanism but also to some extent on the nature of the standard substrate. Unfortunately, it is difficult to predict (assuming a constant aquation mechanism) the effect on m of changing the central metal in $[M(NH_3)_5Cl]^{2+}$ from Co^{III} to Ru^{III}. Considering only complex charge and size, one would expect little variation. On the other hand, in view of the generally more covalent (and less ionic) character of metal–ligand bonds in second- compared to first-row transition-metal complexes, one might reasonably predict that in a hypothetical S_N1 aquation Ru^{III} complexes would show significantly higher m values than the average of 0·3 found for Co^{III}. Thus, with our presently limited knowledge of solvent effects on octahedral aquation, the average m values of *ca.* 0·23 observed here for $[Ru(NH_3)_5Cl]Cl_2$ and *cis*-$[Ru(en)_2Cl_2]Cl$ do not necessarily exclude the presence of appreciable associative contributions.

Nevertheless, it would appear to be somewhat more than fortuitous that m values between 0·2 and 0·35 have now been observed for substitution reactions of analogous aminechloro-complexes of Co^{III}, Rh^{III}, Ir^{III}, and Ru^{III}. Certainly, for the first three systems other evidence [14] supports essentially dissociative mechanisms (albeit with increasing associative character passing down the triad [16]). It would thus appear that Grunwald–Winstein m values may be useful in delineating the broad mechanistic

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[13] J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1964, **3**, 826.

[14] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., John Wiley, New York, 1967, ch. 3.

[15] L. Wilputte-Steinert and P. J. C. Pierens, *Bull. Soc. chim. belges*, 1955, **64**, 308.

[16] E. Borghi, F. Monacelli, and T. Prosperi, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 667.

features of the aquation of octahedral complexes, suggesting an essentially S_N1 mechanism for the Ru^{III} complexes studied here. However, precise estimates of the degree of associative character seem presently beyond the power of the method.

A further interesting feature of the *m* values reported in Table 4 is that, while a constant value ($0{\cdot}23 \pm 0{\cdot}01$) is obtained for $[Ru(NH_3)_5Cl]Cl_2$ with all solvent mixtures, different gradients are observed for different solvent pairs for the related complex *cis*-$[Ru(en)_2Cl_2]Cl{\cdot}OH_2$. This dispersion is also common to Co^{III} aquations,[3,5] and is well documented in the aquation of primary and secondary organic substrates.[17,18] It has been attributed to variations in the nucleophilicity (*N*) of the organic solvent component, and the more comprehensive relation (6) has been proposed [18] to account for both the ionising power (*Y*) and nucleophilicity (*N*) of the solvent. Here *l* is a

$$\log (k/k_0) = lN + mY \qquad (6)$$

measure of the sensitivity of the substrate to changes in nucleophilicity of the solvent. *N* Values have recently been evaluated [19] for aqueous methanol and ethanol and found to be similar. This explains why even primary organic substrates give satisfactory correlations in such solvents using the simple equation (1). On the other hand, a much lower nucleophilicity was calculated [19] for water–acetone mixtures, which is consistent with the lower ' apparent-*m* ' values observed here for this solvent pair. However, the variations in ' apparent-*m* ' values observed here for *cis*-$[Ru(en)_2Cl_2]^+$ cannot be adequately explained in terms of solvent nucleophilicity alone. While the low value for acetone (0·16) is expected, the very high value for methanol (0·33) compared to ethanol (0·22) is inconsistent with the similar nucleophilicities of the alcohols. In addition, it is not obvious why solvent nucleophilicity should be important for *cis*-$[Ru(en)_2Cl_2]^+$ but not $[Ru(NH_3)_5Cl]^{2+}$. Perhaps these different solvent responses reflect differences in aquation mechanism for these two complexes.

Finally, the temperature-dependence data in Table 2 for the aquation of $[Ru(NH_3)_5Cl]Cl_2$ in various ethanol–water mixtures reveal a small dependence of $\Delta H^‡$ and $\Delta S^‡$ on the mol fraction of ethanol. This observation is similar to previous results [4,20] for aquation of $[Co(NH_3)_5Cl]^{2+}$ over similar solvent-composition ranges. The significance of these variations in activation parameters with medium changes is difficult to assess with the present limited data.

Mercury-catalysed Aquation.—Preliminary kinetic results for the Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl][BF_4]_2$ (Table 5) provide strong mechanistic evidence. The failure to observe a second-order rate law (a plot of observed first-order rate constants, $k_{Hg^{2+}}$, against $[Hg^{2+}]$ is curved at $[Hg^{2+}] > 2 \times 10^{-3}$M) rules out a mechanism involving electrophilic attack by Hg^{2+} to remove a chloride ligand, followed by rapid addition of water to the five-co-ordinate intermediate, $[Ru(NH_3)_5]^{3+}$. However, a plot (Figure 4) of log $(1/k_{Hg^{2+}}{}^0)$ against $[Hg^{2+}]^{-1}$ is linear over the entire Hg^{2+}-concentration range studied ($0{\cdot}10 \times 10^{-2}$—$1{\cdot}5 \times 10^{-2}$M). This behaviour is similar to that previously observed for the Hg^{2+}-catalysed aquation of related complexes such as *cis*-$[Co(en)_2Cl_2]^+$ (ref. 21) and indicates the three-step mechanism in equations (7)—(9). The rate law for such a mechanism is (10). Rearranging equation (10) yields (11), which predicts the linear plot observed in Figure 4. From the gradient and intercept of this plot, values for *k* and *K* can

$$[Ru(NH_3)_5Cl]^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} [(H_3N)_5Ru\text{–}Cl\text{–}Hg]^{4+} \qquad (7)$$

$$[(H_3N)_5Ru\text{–}Cl\text{–}Hg]^{4+} \xrightarrow{k} [Ru(NH_3)_5]^{3+} + [HgCl]^+ \qquad (8)$$

$$[Ru(NH_3)_5]^{3+} + H_2O \xrightarrow{\text{fast}} [Ru(NH_3)_5(OH_2)]^{3+} \qquad (9)$$

$$\begin{aligned}\text{Rate} &= \frac{kK[Ru(NH_3)_5Cl^{2+}][Hg^{2+}]}{1 + K[Hg^{2+}]} \\ &= k_{Hg^{2+}}[Ru(NH_3)_5Cl^{2+}] \qquad (10)\end{aligned}$$

$$\frac{1}{k_{Hg^{2+}}} = \frac{1}{kK[Hg^{2+}]} + \frac{1}{k} \qquad (11)$$

be calculated. The equilibrium constant *K* for formation of the chloro-bridged intermediate is $3{\cdot}12 \times 10^3$ l mol^{-1}, while the rate constant *k* for its S_N1 dissociation is $4{\cdot}55 \times 10^{-6}$ s^{-1}.

In contrast to spontaneous aquation, plots of log $k_{Hg^{2+}}$ against *Y* for the Hg^{2+}-catalysed aquation of $[Ru(NH_3)_5Cl]Cl_2$ in mixed water–organic solvents are non-linear (Figure 3). However, it is interesting that good correlations are in fact observed for solvents containing 10—40% organic component (*m* $0{\cdot}24 \pm 0{\cdot}05$). An abrupt break occurs in all plots at *ca.* 10% organic component, being most striking for the water–alcohol mixtures where the gradient changes sign (from positive to negative). The characteristic V-shaped curves might suggest a change in reaction mechanism near 10% organic component. However, the behaviour shown in Figure 3 may be accommodated by the mechanism in equations (7)—(9) which was shown above to operate in aqueous solution. Solvent variations should effect *k* and *K* differently. The rate constant *k* for the slow dissociative step (8) is expected to show a similar solvent dependence to that observed above for spontaneous aquation (*i.e.* *m* + 0·25, Table 4). In contrast, since the pre-equilibrium formation of the bridged species $[(H_3N)_5Ru\text{–}Cl\text{–}Hg]^{4+}$ will involve some desolvation,[22] replacing solvent water by organic components of lower solvating ability (*Y*) should increase *K*. The curves observed for the alcohol–water solvent mixtures may thus be rationalised in terms of these opposing influences. However, no

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[17] S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700.

[18] S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Amer. Chem. Soc.*, 1957, **79**, 4146.

[19] T. W. Bentley, F. L. Schadt, and P. V. R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 992.

[20] K. O. Watkins and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1964, **26**, 469.

[21] C. Bifano and R. G. Linck, *Inorg. Chem.*, 1968, **7**, 908.

[22] S. C. Chan and S. F. Chan, *Austral. J. Chem.*, 1971, **24**, 895.

explanation is apparent for the completely different solvent-dependence behaviour of water–acetone mixtures, in which a different mechanism is perhaps operating.

The behaviour of $[Ru(NH_3)_5Cl]^{2+}$ during Hg^{2+}-catalysed aquation in mixed solvents is unique, since analogous studies[3] of the related $[M(NH_3)_5Cl]^{2+}$ ($M = Co^{III}$ or Rh^{III}) complexes yielded straightforward linear plots, with negative gradients of *ca.* —0·3. This strikingly different behaviour is not surprising, since kinetic studies[23] of the Hg^{2+}-catalysed aquation of $[Co(NH_3)_5Cl]^{2+}$ in pure aqueous solution yielded a second-order rate law, Rate $= k'[Co(NH_3)_5Cl^{2+}][Hg^{2+}]$, over a wide range of Hg^{2+} concentrations. These results for $[Co(NH_3)_5Cl]^{2+}$ are consistent with the mechanism in equations (7)—(9) only provided $K \ll 1$.

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[23] F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, 1957, **79**, 255.