(4) The k_{2d} value for the TPTZ complex is 4000 times greater than the k_{2d} value for $Fe(terpy)_2^{2+}$, paralleling the relative stability constants of the complexes. In the absence of hydrogen ion or hydroxide ion acceleration of the rate-determining step is the third bond dissociation of TPTZ.

(5) The dissociation of $Fe(TPTZ)_2^{2+}$ is accelerated by hydrogen ion and by hydroxide ion and in both cases prior dissociation steps can become rate limiting. As a result a complete stepwise mechanism can be identified in the loss of the first TPTZ.

(6) Above pH 9 direct reaction is observed between $Fe(TPTZ)_2^{2+}$ and hydroxide ion. This is similar to the reaction of $Fe(phen)_3^{2+}$ with OH^- but with TPTZ the hydroxide ion rate constant is 3000 times greater.[11] Hence hydroxide ion can attack the complex directly as well as taking part in the stepwise dissociation.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SCHOOL OF GENERAL STUDIES,
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Substitution Reactions of Ruthenium(III)–Ethylenediamine and Related Complexes. I. Acid Hydrolysis of *cis*-Dihalogenobis(ethylenediamine), (—)-1,2-Diaminopropane, Triethylenetetramine, and Ammonia Complexes

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Kinetics and stereochemistry of primary and secondary aquation of *cis*-dihalogenobis(ethylenediamine)ruthenium(III), *cis*-dichlorobis((−)-1,2 diaminopropane)ruthenium(III), *cis*-α-dichlorotriethylenetetramineruthenium(III), and *cis*-dichlorotetraammineruthenium(III) have been studied together with acid hydrolyses of bromo- and iodopentaammineruthenium(III) cations. The aquation reactions take place with complete retention of configuration. Charge has no effect on the rates, while increased chelation results in progressively faster rates. These results can be explained by an SN2 mechanism for aquation. The equilibria pertaining to *cis*-diaquobis(ethylenediamine)ruthenium(III) with chloride or bromide ions and aquopentaammineruthenium(III) with bromide or iodide ions have been studied as a function of temperature. pK_a values of 5.30 ± 0.05 at 23° have been measured for *cis*-$RuXH_2O(en)_2^{2+}$ (X = Cl, Br).

Introduction

The first study of the substitution processes in ruthenium(III) ammines was concerned with the $RuCl(NH_3)_5^{2+}$ cation.[2] Though this complex behaved similarly to Co(III), Cr(III), and Rh(III) with respect to acid hydrolysis, in basic solution loss of the chloro ligand was very fast and therefore similar to the well-known Co(III) system. To obtain information on the stereochemistry of ruthenium(III) reactions we have, therefore, studied the bis-bidentate chelate complexes *cis*-$[RuX_2(en)_2]X$ (X = Cl, Br, I; en = ethylenediamine) and *cis*-$[RuCl_2((-)pn)_2]Cl$ ((−)pn = (−)-1,2-diaminopropane) and the related *cis*-α-$[RuCl_2(trien)]Cl$ (trien = triethylenetetramine) and *cis*-$[RuCl_2(NH_3)_4]Cl$. The initial work on $[RuCl(NH_3)_5]Cl$ has also been extended to include $RuBr(NH_3)_5^{2+}$ and $RuI(NH_3)_5^{2+}$. The syntheses and characterization of these chelate complexes have been described earlier.[3] In this paper the results of kinetic studies in acid solution are given.

Experimental Section

Materials.—*cis*-$[RuCl_2(NH_3)_4]Cl \cdot H_2O$ was obtained by the action of concentrated HCl on $[RuC_2O_4(NH_3)_4]I$[4,5] and was recrystallized as orange needles from dilute HCl (2 *M*). *Anal.* Calcd for $H_{14}N_4Cl_3ORu$: N, 19.1; Cl, 36.2. Found: N, 18.5; Cl, 36.1. The absorption spectrum agreed with previous work[6] and also corresponded closely to that of *cis*-$RuCl_2(en)_2^+$.

***cis*-Bromoaquobis(ethylenediamine)ruthenium(III) *p*-Toluenesulfonate Monohydrate, $[RuBrH_2O(C_2H_8N_2)_2](C_7H_7SO_3)_2 \cdot H_2O$.**—This light brown compound was prepared by a method analogous to that described for the corresponding chloro complex. *Anal.* Calcd for $C_{18}H_{34}BrS_2N_4O_8Ru$: C, 31.8; H, 5.0; Br, 11.8; S, 9.4; N, 8.2. Found: C, 31.9; H, 5.0; Br, 12.4; S, 8.6; N, 8.5.

***cis*-Iodoaquobis(ethylenediamine)ruthenium(III) *p*-Toluenesulfonate, $[RuIH_2O(C_2H_8N_2)_2](C_7H_7SO_3)_2$.**—This complex could not be obtained pure by the methods[3] which were successful for the chloro and bromoaquo counterparts. In this procedure the addition of ethanol resulted in dissolution of the purple reaction product. For the kinetic studies the complex was best formed *in situ* by treating *cis*-$[RuI_2(en)_2]I \cdot H_2O$ with base followed by acidification with *p*-toluenesulfonic acid.

***cis*-α-Chloroaquotriethylenetetramineruthenium(III) *p*-Toluenesulfonate Monohydrate, $[RuClH_2O(C_6H_{18}N_4)](C_7H_7SO_3)_2 \cdot H_2O$.**—This pale yellow complex was prepared as for the $RuClH_2O(en)_2^{2+}$

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(1) On sabbatical leave at Stanford University, Stanford, Calif., from Australian National University, Canberra, Australia.

(2) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).

(3) J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc., A*, 546 (1967).

(4) K. Gleu and W. Breuel, *Z. Anorg. Allgem. Chem.*, **237**, 326, 335, 350 (1938).

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(6) H. Hartmann and C. Bushbeck, *Z. Physik. Chem.* (Frankfurt), **11**, 120 (1957).

complex, starting with *cis*-α-[$RuCl_2$(trien)]Cl·$2H_2O$. *Anal.* Calcd for $C_{20}H_{38}ClS_2N_4O_8Ru$: C, 36.3; H, 5.5; S, 9.7; N, 8.5. Found: C, 36.3; H, 5.4; S, 8.6; N, 9.1.

Absorption Spectral Studies.—Repetitive scanning of the ultraviolet–visible spectral region during hydrolysis in 0.1 *M* *p*-toluenesulfonic acid gave well-defined isosbestic points for *cis*-$RuX_2(en)_2^+$ (X = Cl, Br, I) and *cis*-$RuCl_2(AA)_2^+$ (AA = $2NH_3$, (−)pn, 0.5trien) but only for the first 25–30% of the primary aquation stage. Typical spectral changes are illustrated for *cis*-$RuCl_2(en)_2^+$ and *cis*-$RuBr_2(en)_2^+$ in Figures 1 and 2, and the spectra of *cis*-$RuXH_2O(en)_2^{2+}$ (X = Cl, Br) have been included. It is seen that their spectra pass through the isosbestic points characteristic of the initial stages of primary aquation. Within experimental error (±2 mμ) the spectra of *cis*-$RuClH_2O(AA)_2^{2+}$ (AA = (−)pn, $2NH_3$, 0.5trien) likewise passed through the corresponding isosbestic points for the initial aquations of the *cis*-$RuCl_2(AA)_2^+$ parent complexes.

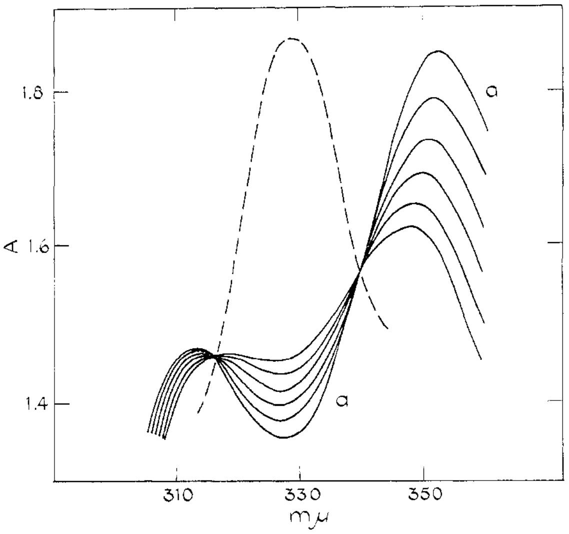

Figure 1.—Absorption spectral changes during primary aquation of *cis*-$RuCl_2(en)_2^+$ at 35.5°. Curve a is the initial trace followed successively by traces at 9, 17.5, 25, 35, and 40 min reaction. The dotted line gives the spectrum of *cis*-$RuClH_2O(en)_2^{2+}$.

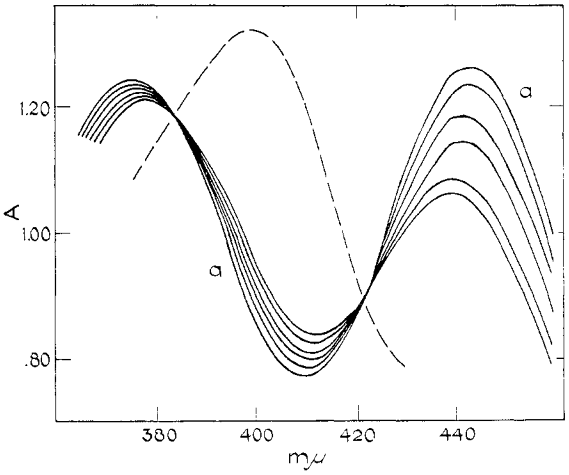

Figure 2.—Absorption spectral changes during primary aquation of *cis*-$RuBr_2(en)_2^+$ at 35.1°. Curve a is the initial trace followed successively by traces at 4.5, 15, 24, 37, and 40 min reaction. The dotted line gives the spectrum of *cis*-$RuBrH_2O(en)_2^{2+}$.

Spectral changes accompanying the aquation of *cis*-$RuClH_2O(en)_2^{2+}$ are illustrated in Figure 3. Here a single sharp isosbestic point is obtained throughout the entire reaction. Similar behavior is found for the other secondary aquations reported in this work.

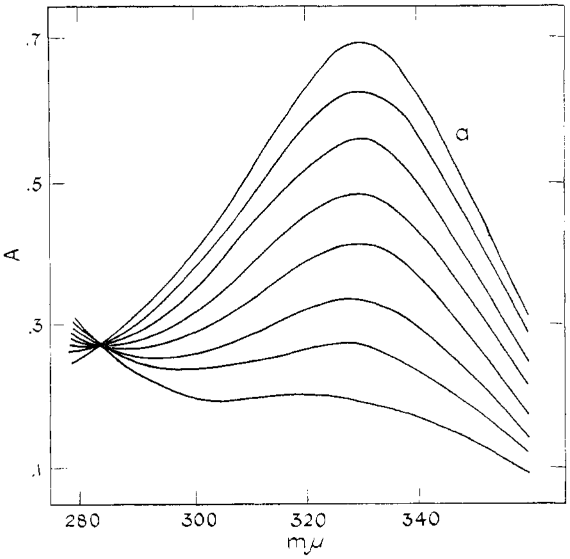

Figure 3.—Absorption spectral changes during aquation of *cis*-$RuClH_2O(en)_2^{2+}$ at 45°. Curve a is the initial trace followed successively by traces at 7, 15, 27, 40, 60, 80, and 130 min reaction.

Conclusive proof of retention of geometrical configuration during the primary and secondary aquation reactions for the substrates *cis*-$RuCl_2(en)_2^+$ and *cis*-$RuCl_2((-)pn)_2^+$ was obtained from the following experiments, using optically active samples.

Retention Experiments.—*cis*-(−)[$RuCl_2(en)_2$]I (0.0084 g) was converted to the chloride salt by shaking for 5 min at room temperature with an aqueous suspension of freshly prepared silver chloride. The silver halides were filtered off and washed with water. *p*-Toluenesulfonic acid (0.4 g) was added to the filtrate and washings and the volume was made up to 25 ml with water, giving a concentration of *cis*-(−)[$RuCl_2(en)_2$]Cl of 7.97 × 10^{-4} *M*. The optical rotary dispersion (ORD) curve was then recorded by means of a Jasco UV-5 recording spectropolarimeter. The solution was next removed and heated at 58° for 3 hr, after which time the spectrum showed that formation of the $Ru(H_2O)_2(en)_2^{3+}$ complex was 82% complete. Concentrated hydrochloric acid (0.3 ml) was added to 2 ml of the solution, which was allowed to age 24 hr at room temperature. The ORD was again measured and found to be identical with that of *cis*-$RuCl_2(en)_2^+$. In another experiment carried out in a similar fashion, but using a more concentrated solution (1.47 × 10^{-2} *M*) of the parent complex, rotations were measured visually by means of a conventional Schmidt and Haensch polarimeter. In this case the reaction was followed at 5890 Å and the solution had reached zero rotation at the stage where the regeneration reaction was initiated. Within experimental error, 100% of the expected rotation was regenerated.

Retention of optical activity has also been shown for the acid hydrolysis of *cis*-(+)[$RuCl_2((-)pn)_2$]Cl. A 0.0134% solution of this complex was allowed to hydrolyze in 0.1 *M* *p*-toluenesulfonic acid for 7 hr at 45°. At this stage the spectrum indicated that aquation of both chloride ligands was almost complete. Concentrated hydrochloric acid was added to give a final chloride ion concentration of 2 *M* and complex concentration of 0.0107%. The ORD and absorption spectrum were recorded after the solution had aged 24 hr at room temperature. Again the rotatory dispersion after regeneration was in accord with the values for pure (+)[$RuCl_2((-)pn)_2$]Cl. The absorption spectrum of the regenerated complex also agreed with that of the *cis*-dichlorobis((−)-1,2-diaminopropane)ruthenium(III) complex.

Kinetic Studies.—For the various ruthenium(III) bis-bidentate complexes studied, aquation involved the reactions

$$cis\text{-}RuX_2(AA)_2^+ + H_2O \underset{}{\overset{k_1}{\rightleftarrows}} cis\text{-}RuXH_2O(AA)_2^{2+} + X^- \quad (1)$$

$$cis\text{-}RuXH_2O(AA)_2^{2+} + H_2O \underset{}{\overset{k_2}{\rightleftarrows}} cis\text{-}Ru(H_2O)_2(AA)_2^{3+} + X^- \quad (2)$$

The positions of these equilibria corresponded to the release of 60–95% of the total halide originally present in $RuX_2(AA)_2^+$ (see Table I). In this work, knowledge of the absorption spectra of the intermediate *cis*-$RuXH_2O(AA)_2^{2+}$ complexes has permitted evaluation of the rate constants for both forward and reverse stages of reactions 1 and 2. It is the forward reactions that will concern us in this paper.

TABLE I

TYPICAL DATA ILLUSTRATING THE EXTENT OF THE ACID HYDROLYSIS REACTIONS OF *cis*-$[RuCl_2(en)_2]Cl \cdot H_2O$ AND *cis*-α-$[RuCl_2(trien)]Cl \cdot 1.5H_2O$

Temp, °C	10^4[complex], *M*	% total chloride released at equil
45.0	0.96[a]	95[c]
45.0	23.9[a]	60[c]
25.0	2.99[a]	95[c]
25.1	4.55[b]	80.1[d]
35.5	5.16[b]	77.5[d]
45.0	5.12[b]	73.5[d]

[a] *cis*-$[RuCl_2(en)_2]Cl \cdot H_2O$. [b] *cis*-$\alpha$-$[RuCl_2(trien)]Cl \cdot 1.5H_2O$. [c] By mercurimetric titration. [d] Spectrophotometrically.

Previous studies with $RuCl(NH_3)_5^{2+}$ had shown that hydrolysis in nitric or perchloric acids led to the rapid formation of unknown brown products.[2] Similar behavior was also observed for the ethylenediamine complexes; consequently, the hydrolyses were carried out in *p*-toluenesulfonic acid.

The wavelengths (mμ) used for the kinetic studies of each *cis* complex were as follows: $RuCl_2(en)_2^+$, 355; $RuBr_2(en)_2^+$, 445; $RuI_2(en)_2^+$, 655; $RuCl_2(NH_3)_4^+$, 352; α-$RuCl_2(trien)^+$, 352; $RuCl_2((-)pn)_2^+$, 354; $RuClH_2O(en)_2^{2+}$, 329; $RuBrH_2O(en)_2^{2+}$, 398; $RuIH_2O(en)_2^{2+}$, 549; $RuClH_2O(trien)^{2+}$, 336. For individual complexes, exposure to the spectrophotometer light beam had no effect on the rates. The titrimetric method was essentially that described previously.[2] Chloride was determined with mercuric nitrate using sodium nitroprusside indicator.[7]

The rates of acid hydrolyses were usually determined by the spectrophotometric method. Solutions of all complexes were found to obey Beer's law. For *cis*-$RuCl_2(en)_2^+$, the titration method was also used but was not employed more widely owing to a lack of materials.

Attempts to follow the acid hydrolyses by measurements of the electrical resistance failed as reaction at, or with, the platinum electrodes took place. For *cis*-$RuCl_2(en)_2^+$ (and also *cis*-$RuClH_2O(en)_2^{2+}$) a deep yellow color originated at the electrode and corresponded with an absorption in the visible spectrum at 450 mμ. Similar absorption spectra were obtained from aqueous solutions of these complexes that had aged for several days.

In the spectrophotometric method *p*-toluenesulfonic acid solutions of the reactants were thermostated at the desired temperature (±0.05°) in a water bath. An accurate weight of complex was then added sufficient to give a final complex concentration of 5×10^{-4} *M*, and the solid rapidly dissolved by shaking. The solution was transferred quickly to a 1-cm silica cell previously thermostated in a Beckman DK-2A spectrophotometer. Appropriate reference solutions were used in all cases. Progress of a reaction was followed either at a single wavelength or, in some cases, at several wavelengths. For example, the disappearance of *cis*-$RuX_2(en)_2^+$ and the appearance of *cis*-$RuXH_2O(en)_2^{2+}$ were conveniently recorded together (see Figures 1 and 2).

Kinetics of Primary Aquation.—Acid hydrolyses as represented in eq 1 were found to follow a simple, first-order rate law. Rate constants have been calculated from the slopes (m) of the plots of log $[(A_\infty - A_0)/(A_\infty - A_t)]$ *vs.* time, where $k_1 = 2.303\ m$. Here A_0 and A_t refer the absorbance initially and at time t, while A_∞ is the absorbance of the products which was obtained independently from the spectra of pure *cis*-$RuXH_2O(AA)_2^{2+}$. The A_∞ used did not correspond to the actual values taken from a rate run since reaction 2 interfered. Titrimetric rate constants have similarly been evaluated using the measured chloride ion concentrations and an infinity value corresponding to the release of one chloride ligand. The first-order rate plots were linear for 25–30% of reaction 1 and then deviated to curves of increased slopes. This loss of linearity corresponded in time to the disappearance of the sharp isosbestic points in the absorption spectra and is accounted for by the presence of reaction 2. For each of the complexes reported here, the rates increase rather than decrease with time so that the possible attainment of equilibrium at stage 1 may be discounted. The retention experiments prove that, at least for *cis*-$RuCl_2(en)_2^+$, *cis*-$RuBr_2(en)_2^+$ and *cis*-$RuCl_2((-)pn)_2^+$, isomerization to the *trans* species is not a complication.

Kinetics of Secondary Aquation.—Acid hydrolyses of *cis*-$RuXH_2O(AA)_2^{2+}$ complexes were found to obey an opposed first-order–second-order rate law. Rate constants (k_2) have been calculated from the plots of log $\{ax_e + [x(a - x_e)/a(x_e - x)]\}$ *vs.* time. Straight lines were obtained in which the slope is equal to $k_2(2a - x_e)/2.303x_e$. Here a is the initial concentration of $RuXH_2O(AA)_2^{2+}$, x is the concentration of $Ru(H_2O)_2(AA)_2^{3+}$ at time t, and x_e is the concentration of the diaquo species at equilibrium. x is given by the expression $(\epsilon_1 a - A_t)/(\epsilon_1 - \epsilon_2)$, where ϵ_1 and ϵ_2 are the respective extinction coefficients at the relevant wavelengths of $RuXH_2O(AA)_2^{2+}$ and $Ru(H_2O)_2(AA)_2^{3+}$, and A_t is the absorbance of the reaction solution at time t.

Since the equilibrium in reaction 2 was well to the right, it was more convenient to use a simple first-order treatment to calculate k_2 values. Plots of log $[(A_\infty - A_0)/(A_\infty - A_t)]$ against time were linear for about 2 half-lives. Rate constants agreed within experimental error with those obtained using the opposed first-order–second-order calculations. Most of the rate data have been evaluated by this alternative method.

Acid Hydrolyses of $RuBr(NH_3)_5^{2+}$ and $RuI(NH_3)_5^{2+}$.—Rate data for these complexes were obtained by methods[2] analogous to those described for $RuCl(NH_3)_5^{2+}$.

Equilibrium Studies.—Values of x_e from the kinetic studies permitted calculations of the equilibrium quotients K for the anation reactions

$$Ru(H_2O)_2(en)_2^{3+} + X^- \rightleftharpoons RuXH_2O(en)_2^{2+} + H_2O \quad (X = Cl, Br)$$

$$RuH_2O(NH_3)_5^{3+} + X^- \rightleftharpoons RuX(NH_3)_5^{2+} + H_2O \quad (X = Br, I)$$

where $K = (a - x_e)/x_e^2$. Values of K are given in Tables II–IV.

pK_a Measurements.—The 10^{-3} *M* solutions of *cis*-$[RuClH_2O(en)_2](C_7H_7SO_3)_2 \cdot H_2O$ and *cis*-$[RuBrH_2O(en)_2](C_7H_7SO_3)_2 \cdot H_2O$ in carbon dioxide free water were titrated with freshly prepared potassium hydroxide (10^{-2} *M*). The pH was measured with a Beckman glass-electrode pH meter. Values of pK_a for each complex were read from the half-neutralization stage of the titration and were also calculated at selected intervals along the curves. Duplicate determinations gave identical pK_a values for both complexes of 5.30 ± 0.05 at 23°.

Results and Discussion

Table V cites results for the effects of changes in complex concentrations, ionic strength, acid concentration, and temperature on the acid hydrolysis rates. It is seen that variations in acid over the range 10^{-3}–10^{-1} *M* had no significant effect on rates. Activation energies and log A factors have been obtained from the usual Arrhenius plots analyzed by the method of least squares and are collected in Table VI.

While the pseudo-first-order rate laws found with these complexes by themselves disclose nothing about the molecularity of the reactions, some information on the mechanisms can be obtained. An examination of

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(7) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1953, pp 460, 547–549.

TABLE II

EQUILIBRIUM DATA FOR THE REACTION *cis*-$Ru(H_2O)_2(en)_2^{3+}$ + $Cl^- \rightleftarrows$ *cis*-$RuClH_2O(en)_2^{2+}$ + H_2O IN 0.1 *M* *p*-TOLUENESULFONIC ACID

Temp, °C	10^4[chloroaquo complex], *M*	$K^{b,c}$	F^d
24.9	3.41	277	0.920
35.5	4.24	316	0.891
45.0	4.25	368	0.879
45.0	4.63	318	0.885
45.0	18.1	291^a	0.724
54.7	4.03	316	0.891
54.7	4.22	406	0.869
54.7	9.04	330^a	0.881

[a] By chloride titration. [b] Ionic strength 0.1 *M*. [c] Error ±13%. [d] *F* is the fraction of *cis*-$Ru(H_2O)_2(en)_2^{3+}$ formed at equilibrium.

TABLE III

EQUILIBRIUM DATA FOR THE REACTION *cis*-$Ru(H_2O)_2(en)_2^{3+}$ + $Br^- \rightleftarrows$ *cis*-$RuBrH_2O(en)_2^{2+}$ + H_2O IN 0.1 *M* *p*-TOLUENESULFONIC ACID

Temp, °C	10^4[bromoaquo complex], *M*	$K^{a,b}$	F^d
54.5	4.22	100	0.961
54.5	3.85	77	0.972
59.9	4.63	120	0.950
59.9	4.41	106	0.957
65.0	3.99	112	0.959
65.0	3.85	89	0.968
65.0	13.9	134^c	0.862
69.9	3.97	121	0.956
69.9	4.13	97	0.963
69.9	4.13	97	$(0.99 \pm 0.03)^c$

[a] Ionic strength 0.1 *M*. [b] Error ±16%. [c] By bromide titration. [d] *F* is the fraction of *cis*-$Ru(H_2O)_2(en)_2^{3+}$ formed at equilibrium.

TABLE IV

EQUILIBRIUM DATA FOR THE REACTION $RuH_2O(NH_3)_5^{3+}$ + $X^- \rightleftarrows RuX(NH_3)_5^{2+}$ + H_2O (X = Br, I) IN 0.1 *M* *p*-TOLUENESULFONIC ACID

Temp, °C	10^4[complex], *M*	K_{Br}	K_I
54.7	4.38	83	. . .
54.7	3.30	94	. . .
70.0	8.08, 3.95^b	89^a	132
80.1	3.92, 3.89^b	104	123
80.1	4.23	92	. . .
90.5	4.13, 4.00^b	101	140

[a] By titration. [b] For the iodo complex.

TABLE V

RATE DATA FOR RUTHENIUM(III)–AMINE COMPLEXES[h]

Temp, °C	10^4k_1,[a] sec^{-1}	Temp, °C	10^4k,[a] sec^{-1}
cis-$[RuCl_2(en)_2]Cl \cdot H_2O$		*cis*-$[RuBr_2(en)_2]Br \cdot H_2O$	
24.9	0.39	30.0	0.594
24.9	0.38^b	35.1	1.14
24.9	$0.37,^c\ 0.34^d$	45.0	3.47, 3.36^e
44.9	3.70, 3.1^g	49.9	5.55
44.9	$3.77,^e\ 2.97^f$	54.4	7.98
35.5	1.34, 1.17^g		
		cis-$[RuI_2(en)_2]I \cdot H_2O$	
cis-$[RuCl_2(NH_3)_4]Cl \cdot H_2O$		35.5	0.359
25.1	0.078	40.0	0.599
45.0	0.875	45.0	1.13
54.7	2.32	50.0	1.83
		54.5	3.24
cis-α-$[RuCl_2trien]Cl$		60.0	5.30
25.1	5.85, 6.85^c		
35.5	17.1	*cis*-$[RuCl_2((-)pn)_2]Cl$	
40.0	26.2	35.5	1.06
		45.0	2.82
cis-$[RuClH_2O(en)_2](C_7H_7SO_3)_2$		54.7	6.36
24.9	0.158		
35.5	0.565	*cis*-$[RuBrH_2O(en)_2](C_7H_7SO_3)_2$	
45.0	1.44, 1.43^b	25.0	0.133
45.0	1.38^e	54.5	3.98
54.7	3.54^g	59.9	7.12
		60.0	$7.22,^b\ 7.02^i$
cis-$[RuIH_2O(en)_2](C_7H_7SO_3)_2$		65.0	11.8
45.1	0.358	69.9	18.2
49.9	0.618		
55.3	1.22	*cis*-$[RuClH_2Otrien](C_7H_7SO_3)_2$	
		25.1	2.00
$[RuBr(NH_3)_5]Br_2$			
54.7	0.310	$[RuI(NH_3)_5]I_2$	
70.0	1.54	70.0	0.583
80.1	3.98	80.1	1.64
90.5	10.6	90.5	4.27

[a] In 0.1 *M* *p*-toluenesulfonic acid and at ionic strength 0.1 *M* unless otherwise stated; average reproducibility ±3%. [b] 10^{-2} *M* acid. [c] 10^{-3} *M* acid. [d] 10^{-4} *M* acid. [e] Acid concentration and ionic strength 0.001 *M*. [f] Acid concentration and ionic strength 1.0 *M*. [g] By titration. [h] Complex concentrations were varied in the range 3.3×10^{-4}–2.2×10^{-3} *M*. [i] Ionic strength 0.01 *M*.

TABLE VI

ARRHENIUS PARAMETERS AND RATE CONSTANTS FOR ACID HYDROLYSIS OF RUTHENIUM(III) COMPLEXES AT 54.5°

Complex ion	10^4k, sec^{-1}	E_a,[c] kcal mol^{-1}	Log *A* (sec^{-1})
cis-$RuCl_2(en)_2^+$	8.68	20.5 ± 0.7	10.6 ± 0.9
cis-$RuBr_2(en)_2^+$	7.98	21.1 ± 0.6	11.0 ± 0.7
cis-$RuI_2(en)_2^+$	3.24	22.7 ± 0.5	11.6 ± 0.7
cis-$RuCl(H_2O)(en)_2^{2+}$	3.86	20.7 ± 0.3	10.4 ± 0.5
cis-$RuBr(H_2O)(en)_2^{2+}$	4.08	22.4 ± 0.4	11.6 ± 0.6
cis-$RuI(H_2O)(en)_2^{2+}$	1.22	25.0 ± 0.7	12.7 ± 0.8
$RuCl(NH_3)_5^{2+}$[b]	3.28^a	23.2	10.8
$RuBr(NH_3)_5^{2+}$	3.99^a	23.2 ± 0.2	11.0 ± 0.4
$RuI(NH_3)_5^{2+}$	1.64^a	24.5 ± 0.1	11.4 ± 0.4

[a] Temperature 80.1°. [b] Reference 2. [c] Errors are the standard deviations obtained *via* the method of least squares.

Table VI shows that acid hydrolysis rates are almost independent of the over-all complex charge. For example, after allowance is made for the statistical factor of 2 favoring the *cis*-$RuX_2(en)_2^+$ cations (X = halide ion), their rates are closely comparable to those of *cis*-$RuXH_2O(en)_2^{2+}$. This indicates that bond breaking alone is not of major importance; otherwise the dipositive cations might be expected to react more slowly than the unipositive cations. As the leaving group is changed from chloride to bromide or iodide, the reaction rates are found in the order Cl ~ Br > I for both the pentaammine and the ethylenediamine complexes. This relative rate sequence is not that predicted on the basis of simple electrostatic considerations.

If the mechanism were of the dissociative (SN1 limiting) type, then the iodo complexes would be expected to show the fastest reactions instead of the slowest. These slower rates may be attributed to the higher activation energy terms. The results suggest that bond making is of more importance for ruthenium(III) than for cobalt(III). If we assume an SN2 mechanism for ruthenium(III) in both primary and secondary aquation, then the recent ideas of Pearson and Songstad[8] may be tested, using the data in Table VI. The prediction is that replacement of the hard base, H_2O, by bases such as Cl^-, Br^-, or I^-, where the hardness is decreasing, should lead to a destabilization of the transition state in an SN2 process and, consequently, slower reactions with high E_a values. The lower rates and higher activation energies for the iodo complexes are in good agreement with this prediction. Differences between the chloro and bromo complexes are marginal, though they do reflect the expected activation energy increase with increased softness of the leaving group. It seems worth noting here that corresponding aquation studies on rhodium(III) halogenopentaammine[9] and bis(ethylenediamine) systems[10] have been interpreted in terms of SN2 mechanisms. The slowest rates and highest activation energies are again found for the iodo complexes, which is in agreement with these symbiotic effect predictions assuming the presence of an SN2 mechanism.

The effects of chelation on the acid hydrolyses are shown in Table VII. For ruthenium there is a marked increase in rates with increased chelation accompanied by an associated decrease in activation energies. The relative order is unchanged over the temperature range investigated and is the direct *opposite* to that found for the analogous Co(III), Cr(III), and Rh(III) cases.

TABLE VII
INFLUENCE OF CHELATION ON PRIMARY AQUATION OF RUTHENIUM(III) COMPLEXES

Complex ion	10^4k, sec^{-1} (25°)	E_a,[b] kcal mol^{-1}	Log A (sec^{-1})
cis-$RuCl_2(NH_3)_4^+$	0.88	22.4 ± 0.5	11.3 ± 0.9
cis-$RuCl_2(en)_2^+$	3.70	20.5 ± 0.7	10.6 ± 0.9
cis-α-$RuCl_2trien^+$	42[a]	18.7 ± 0.1	10.5 ± 0.4
cis-$RuCl_2((-)pn)_2^+$	2.82	18.8 ± 0.8	9.3 ± 0.9

[a] Calculated from Arrhenius parameters. [b] Errors are the standard deviations obtained *via* the method of least squares.

It is possible to give an account of the effects of chelation which incorporates not only the information of Table VII but also that for other metal systems studied to date. In their original discussion of chelation effects in Co(III) acid hydrolyses, Basolo and Pearson[11] pointed out that increased chelation, with its removal of peripheral hydrogen atoms, reduces the effectiveness of positive charge distribution and leads to less efficient solvation in the transition state. This would always predict that rates decrease as chelation increases and certainly does not agree with the Ru(III) results. However, by this same argument, the decreased opportunity for the metal to distribute positive charge with increased chelation must have the effect of increasing the positive charge on the central metal. While this will depend to some extent on the metal (and on its electron affinity), the logical conclusion is that dissociative processes are made more difficult while associative processes are assisted. The decreased rates for Co(III),[11,12] Cr(III),[13] and Rh(III)[14] are then seen as arising mainly from a decrease in the SN1 character of the reactions. For Ru(III), the progressive increase in rates with increased chelation is interpreted as reflecting increased susceptibility toward reaction by an SN2 pathway. Recent information on the β isomers of the triethylenetetramine complexes of Cr(III)[13] and Co(III)[12] shows them to react much faster than the α isomers and faster than the related complexes having fewer chelate rings. It seems probable that the β (and also the *trans*) triethylenetetramine complexes provide less steric hindrance in an associative mechanism than the α isomers and should, therefore, show faster rates. It is noteworthy that aquation studies on the β isomers of the Co(III) complexes have been interpreted in favor of an increase in SN2 character.[12]

When the above discussion is considered along with the experiments showing that there is complete retention of optical activity, then a reasonable picture of the transition state for aquation may be given in terms of the seven-coordinate "octahedral wedge" geometry.[15]

The equilibrium data given in Tables II–IV are subject to considerable error as a consequence of the spectrophotometric method used and the fact that aquation proceeds almost to completion. Thus the differences between the equilibrium complex concentrations and the initial concentrations are small, leading to large over-all errors. Nevertheless, the order of stabilities Cl > Br < I for similar complexes is established, suggesting a borderline class a–class b character with class a being somewhat more dominant for Ru(III). Equilibrium constants for the halogenopentaammineruthenium(III) complexes have also been reported by Endicott and Taube,[16] using a ruthenium(II) catalysis method, and give a similar order of preference for the halide ligands to that reported here.

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