Structural and Mechanistic Studies of Co-ordination Compounds. Part 19.[1] Acid Hydrolysis of Some *trans*-Tetra-aminedichlororuthenium(III) Cations

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The preparation and characterization of *trans*-$[RuCl_2\{(R,S)\text{-3,7NH-nd}\}]^+$ (3,7NH-nd = 3,7-diazanonane-1,9-diamine) are described. A study of the acid-hydrolysis and isotopic chloride-exchange reactions of complexes of the type *trans*-$[RuCl_2L]^+$ has indicated that the reactions are stereoretentive and that the first-order rate constants decrease with increasing chelation of L: $(NH_3)_4 \approx (en)_2 > (R,S)$-3,7NH-nd > cyclam (en = ethylenediamine, cyclam = 1,4,8,11-tetra-azacyclotetradecane), with a corresponding increase in the enthalpies of activation. The entropies of activation have negative values. A dissociative mechanism involving square-pyramidal intermediates has been suggested. The relation between the acid hydrolysis of both the *cis* and *trans* series of tetra-aminedichlororuthenium(III) cations with that of corresponding cobalt(III), chromium(III), and rhodium(III) complexes is discussed. The importance of the σ-*trans* effect of nitrogen donors, the nephelauxetic effect of amine ligands, and solvation effects have been invoked to explain the chelation and *cis versus trans* effects of amine ligands on the acid hydrolysis of these complexes.

As part of our programme to extend the studies of ligand-substitution kinetics and mechanisms of octahedral amine complexes to systems other than those of the extensively explored Co^{III} [2-7] and Cr^{III},[7-10] we report the acid hydrolysis of *trans*-$[RuCl_2L]^+$ $\{L = (NH_3)_4$,

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[2] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966.

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

[4] M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377.

[5] C. K. Poon, *Inorg. Chim. Acta*, 1970, **4**, 123.

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[7] C. H. Langford and V. S. Sastri in 'Reaction Mechanisms in Inorganic Chemistry,' ed. M. L. Tobe, Butterworths, London, 1972, ch. 6.

[8] C. S. Garner and D. A. House in 'Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker, New York, 1970, vol. 6, p. 61.

[9] E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1781.

[10] W. G. Jackson, P. D. Vowles, and W. W. Fee, *Inorg. Chim. Acta*, 1976, **19**, 221.

$(en)_2$ (bisethylenediamine), 3,7NH-nd [(*R*,*S*)-3,7-diazanonane-1,9-diamine], and cyclam (1,4,8,11-tetraazacyclotetradecane)}. Until recently, very little kinetic work had been done on ligand-substitution reactions of ruthenium(III) amine complexes.[11-17] The first systematic study[12] on the *cis*-tetra-amineruthenium(III) series of complexes indicated that acid hydrolysis took place with complete retention of configuration. It was also noted that charge had little effect on the rates of hydrolysis while increased chelation resulted in progressively faster rates. An S_N2 mechanism was invoked for these aquation reactions.[12] However, a more recent study on the aquation of *cis*-$[RuCl_2(en)_2]^+$ in mixed solvents[16] indicated a dissociative S_N1 mechanism. The aim of this investigation is therefore to obtain a deeper insight into the stereochemistry and chelation effect on the aquation of the *trans* series of complexes in order to resolve this mechanistic ambiguity. A brief account of this work has been reported previously.[17]

EXPERIMENTAL

trans-*Dichloro*{(R,S)-3,7-*diazanonane*-1,9-*diamine*}-*ruthenium*(III) *perchlorate*, *trans*-$[RuCl_2\{(R,S)\text{-}3,7NH\text{-}nd\}][ClO_4]$, was prepared by refluxing a mixture of $K_2[RuCl_5(OH_2)]$ (Johnson, Matthey and Co.; 4 g, 0.01 mol) and 3,7NH-nd (twice redistilled; 1.7 g, 0.01 mol) in methanol (300 cm^3) for 6 d. The dark brown mixture was centrifuged (*ca.* 2 000 revolution min^{-1}) and the brown supernatant was evaporated to dryness. The residue was recrystallized from HCl (0.1 mol dm^{-3}). The perchlorate salt was then prepared by dropwise addition of a saturated solution of $Na[ClO_4]$ to a solution of the solid in HCl (0.1 mol dm^{-3}) to give a light brown solid which was redissolved in hot water and filtered. On cooling the filtrate, brown crystals separated out and these were filtered off, washed with acetone and diethyl ether, and dried *in vacuo* at 70 °C (yield 60%) (Found: C, 19.3; H, 4.6; Cl, 24.9; N, 13.0. Calc. for $C_7H_{20}Cl_3N_4O_4Ru$: C, 19.5; H, 4.6; Cl, 24.7; N, 13.0%).

The complex *trans*-$[RuCl_2(NH_3)_4]Cl{\cdot}H_2O$ was prepared by the literature method[18,19] and was recrystallized from HCl (0.02 mol dm^{-3}) as orange crystals (Found: H, 4.8; Cl, 36.2; N, 19.1. Calc. for $H_{14}Cl_3N_4ORu$: H, 4.8; Cl, 36.3; N, 19.1%). Other complexes, *trans*-$[RuCl_2(en)_2][ClO_4]$ and *trans*-$[RuCl_2(cyclam)]Cl$, were prepared as described previously.[20] The temperature control was good to *ca.* ±0.1 °C.

Kinetics.—The acid hydrolysis was followed spectrophotometrically *in situ* using Unicam SP 700 or 8000 recording spectrophotometers, separately equipped with a thermostatted cell holder and a suitable set of scale-expansion and digital-printer accessories, in a conventional manner as described previously.[21]

Solutions for the isotopic chloride-exchange reactions between unlabelled complexes and labelled chloride were made up at room temperature and samples put into Pyrex tubes which were sealed and placed 'simultaneously' in a thermostatted oil-bath. After thermal equilibrium had been attained (*ca.* 20 min), tubes were withdrawn at suitable intervals and quickly cooled in an ice-bath. The solutions were then warmed to room temperature. One portion was passed through a cation-exchange column of Amberlite IR-120 resin in the acid form. The effluent and washings which contained the labelled HCl were made up to a known volume. The solution (10 cm^3) was sampled into an MX124 tube which was placed into an M6H Geiger-Müller tube holder connected to a PANAX P7201 scaler and timer. An equal portion of the reaction solution was passed through an anion-exchange column of IRA-400 resin in the toluene-*p*-sulphonate form. The effluent and washings which now contained the labelled complex cations were also made up to a known volume and similarly counted.

RESULTS

Spectrophotometric changes associated with the acid hydrolysis of these complexes in 0.1 mol dm^{-3} toluene-*p*-sulphonic acid (E. Merck, G.R. grade, m.p. 103—105 °C) revealed isosbestic points [$L = (NH_3)_4$, at 294 and 318; $(en)_2$, 304 and 327; and 3,7NH-nd, 311 and 334 nm] for at least two half-lives in each case. The initial spectra were identical with those of the starting complexes. Volhard's titration confirmed that chloride was released in the course of reactions. Addition of excess of chloride reversed the reactions, retracing the same isosbestic points. It has been observed[14] that anation of *cis*-tetra-amine aquahalogenoruthenium(III) cations is stereoretentive. This means that if any *cis* isomer has been formed in the forward aquation process it would have appeared in the anation products. However, the final spectra obtained after anation were identical to those of the pure *trans*-dichloro-complexes. This strongly suggested that only a single product was formed in both the forward and reverse reactions and that these reactions were stereoretentive, as represented by equation (1). After *ca.* 2 half-lives, deviations from isosbestic points were noted. These were attributed to the beginning of reaction (2) which was confirmed by Volhard's titration. Addition of excess of chloride almost instantaneously pushed the reaction back to reaction (1). As analytically pure samples of *trans*-$[RuCl(L)(OH_2)]^{2+}$ were not available, reaction (2) was not followed although it was clear that it proceeded at much slower rates than (1). The kinetics of reaction (1) were, therefore, followed spectrophotometrically at a fixed wavelength for *ca.* 2 half-lives [$L = (NH_3)_4$, at 332; $(en)_2$, 343; and 3,7NH-nd, 348 nm], and the first-order rate constants were obtained by Guggen-

$$\textit{trans}\text{-}[RuCl_2(L)]^+ + H_2O \rightleftharpoons \textit{trans}\text{-}[RuCl(L)(OH_2)]^{2+} + Cl^- \quad (1)$$

$$\textit{trans}\text{-}[RuCl(L)(OH_2)]^{2+} + H_2O \rightleftharpoons \textit{trans}\text{-}[Ru(L)(OH_2)_2]^{3+} + Cl^- \quad (2)$$

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[14] J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, 1971, **10**, 85.

[15] J. A. Broomhead, L. Kane-Maguire, and D. Wilson, *Inorg. Chem.*, 1975, **14**, 2575.

[16] L. A. P. Kane-Maguire and G. Thomas, *J.C.S. Dalton*, 1975, 1324.

[17] D. A. Isabirye and C. K. Poon, *Proc. 17th Internat. Conf. Co-ordination Chem.*, Hamburg, 1976, p. 216.

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heim's method.[22] These data, which are independent of acid (0.001—1.0 mol dm^{-3}) and complex concentration (1.0×10^{-4}—3.0×10^{-4} mol dm^{-3}), are collected in Table 1.

TABLE 1

First-order aquation rate constants of some complexes of the type *trans*-$[RuCl_2L]^+$ in toluene-*p*-sulphonic acid

L	θ_c/°C	$10^4k/s^{-1}$ [a]
$(NH_3)_4$ [b]	44.4	0.17
	53.3	0.46
	58.6	0.77
	68.4	2.0
	70.2	2.6
$(en)_2$ [b]	45.4	0.55
	47.9	0.76
	51.4	1.10
	58.0	2.4
	58.6	2.5
	63.1	4.0
(*R*,*S*)-3,7NH-nd [b]	55.4	0.24
	61.3	0.50
	67.6	0.99
	70.3	1.3
	81.0	4.1
cyclam [c]	102	0.003

[a] Each entry represents an average from two to four different determinations. [b] These rate constants are independent of acid (1.0×10^{-3}—1.0 mol dm^{-3}) and complex concentration (1.0×10^{-4}—3.0×10^{-4} mol dm^{-3}). Most reactions were carried out in 0.1 mol dm^{-3} acid. [c] Isotopic chloride-exchange reaction in 1.0×10^{-3} mol dm^{-3} and 5.0×10^{-3} mol dm^{-3} HCl. The temperature control was good to *ca.* ±1 °C.

For *trans*-$[RuCl_2(cyclam)]^+$ there was virtually no detectable spectral change nor detectable chloride release even after standing the complex in varying concentrations of acid for weeks at 80 °C. This indicated either that the complex did not react at all or that it reacted according to equation (1) with an unfavourable equilibrium constant. An isotopic chloride-exchange study showed that the complex indeed reacted but very slowly($t_{\frac{1}{2}} > 3$ weeks at 102 °C) and that the two chlorides are kinetically equivalent. It was not practical to follow this extremely slow reaction in detail. The reaction was followed only at one temperature and for two different concentration conditions. The infinity data were calculated by assuming an equal statistical distribution of the labelled chloride in both co-ordinated and ionic forms. This is a reasonable assumption and was confirmed at least for the corresponding 3,7NH-nd system reported below.

An isotopic chloride-exchange study of *trans*-$[RuCl_2\{$(*R*,*S*)-3,7NH-nd$\}]^+$ showed that the two co-ordinated chlorides were kinetically non-equivalent. The Mckay plot [22] of log ($a_\infty - a_t$) against time, where a_t and a_∞ represent the specific activities of the complex at time *t* and at infinity respectively, was curved and could be resolved into two parallel first-order reactions.[22,23] The specific activity obtained by extrapolating the slower reaction to 'zero time' agreed with the theoretical value expected for one of the two co-ordinated chlorides being fully exchanged. This strongly indicated that only one isomeric form of *trans*-$[RuCl_2(3,7NH\text{-}nd)]^+$ was reacting (see Discussion section). The presence of two isomers would have required them to be present in equal amounts. This seemed unlikely after repeated recrystallization of the complex. The reaction was followed at only one temperature (71.0 °C) and the rate constant obtained for the faster step (1.8×10^{-4} s^{-1}) agreed reasonably well with the value (1.5×10^{-4} s^{-1}) extrapolated from the aquation data at other temperatures (Table 1). At this temperature the rate constant for the exchange of the less-labile chloride is 3.6×10^{-5} s^{-1}.

The equilibrium constants for reaction (1) were determined spectrophotometrically, but first it was necessary to determine the spectra of *trans*-$[RuCl(L)(OH_2)]^{2+}$ [L = $(NH_3)_4$, $(en)_2$, or (*R*,*S*)-3,7-NH-nd] which we were not able to isolate as pure salts. This was done by allowing a known solution of *trans*-$[RuCl_2(L)]^+$ to aquate for *ca.* 1 half-life at *ca.* 60 °C. The solution was then cooled and the absorption spectrum recorded. A known quantity of the solution was immediately passed through a cation-exchange column of Amberlite IR-100 resin in the acid form and the amount of ionic chloride in the effluent and washings was determined by Volhard's method. Using the known values of the molar absorption coefficients of the starting dichloro-complex and the above information, the absorption spectrum of the corresponding aquachloro-complex could be determined. The equilibrium constant was then determined by adding an appropriate amount of NaCl to a known solution of the dichloro-complex so that equilibrium for reaction (1) would be reached with only *ca.* 50% of the starting complex being hydrolysed. The absorption spectrum of the equilibrated solution was then recorded. Knowing the molar absorption coefficients of both the dichloro- and the corresponding aquachloro-complexes at a suitable wavelength corresponding to a relatively large change in the two coefficients [$(NH_3)_4$, ε 5 270 and 687 at 331; $(en)_2$, ε 3 850 and 1 440 at 343; (*R*,*S*)-3,7NH-nd, ε 3 350 and 2 040 dm^3 mol^{-1} cm^{-1} at 350 nm, for the dichloro- and aquachloro-complexes respectively], the equilibrium concentrations of these two species and hence the equilibrium constant were determined. These data are collected in Table 2.

TABLE 2

Equilibrium constants for the following reaction in 0.1 mol dm^{-3} toluene-*p*-sulphonic acid at 60.1 °C and at I = 0.1 mol dm^{-3}: *trans*-$[RuCl_2L]^+ + H_2O \overset{K}{\rightleftharpoons}$ *trans*-$[RuCl(L)(OH_2)]^{2+} + Cl^-$

L	K [a]/mol dm^{-3}
$(NH_3)_4$	2.6×10^{-3}
$(en)_2$	2.8×10^{-3}
(*R*,*S*)-3,7NH-nd	9.3×10^{-4}
cyclam	$<10^{-6}$ [b]

[a] An average from two determinations. [b] At *ca.* 80 °C.

The equilibrium constants for reaction (2) were not determined. However, titration of the amount of chloride released at the end of both reactions indicated that *ca.* 85—95% of both co-ordinated chlorides had been released. The aquation equilibrium constant of *trans*-$[RuCl_2(cyclam)]^+$ could not be determined directly as we could not detect any hydrolysis reaction. However, with reference to the limits of accuracy we could expect from our spectrophotometric and titrimetric studies, an upper limit could be assigned to the equilibrium constant of this complex (Table 2).

DISCUSSION

The isomeric purity of the new 3,7NH-nd complex was checked in two different ways. The first method was by absorbing the cation on Dowex 50W-X8 (20—50 mesh) resin. Only a single band developed on the column

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[22] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanisms,' 2nd edn., Wiley, New York, 1961.

[23] W. K. Chau and C. K. Poon, *J. Chem. Soc. (A)*, 1971, 3087.

which could be eluted out. The second method was by observing that the u.v. spectrum of the complex [$\lambda_{max.}$ 350 (ε 3 090), 300 (1 370), and 280 (sh) nm (1 060 dm^3 mol^{-1} cm^{-1})] was unaffected by repeated recrystallization. The assignment of a *trans* configuration was made on the basis that the i.r. spectrum shows only one sharp NH_2 bending vibration at 1 600 cm^{-1}.[24] The free ends of this linear tetra-amine on co-ordination might be expected to give an i.r. spectrum rather similar to that of two co-ordinated ethylenediamine molecules.[24] On the other hand, the presence of a doublet at *ca.* 900 cm^{-1} (876 and 892 cm^{-1}) and a singlet at 806 cm^{-1} is very similar to the i.r. spectrum of all the known cyclam complexes having a *trans* configuration.[25,26] It is not surprising that the i.r. spectra of corresponding cyclam and 3,7NH-nd complexes are rather similar, at least for those vibrations which arise predominantly from secondary nitrogens and methylene chains. The observation of one relatively sharp and intense band at 320 cm^{-1}, which might be assigned to the Ru–Cl stretch,[20] further confirms this assignment of a *trans* configuration. The visible and u.v. spectra of *cis*- and *trans*-$[RuCl_2(en)_2]^+$ are rather similar,[20] and they are, therefore, not useful for this isomeric differentiation. The assignment of a *trans* configuration does not fully characterize this complex. The flexible ligand 3,7NH-nd has been known [27,28] to form two *trans* isomeric complexes, *viz.* (*R*,*S*)-N-*meso* and (*RR*,*SS*)-N-*rac*. In the present case, the relatively more stable (*R*,*S*) configuration has been assigned on the basis of the kinetics of isotopic chloride-exchange. As the two chlorides are non-equivalent in this configuration, they would be expected to exchange at different rates as observed here.

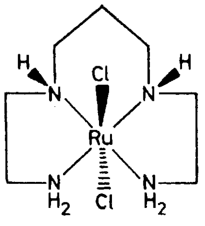
TABLE 3

First-order aquation rate constants at 25.0 °C and activation parameters for some complexes of the type *cis*- and *trans*-$[MCl_2L]^+$

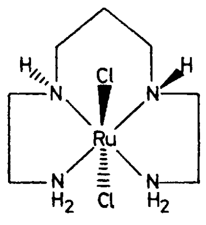
M	L	k_t [a] s^{-1}	$\Delta H_t^‡$ [a] kJ mol^{-1}	$\Delta S_t^‡$ [a] J K^{-1} mol^{-1}	k_c [a] s^{-1}	$\Delta H_c^‡$ [a] kJ mol^{-1}	$\Delta S_c^‡$ [a] J K^{-1} mol^{-1}	k_c/k_t [a]
Ru	$(NH_3)_4$	1.7×10^{-6} [b]	91.2	−50	8.8×10^{-5} [c]	91.2	−37	34
	$(en)_2$	4.2×10^{-6} [b]	97.5	−21	3.7×10^{-4} [c]	83.8	−49	88
		4.5×10^{-6} [d]	89.0	−49				
	α-trien				5.8×10^{-4} [e]	76.0	−52	
	(*R*,*S*)-3,7NH-nd	4.8×10^{-7} [b]	103	−20				
	cyclam	3×10^{-7} [f]						
Co	$(NH_3)_4$	1.8×10^{-3} [g]	98.7	33	Very fast [h]			
	$(en)_2$	3.5×10^{-5} [i,j]	110	59	2.4×10^{-4} [i]	90.0	−21	6.9
	3,7NH-nd	1.5×10^{-5} [k]	102	4	1.1×10^{-3} [k]	93.3	8	73
	cyclam	1.1×10^{-6} [l]	103	−15	1.6×10^{-2} [m]	76.6	−25	15 000
Cr	$(NH_3)_4$	4.9×10^{-5} [n]	87.9	−33	3.3×10^{-4} [o]	83.7	−25	6.7
	$(en)_2$	2.3×10^{-5} [p]	94.6	−29	3.3×10^{-4} [p]	85.8	−25	14
	α-trien				1.9×10^{-4} [q]	86.6	−25	
	cyclam	2×10^{-8} [r]	113	−8	2.5×10^{-5} [r]	93.7	−21	1 300
Rh	$(NH_3)_4$	1.3×10^{-7} [s]	101	−38				
	$(en)_2$	4.9×10^{-8} [t]	104	−36				

[a] k_t, $\Delta H_t^‡$, and $\Delta S_t^‡$ represent the rate constant, activation enthalpy, and activation entropy of *trans*-$[MCl_2L]^+$ respectively; k_c, $\Delta H_c^‡$, and $\Delta S_c^‡$ represent those of the corresponding *cis* isomer. Activation parameters were obtained from least-squares plots of $\ln(k/T)$ against $1/T$. [b] This work. [c] Ref. 12. [d] Extrapolated from data in ref. 15. [e] The rate constant of 4.2×10^{-3} s^{-1} in Table VII of ref. 12 does not agree with the value extrapolated, which is now reported here, from the primary rate data in Table V of the same reference. [f] At 102 °C isotopic chloride-exchange reaction (this work). [g] R. G. Linck, *Inorg. Chem.*, 1969, **8**, 1016. [h] Ref. 34. [i] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 1961, 4637. [j] S. C. Chan, *Austral. J. Chem.*, 1967, **20**, 595. [k] Ref. 28; these data refer to the most stable diastereoisomer of *trans*-(*R*,*S*) and *cis*-(*RR*,*SS*) complexes. [l] C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1967, 2069. [m] C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1968, 1549. [n] D. W. Hoppenjans, J. B. Hunt, and C. R. Gregoire, *Inorg. Chem.*, 1968, **7**, 2506. [o] Ref. 10. [p] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, 1962, **1**, 20. [q] C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta*, 1967, **1**, 17. [r] Ref. 9. [s] Obtained from published data at other temperatures; A. J. Poë and M. V. Twigg, *Canad. J. Chem.*, 1972, **50**, 1089. [t] Obtained from published data at other temperatures; H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc.* (*A*), 1966, 1275.

Table 3 shows the aquation rate constants at 25.0 °C and activation parameters for Ru^{III} together with those of analogous amine complexes of the type *cis*- and *trans*-$[MCl_2(L)]^+$ (M = Co^{III}, Cr^{III}, or Rh^{III}). Four general patterns of behaviour have been noted. First, *cis* complexes are always more reactive than their *trans* counterparts due to more favourable enthalpies of activation ($\Delta H^‡$). Secondly, for the *trans* series of complexes there is a genuine decrease in reactivity with increased chelation. This is accompanied by an increase in $\Delta H^‡$ with the exception of *trans*-$[CoCl_2(en)_2]^+$, see later. However, with the exception of the cobalt(III) system, the difference



N-*meso* (*R*,*S*)



N-*rac* (*RR*,*SS*)

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[24] P. E. Merritt and S. E. Wiberley, *J. Phys. Chem.*, 1955, **59**, 55.

[25] C. K. Poon, *Inorg. Chim. Acta*, 1971, **5**, 322.

[26] P. K. Chan and C. K. Poon, *J.C.S. Dalton*, 1976, 858.

[27] H. G. Hamilton, jun., and M. D. Alexander, *J. Amer. Chem. Soc.*, 1967, **89**, 5065.

[28] R. Niththyanathan and M. L. Tobe, *Inorg. Chem.*, 1969, **8**, 1589.

in reactivity between *trans*-$[MCl_2(NH_3)_4]^+$ and the corresponding *trans*-$[MCl_2(en)_2]^+$ (M = Ru, Cr, or Rh) is only marginal with the ruthenium(III) tetra-amine complex even slightly less labile than the corresponding bis(ethylenediamine) complex. Thirdly, for the *cis* series of complexes there seems to be no general reactivity pattern with increased chelation. The reactivity of complexes of Ru^{III} increases, that of Cr^{III} decreases, and that of Co^{III} first decreases and then increases with increased chelation. However, $\Delta H^‡$ values follow the pattern closely, *i.e.* $\Delta H^‡$ decreases in the ruthenium(III) series, increases for Cr^{III}, and changes less regularly for Co^{III}. Fourthly, the aquation of all the complexes, with the exception of *trans*-$[CoCl_2L]^+$ [L = $(NH_3)_4$ or $(en)_2$], is stereoretentive with relatively low entropies of activation ($\Delta S^‡$).* It is, therefore, clear that, based on this extended set of kinetic data, the original idea[12] that the relative rates of *cis*-amine complexes of Ru^{III} increase with increased chelation *in contrast to* Co^{III}, Cr^{III}, and Rh^{III} is incorrect. With the apparent exception of the third point mentioned above, these four metal systems behave quite similar to each other and a dissociative mechanism, which is well established for Co^{III} [2,3,5] and very recently also for Cr^{III},[29] is assigned to the aquation of these complexes.

Recently, the importance of the role of the σ-*trans* effect of non-labile ligands in affecting the kinetic lability of complexes has been recognised.[2,10,30,31] It seems possible to explain the above observations in terms of this σ-*trans* effect in conjunction with nephelauxetic[6,32,33] and solvation effects.[34] It has been demonstrated that protons on nitrogen *trans* to chloride in cobalt(III) amine complexes exchange with deuterium ion much faster than the other protons on nitrogen *trans* to another nitrogen donor in the same complex.[35-37] This implies that in the H-N-Co-Cl system the N-H bond is relatively weaker and hence the Co-N bond stronger than in the H-N-Co-N system in the same complex. This means that nitrogen has a greater σ-*trans*-labilizing effect than chloride. In the *trans* complexes the leaving chloride lies *trans* to another chloride, while in the *cis* complexes the leaving chloride is *trans* to a nitrogen. Since corresponding pairs of *cis* and *trans* complexes only differ in the relative position of the ligands, it is reasonable to expect that *cis* complexes would react faster than their *trans* counterparts due primarily to favourable enthalpies of activation (*i.e.* $\Delta H_c^‡ < \Delta H_t^‡$). The above discussion assumes that the difference in σ-*trans* effect between a nitrogen and a chloride donor is independent of the nature of the central metal ion.

This idea concerning the role of the σ-*trans* effect in affecting the relative reactivity of *cis*- and *trans*-$[MCl_2L]^+$ is further supported by comparing the kinetic data of corresponding pairs of *cis*- and *trans*-$[CoA(Cl)(en)_2]^{n+}$ (Table 4). Depending on the nature of the orientating ligand A, three classes of kinetic behaviour are evident. For π-neutral nitrogen-donating ligands, such as NH_3 which has a similar σ-*trans* effect to en, both the *cis* and *trans* isomers have similar reactivity. For ligands A such as $[CN]^-$ and $[NO_2]^-$, which are expected to have a greater σ-*trans*-labilizing effect than en due to their co-operative π-accepting character, the *cis* isomers are less reactive than their *trans* counterparts. Lastly, ligands such as Cl^-, Br^-, $[OH]^-$, and $[NCS]^-$ might have a weaker σ-*trans*-labilizing effect than en due to their competing π-donating character. Hence, their *cis* isomers with a ethylenediamine nitrogen *trans* to the leaving group would be expected to react faster than their *trans* counterparts. The position of the ligand A = $[N_3]^-$ is less clear cut since it can behave as π-neutral, π-accepting, or π-donating. The observation that both the *cis* and *trans* isomers are similar in their reactivity puts it in the class I behaviour.

TABLE 4

First-order aquation rate constants at 25.0 °C of some complexes of the type *cis*- and *trans*-$[CoA(Cl)(en)_2]^{n+}$

A	k_c [a]/s^{-1}	k_t [a]/s^{-1}	k_c/k_t [a]	Classification
NH_3	3.7×10^{-7} [b]	2.9×10^{-7} [c]	1.3	I
$[N_3]^-$	2.4×10^{-4} [d]	2.6×10^{-4} [e]	0.92	I
$[NO_2]^-$	1.2×10^{-4} [f]	9.8×10^{-4} [f]	0.12	II
$[CN]^-$	6.2×10^{-6} [g]	7.8×10^{-5} [h]	0.079	II
Cl^-	2.4×10^{-4} [i]	3.5×10^{-5} [i]	6.9	III
Br^-	1.4×10^{-4} [j]	4.5×10^{-5} [j]	3.1	III
$[OH]^-$	1.2×10^{-2} [i]	1.6×10^{-3} [i]	7.5	III
$[NCS]^-$	1.1×10^{-5} [k]	4.5×10^{-8} [l]	24	III

[a] k_c and k_t represent the first-order aquation rate constant of the *cis* and *trans* isomer respectively. [b] S. C. Chan, *J. Chem. Soc.* (*A*), 1967, 291. [c] M. L. Tobe, *J. Chem. Soc.*, 1959, 3776. [d] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4803. [e] V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1785. [f] S. Asperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862. [g] Ref. 31. [h] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 514. [i] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 1961, 4637. [j] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 5700. [k] M. E. Baldwin and M. L. Tobe, *J. Chem. Soc.*, 1960, 4275. [l] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1956, 1691.

It was pointed out[34] that the major effect associated with increased chelation might be solvation. On the basis of a dissociative mechanism it was argued[34] that increased chelation with its gradual removal of peripheral acidic hydrogens (N-H hydrogens) might lead to less-efficient solvation, more seriously in the transition state which has one unit of positive charge more than in the ground state. Hence the rate would decrease with increased chelation. Obviously, as shown in Table 3, this solvation effect which might be real is not the only factor affecting the reactivity of, at least, the *cis* series of ruthenium(III) and cobalt(III) complexes. This

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* It is not clear why the $\Delta S^‡$ values for the stereoretentive aquation of the cobalt(III) complexes of 3,7NH-nd are positive. In any case, these values are still rather small.

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implies that other factors besides solvation might have to be considered.

Recently, attention has been drawn [32,33] to the importance of the nephelauxetic effect of amine ligands in affecting the thermodynamic and kinetic stability of octahedral amine complexes. It was pointed out [32,33] that increased chelation was accompanied by an increased nephelauxetic effect leading to a greater expansion of the *d*-electronic cloud away from the central metal ion and hence causing the metal ion to experience a greater demand for electron pairs from donor atoms. In the *trans* series of complexes the amine ligands are in the equatorial plane and so the increased nephelauxetic effect with increased chelation is to be shared out equally between the two chlorides which are *trans* to each other. Hence increased chelation makes the Co–Cl bond stronger and its dissociation more difficult. In other words, as chelation increases, the non-bonding or weakly antibonding π electrons of the central metal ion will be further away and hence the metal ion will be less likely to expel a chloride in order to gain a greater delocalization of the *d* electrons into the vacated orbital to release the ground-state electronic repulsion in the transition state. Therefore, the reaction rate gradually decreases. Here both solvation and nephelauxetic effects work in the same direction and result in a gradual increase in the enthalpies of activation with increased chelation {*trans*-$[CoCl_2(en)_2]^+$ is an exception, see later}. Since the nephelauxetic effect is expected to be relatively more pronounced in the low-spin d^6 cobalt(III) system where there is a maximum number of electrons in the non-bonding or weakly antibonding π orbitals, the similarity in the spread of k_t (first-order aquation rate constants for the *trans* series) for both Co^{III} and Cr^{III} seems to indicate that this effect cannot be more important than the solvation effect in affecting the reactivity of these *trans* series of complexes.

The situation is less straightforward for the *cis* series of complexes. Here, the nephelauxetic influence is shared unequally between the nitrogen and the chloride *trans* to each other. With increased chelation, nitrogen having a greater donor ability will progressively increase its binding to a larger extent than chloride. The consequence is that the σ-*trans* effect of nitrogen in labilizing a chloride increases and hence the reaction rate increases. This behaviour is, to some extent, rather reminiscent of the antisymbiotic effect [38] whereby two soft ligands in mutual *trans* positions will have a destabilizing effect on each other when attached to soft metal atoms, although soft prefers soft is the more common phenomenon. Therefore, for these *cis* series of complexes, the solvation and nephelauxetic effects operate in opposite directions. The net chelation effect will depend more critically on the balance of these two opposing factors, and the presence of some minor factors may be important in tipping the balance to any one side. In any case, the overall chelation effect here, *i.e.* the gross variation in the reaction rate constants, will be much less prominent, as observed, than that in the corresponding *trans* series of complexes. For the relatively more bulky *cis* complexes of Ru^{III}, the solvation effect may become less important, resulting in a slight increase in reactivity and a corresponding decrease in the activation enthalpies, with increased chelation. For the relatively small complexes of Co^{III} and Cr^{III} the solvation effect might be rather important. However, as pointed out previously, since the nephelauxetic effect is expected to be rather pronounced in the cobalt(III) system this factor seems to control the chelation effect.

The *trans*-$[CoCl_2(NH_3)_4]^+$ cation with many peripheral acidic hydrogens, on the other hand, might be much more susceptible to solvation effects than other members of the series. It is, therefore, not surprising that this effect overcomes the nephelauxetic effect and makes the tetra-ammine complex relatively much more reactive. The delicate balance of these two effects is reflected in the non-systematic change in activation enthalpies with increased chelation. Amine complexes of Cr^{III} are rather peculiar in that amine ligands may be released during acid hydrolysis.[8] This implies that the Cr–N binding and hence the σ-*trans* effect of nitrogen is relatively weak as compared to those in the corresponding cobalt(III) and rhodium(III) systems. Furthermore, the nephelauxetic effect is not expected to play an important role in chromium(III) complexes of d^3 configuration where the interelectronic repulsion between the 3*d* electrons is less important. It is, therefore, not surprising that the chelation here is controlled mainly by the solvation effect.

It has been suggested [39] that low entropies of activation and stereoretention indicate a square-pyramidal intermediate for dissociative reactions. Following this argument, the dissociative acid hydrolysis of these ruthenium(III) complexes probably generates square-pyramidal intermediates. For complexes of a second-row transition metal formation of a square-pyramidal rather than a trigonal-bipyramidal intermediate is preferable as the former would involve a minimum loss of ligand-field stabilization energy which is much more significant than that in reactions of first-row metal complexes. For *trans*-$[CoCl_2L]^+$ [$L = (NH_3)_4$ or $(en)_2$], the high values of $\Delta S^\ddagger$ and stereochemical changes indicate the presence of trigonal-bipyramidal intermediates in their aquation reactions, the additional energy needed for their formation making the enthalpies of activation higher than what they would have been if square-pyramidal intermediates had been generated.

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