Structural and Mechanistic Studies of Co-ordination Compounds. Part 37.[1] Ligand-substitution Kinetics of Some Halogeno Tetra-amine Complexes of Cobalt(III), Ruthenium(II), and Ruthenium(III)

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The first-order rate constants for the replacement of X^- from 21 different complexes of the type *trans*-$[ML(A)X]^{n+}$ [M = Co^{III}, Ru^{III}, or Ru^{II}; L = either two bidentate or one quadridentate amine ligand; and (A)X = (Cl)Cl, (Cl)Br, (Br)Cl, or (Br)Br] have been determined over a range of temperature. It has been found that the ruthenium(II) (d^6) complexes behave much more like the corresponding ruthenium(III) (d^5) than the cobalt(III) (d^6) and rhodium(III) (d^6) systems.

As part of our programme to examine the chemistries of ruthenium and cobalt amine complexes, we report in this paper the kinetics of ligand-substitution reactions of several mixed bromochlorotetra-amine complexes of ruthenium(II), ruthenium(III), and cobalt(III). Ligand abbreviations used in this paper are as follows: L^1 = two ethane-1,2-diamine ligands; L^2 = two propane-1,3-diamine ligands; L^3 = two *N,N'*-dimethylethane-1,2-diamine ligands; L^4 = 4,7-diazadecane-1,10-diamine; L^5 = 3,7-diazanonane-1,9-diamine; L^6 = 4,8-diazaundecane-1,11-diamine; L^7 = 1,4,8,11-tetra-azacyclotetradecane; L^8 = 1,4,8,12-tetra-azacyclopentadecane; L^9 = *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane; L^{10} = 2,3-dimethyl-1,4,8,11-tetra-azacyclotetradeca-1,3-diene; and L^{11} = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene.

Experimental

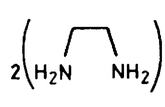
All the ruthenium(III) [2] and cobalt(III) [3-5] complexes, with the exception of *trans*-$[CoL^7Br_2]NO_3$, were prepared by published methods.

trans-*Dibromo*(1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *Nitrate*.—The perchlorate salt reported in the literature [3] was not soluble enough for kinetic studies. The nitrate salt was prepared by drawing air through an ethanolic solution (100 cm^3, 95%) of L^7 (2 g) and cobalt(II) bromide (4 g) for 0.5 h. Bromine-free hydrobromic acid (1 cm^3, 48%) was added and air was drawn for another 0.25 h. A greenish precipitate appeared. The solution was concentrated to a smaller volume to increase the yield. The greenish precipitate of the bromide salt was filtered off and dissolved in the minimum amount of water. Concentrated nitric acid was added dropwise to the cooled solution to precipitate the nitrate salt which was collected and recrystallized from boiling water (yield 70%) (Found: C, 24.8; H, 5.00; Br, 33.2; N, 14.4. Calc. for $C_{10}H_{24}Br_2CoN_5O_3$: C, 25.0; H, 5.05; Br, 33.2; N, 14.6%).

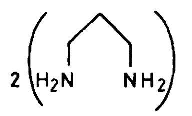
The complex *trans*-$[CoL^{10}X_2]ClO_4$ (X = Cl or Br) was prepared by a slight modification of the published method.[5] After the addition of biacetyl to a cooled mixture of HX and *N,N'*-bis(3-aminopropyl)ethane-1,2-diamine, the solution was stirred for 15 min. Stirring for 0.5 h as reported would have resulted in a dark brown instead of a yellowish brown solution. The complex could be recrystallized by dissolving it in the minimum amount of sodium hydroxide (0.01 mol dm^{-3}) followed by the acidification with HX.

Several attempts to prepare pure *trans*-$[CoL(Cl)Br]^+$ (L = L^7, L^9, or L^{10}) in crystalline salts were unsuccessful. These complex cations were freshly generated in solution for subsequent kinetic studies in the following manner. For the L^9 and L^{10} complexes, a solution containing a mixture of *trans*-$[CoL(OH_2)X]^{2+}$ and *trans*-$[CoL(OH_2)_2]^{3+}$ was first prepared by allowing an acidic solution (0.01 mol dm^{-3}, HNO_3) of *trans*-$[CoLX_2]^+$ (X = Cl or Br) to stand for 10 aquation half-lives at a suitable temperature and then passing the solution through an anion-exchange column of Amberlite IRA-400 resin in the nitrate form. A known volume of this solution was quickly brought to the temperature desired for kinetic studies and was then treated with a known quantity of either sodium chloride or sodium bromide as appropriate. For example, the addition of sodium chloride to a solution containing *trans*-$[CoL(OH_2)Br]^{2+}$ and *trans*-$[CoL(OH_2)_2]^{3+}$ would relatively quickly generate a mixture of *trans*-$[CoL(Cl)Br]^+$ and *trans*-$[CoLCl_2]^+$ in the presence of excess of chloride. The subsequent chemical reaction to be followed corresponds to the chloride substitution of *trans*-$[CoL(Cl)Br]^+$ to give *trans*-$[CoLCl_2]^+$. Similarly, the addition of sodium bromide to a solution containing *trans*-$[CoL(OH_2)Cl]^{2+}$ and *trans*-$[CoL(OH_2)_2]^{3+}$ generates *trans*-$[CoL(Br)Cl]^+$ suitable for the kinetic study of its substitution by bromide to give *trans*-$[CoLBr_2]^+$. The complex *trans*-$[CoL^7(Cl)Br]^+$ in the presence of some *trans*-$[CoL^7Cl_2]^+$ and excess of chloride was similarly prepared from *trans*-$[CoL^7Br_2]^+$. However, the method of preparation of *trans*-$[CoL^7(Br)Cl]^+$ from *trans*-$[CoL^7Cl_2]^+$ was slightly different. After having allowed *trans*-$[CoL^7Cl_2]$ in nitric acid (0.01 mol dm^{-3}) to stand for 10 aquation half-lives at 60 °C, a small but sufficient quantity of $NaClO_4$ was added to precipitate the remaining *trans*-$[CoL^7Cl_2]^+$ which was in equilibrium with the *trans*-$[CoL^7(OH_2)Cl]^{2+}$ product. The filtrate was then passed through an anion-exchange resin column in the nitrate form to remove the excess of perchlorate ion before it was treated with excess of sodium bromide.

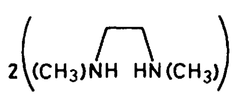
Kinetics.—All the reactions, aquation and halide and thiocyanate substitutions, of cobalt(III) and ruthenium(III) complexes were followed spectrophotometrically, either *in situ* or by the sealed-tube method, using either a Beckman Acta CIII or a Unicam SP8000 recording spectrophotometer equipped with a Weyfringe ADCP-2 digital printer. The reactions of cobalt(III) complexes were most conveniently studied in nitric acid. However, nitric acid was found to be unsuitable [6] for ruthenium(III) amine systems which were therefore followed in toluene-*p*-sulphonic acid. The reaction temperature was maintained to ±0.1 °C by circulating thermostatted water through the cell holder using either a Lauda model WB-20/R or a Forma Scientific model 2800 refrigerated bath and circulator. The actual reaction temperature was determined by inserting a Doric 400A semi-micro temperature sensor into a blank test solution in the cell holder before the reaction and



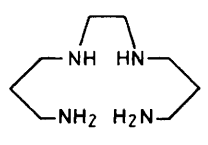
L^1



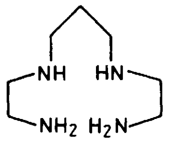
L^2



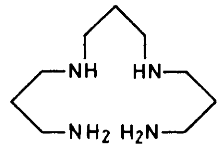
L^3



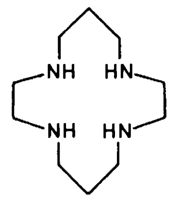
L^4



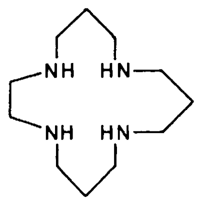
L^5



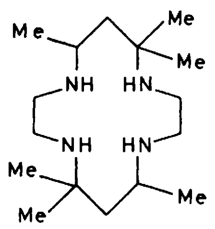
L^6



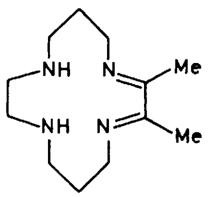
L^7



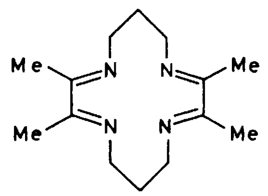
L^8



L^9



L^{10}



L^{11}

again directly into the reaction solution at the end of the reaction. Both temperature readings agreed to ±0.1 °C. The kinetics of aquation of ruthenium(II) complexes were followed by cyclic voltammetry of the parent ruthenium(III) complexes as described previously,[7] using Princeton Applied Research (PAR) instruments: model 175 (Universal Programmer) and model 173 (Potentiostat-Galvanostat). A PAR model 9323 hanging-mercury-drop electrode (h.m.d.e.) was used as the working electrode. The reaction cell was a standard PAR model K64 three-electrode jacketted polarographic cell which was maintained to ±0.1 °C by thermostatted water. Cyclic voltammograms were recorded with a Houston model 2000 X-Y recorder at slow scan rates (<1 V s^{-1}) and with a Tektronix model 5103N storage oscilloscope at high scan rates (>1 V s^{-1}).

Results

The changing u.v. and visible spectra associated with the acid hydrolysis of *trans*-$[RuLBr_2]^+$ [L = $(NH_3)_4$ or L^1] in toluene-*p*-sulphonic acid, Hpts (0.01—1.0 mol dm^{-3}), maintained isosbestic points for over 2 half-lives. The initial spectra were identical to those of the starting complexes and the absorption peaks shifted to shorter wavelengths as the reactions proceeded. Addition of excess of sodium bromide reversed the reactions, retracing the same isosbestic points. This suggested that the primary aquation was stereoretentive. Volhard's titration after 10 half-lives of the primary aquation showed that the release of bromide in both cases was more than 100% with respect to one co-ordinated bromide. This was consistent with the release of the second bromide, as suggested by the deviation of the changing spectra from the isosbestic points in the later part of the reactions.

The substitution reactions of *trans*-$[RuL^1Cl_2]^+$ by various anions Y^{n-} (Br^-, $CH_2ClCO_2^-$, $H_2PO_4^-$, and SO_4^{2-}) in toluene-*p*-sulphonic acid also revealed isosbestic points for *ca.* 2 half-lives. The initial spectrum in each case was identical to that of the starting *trans*-$[RuL^1Cl_2]^+$. A second set of isosbestic points eventually appeared which was maintained till the end of the reactions. The final spectrum was identical to that of the known *trans*-$[RuL^1Y_2]^+$ ($Y^- = Br^-$ or $CH_2ClCO_2^-$]. It seems reasonable to assume that the first reaction in each case corresponded to the stereoretentive replacement of one co-ordinated chloride by Y^{n-}. The presence of co-ordinated sulphate in the appropriate reaction product was confirmed by passing the solution, which had reacted for *ca.* 2 half-lives, through a column of anion-exchange resin, Amberlite IRA-400 in the chloride form, to remove all the ionic sulphate. The effluent was then treated with barium chloride. Upon slight warming, a white precipitate of barium sulphate appeared.

The aquation of *trans*-$[RuL^1(Cl)Br]^+$ was complicated by the simultaneous release of both chloride and bromide in a competitive manner. Since the ligand substitution of *trans*-$[RuL^1Cl_2]^+$ by any suitable nucleophile has been shown to give an alternative measure of the aquation of the same complex (see Discussion section), the reaction of *trans*-$[RuL^1(Cl)Br]^+$ was followed in excess of halide. The kinetics of substitution by excess of chloride should give a reliable determination of the aquation of the co-ordinated bromide since the concomitant replacement of the co-ordinated chloride does not give rise to any net reaction. On the other hand, the kinetics of substitution by excess of bromide corresponds to the aquation of the co-ordinated chloride. In each case, isosbestic points were maintained for the entire reaction with the final spectrum identical to that of the corresponding *trans*-$[RuL^1X_2]^+$, where X^- represents the entering halide.

Table 1. Spectrophotometric characteristics of the substitution reactions of some *trans*-$[ML(A)X]^+$ ($M = Ru^{III}$ or Co^{III}) complexes in acidic aqueous solutions [a]: *trans*-$[ML(A)X]^+ + Y^{n-} \longrightarrow$ *trans*-$[ML(A)Y]^{(2-n)+} + X^-$

M	L	A^-	X^-	Y^{n-} [b]	Isosbestic points (λ/nm)	λ [c]/nm
Ru	$(NH_3)_4$	Br^-	Br^-	H_2O	351, 373	400
	L^1	Cl^-	Cl^-	Br^-	360	343
	L^1	Cl^-	Cl^-	SO_4^{2-} [d]	241, 257, 268, 280, 299, 332	343
	L^1	Cl^-	Cl^-	$H_2PO_4^-$	330	343
	L^1	Cl^-	Cl^-	$CH_2ClCO_2^-$	306, 329	343
	L^1	Br^-	Br^-	H_2O	353, 378	409
	L^1	Br^-	Cl^-	Br^-	391	414
	L^1	Cl^-	Br^-	Cl^-	360	343
Co	L^7	Br^-	Br^-	H_2O	508, 640	670
	L^7	Br^-	Cl^-	Br^-	510, 627	430
	L^7	Cl^-	Br^-	Cl^-	476, 609	430
	L^9	Br^-	Cl^-	Br^-	522, 633	690
	L^9	Cl^-	Br^-	Cl^-	507, 619	570
	L^{10}	Cl^-	Cl^-	NCS^-	630	570
	L^{10}	Br^-	Br^-	NCS^-	624	570
	L^{10}	Br^-	Cl^-	Br^-	495, 576	430
	L^{10}	Cl^-	Br^-	Cl^-	459, 562	390
	L^{11}	Cl^-	Cl^-	NCS^-	—	505

[a] Reactions of cobalt(III) complexes were carried out in HNO_3 (0.005—0.05 mol dm^{-3}) and of ruthenium(III) complexes in Hpts (0.01—1.0 mol dm^{-3}). The rate constants were independent of acid concentration. [b] The rate constants were independent of Y^{n-} concentration (0.01—1.0 mol dm^{-3}). [c] Wavelength at which the reaction was followed. [d] In H_2SO_4 (0.01—0.1 mol dm^{-3}).

The behaviour of the aquation of *trans*-$[CoL^7Br_2]^+$ in HNO_3 (0.01 mol dm^{-3}) was very similar to that of *trans*-$[RuL^1Br_2]^+$ described above with a set of isosbestic points maintained for *ca.* 2 half-lives. The reaction was stereoretentive. Volhard's titration confirmed the release of more than one co-ordinated bromide at equilibrium.

The aquation of *trans*-$[CoLX_2]^+$ ($L = L^{10}$ or L^{11}, X = Cl or Br) was first reported by Rillema *et al.*[8] However, the study was complicated by the reversibility of the reactions, and elaborate rate expressions were used to evaluate the forward aquation rate constants. These reactions, except the very fast reaction of *trans*-$[CoL^{11}Br_2]^+$, were re-investigated here by following the thiocyanate-substitution reactions which, on the one hand, proceeded to completion, and, on the other, gave large absorbance changes for a more reliable determination of the rate constants. For the L^{10} complexes, two sets of isosbestic points were maintained corresponding to the stepwise replacements of the halides. However, the spectrum of *trans*-$[CoL^{11}Cl_2]^+$ gradually increased in absorbance in the visible region as the reaction proceeded without establishing any isosbestic point; at *ca.* 10 half-lives it was identical to that of an authentic sample[9] of *trans*-$[CoL^{11}(NCS)Cl]^+$. The replacement of the second chloride was too slow to interfere with the kinetic study of the first substitution reaction.

The spectrophotometric changes for the substitution reactions of *trans*-$[CoL(Cl)Br]^+$ ($L = L^7$, L^9, or L^{10}) by either chloride or bromide were very similar to those of the corresponding ruthenium(III) reactions. A set of isosbestic points was maintained for the entire reaction with the final spectrum identical to that of the appropriate *trans*-$[CoLX_2]^+$.

The spectral characteristics of all the above reactions are collected in Table 1. The kinetics were followed at a fixed wavelength corresponding to a sufficiently large absorbance change for the period of time when the isosbestic points were still maintained. First-order rate constants were calculated by Guggenheim's method. For the thiocyanate-substitution reactions of the cobalt(III) complexes, the rate constants were obtained from the slopes of the linear plots of $\ln(D_\infty - D_t)$ *vs.* time where D_∞ and D_t represent the absorbances at infinity (*ca.* 10 half-lives) and at time *t* respectively. All these rate constants were found to be independent of acid [HNO_3 (0.005—0.05 mol dm^{-3}) for cobalt(III) and Hpts (0.01—1.0 mol dm^{-3}) for ruthenium(III) reactions], and complex concentrations [1.0×10^{-3}—4.0×10^{-3} mol dm^{-3} for cobalt(III) and 1.0×10^{-4}—4.0×10^{-4} mol dm^{-3} for ruthenium(III)], and also of the nature and concentrations of the entering groups (0.1—1.0 mol dm^{-3}).

The electrochemical behaviour of all the *trans*-$[RuLX_2]^+$ complexes investigated here was very similar to that of *trans*-$[RuL^1X_2]^+$ (X = Cl or Br) reported previously.[7] In 0.01 mol dm^{-3} Hpts with 0.2 mol dm^{-3} K(pts) as supporting electrolyte the cyclic voltammogram, at a relatively fast scan rate, was typical of a reversible one-electron redox system. The peak currents began to drop at a slower scan rate with a second set of peaks appearing at more positive potentials. When a solution of known concentration of *trans*-$[RuLX_2]^+$ was subjected to a one-electron controlled-potential electrolysis and then air-oxidized and treated with the corresponding NaX, the course of the reaction, traced by electronic spectroscopy, was identical with the stepwise anation of *trans*-$[RuL(OH_2)_2]^{3+}$ by X^- back to *trans*-$[RuLX_2]^+$. This confirmed that the aquation of *trans*-$[RuLX_2]$ (X = Cl or Br), following a reversible electron-transfer process, was stereoretentive. The first-order rate constants were determined by the method of Nicholson and Shain.[10,11] The aquation of *trans*-$[RuL^1(Cl)Br]$ has been shown to involve the simultaneous release of both chloride and bromide. This is not surprising judging from the similarity of the aquation rate constants of *trans*-$[RuL^1Cl_2]$ and *trans*-$[RuL^1Br_2]$ (0.35 and 0.44 s^{-1} at 25.0 °C respectively[7]). The observed rate constant was, therefore, the sum of the rate constants for the release of chloride and bromide. To determine the individual rate constant, the electrochemical study was carried out in the presence of excess of NaX (X = Cl or Br) in order to suppress the particular path involving release of the corresponding X^-. Most of the reactions were repeated as many times, and over as many possible scan rates, as required (usually 8—10 runs), at a single temperature in order to obtain a more reliable average value of the rate

Table 2. First-order rate constants, *k*, at 25.0 °C and activation parameters for the replacement of the leaving group X^- from some *trans*-$[ML(A)X]^{n+}$ complexes

M	L	A	X	k/s^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}
Ru^{III}	$(NH_3)_4$	Cl	Cl	1.7×10^{-6}[a]	91.2	−50
		Br	Br	3.0×10^{-6}	96.5	−27
	L^1	Cl	Cl	4.2×10^{-6}[a]	97.5	−21
		Br	Br	5.6×10^{-6}	98.5	−15
		Cl	Br	1.7×10^{-6}	106	−1
		Br	Cl	2.1×10^{-6}	101	−16
Ru^{II}	$(NH_3)_4$	Cl	Cl	1.0[b]	72.1	−3
	L^1	Cl	Cl	3.5×10^{-1}[b]	73.0	−9
		Br	Br	4.4×10^{-1}[b]	74.5	−2
		Cl	Br	2.4×10^{-1}		
		Br	Cl	2.4×10^{-1}		
	L^2	Cl	Cl	5.3×10^{-1}	72.9	−6
	L^3	Cl	Cl	6.8×10^{-2}	70.4	−39
	L^4	Cl	Cl	5.9×10^{-2}	74.7	−19
	L^5	Cl	Cl	6.6×10^{-2}[b]	78.6	−4
	L^5	Br	Br	9.4×10^{-2}[b]	72.0	−23
	L^6	Cl	Cl	2.5×10^{-1}	67.2	−31
	L^7	Cl	Cl	2.3×10^{-2}[b]	78.1	−14
	L^8	Cl	Cl	7.4×10^{-2}	78.2	−4
	L^9	Cl	Cl	*ca.* 5.0		
Co^{III}	L^1	Cl	Cl	3.5×10^{-5}[c] 4.2×10^{-5}[d]	110	+37
		Br	Br	1.4×10^{-4}[e] 4.1×10^{-4}[d]	105	+33
		Cl	Br	1.1×10^{-4}[e]	109	+46
		Br	Cl	4.5×10^{-5}[e]	103	+17
	L^7	Cl	Cl	1.1×10^{-6}[f]	103	−15
		Br	Br	2.2×10^{-5}	95.1	−15
		Cl	Br	1.2×10^{-5}	89.3	−40
		Br	Cl	1.6×10^{-6}	96.3	−25
	L^9	Cl	Cl	9.3×10^{-4}[g]	107	+54
		Br	Br	3.8×10^{-2}[h]	92	+32
		Cl	Br	1.3×10^{-2}	98.4	+49
		Br	Cl	1.2×10^{-3}	108	+62
	L^{10}	Cl	Cl	2.5×10^{-4}[i] 2.3×10^{-4}[j]	107	+46
		Br	Br	8.4×10^{-3}[i] 7.8×10^{-2}[j]	108	+77
		Cl	Br	2.7×10^{-4}	98.1	+16
		Br	Cl	4.2×10^{-4}	95.4	+11
	L^{11}	Cl	Cl	1.5×10^{-2}[i] 2.1×10^{-2}[j]	93.6	+34
		Br	Br	1.2×10^{-1}[j]		

[a] Ref. 12. [b] Ref. 7. [c] Activation parameters were calculated from the data of S. C. Chan, *Aust. J. Chem.*, 1967, **20**, 595. [d] W. G. Jackson and C. M. Begbie, *Inorg. Chim. Acta*, 1982, **61**, 167. [e] Activation parameters were calculated from the data of S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 5700. [f] C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1967, 2069. [g] W. K. Chau and C. K. Poon, *J. Chem. Soc. A*, 1971, 3087. [h] J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 1970, **9**, 1504. [i] This work; the rate constants were for thiocyanate-substitution reactions. [j] Ref. 8.

constant. These rate constants are independent of the scan rate and complex and acid concentrations.

All the above reactions were studied over four or five different temperatures. Activation parameters and rate constants extrapolated to 25.0 °C were obtained by the least-squares method from Eyring plots of $\ln(k/T)$ against $1/T$, where k represents the first-order rate constant at the temperature T measured on the absolute scale. These data are collected in Table 2.

Discussion

The first-order rate constants for the substitution reactions of *trans*-$[RuL^1Cl_2]^+$ by various anions, Y^{n-}, have been found to be independent of the nature and concentrations of the entering groups ($Y^{n-} = Br^-$, 5.2×10^{-4}; $CH_2ClCO_2^-$, 5.2×10^{-4}; $H_2PO_4^-$, 5.6×10^{-4}; and SO_4^{2-}, 5.1×10^{-4} s^{-1} at 65.2 °C) and they are equal to the aquation rate constant of the same complex (5.1×10^{-4} s^{-1} at 65.2 °C, by extrapolation of published data[12]). This behaviour is common in the well explored cobalt(III) amine chemistry. It implies that the incoming anions, Y^{n-}, do not attack the ruthenium(III) substrate directly, and is consistent with a mechanism in which the formation of *trans*-$[RuL^1(Cl)Y]^{(2-n)+}$ goes *via* a slow rate-determining aquation of the substrate [equation (1)], followed by a fast anation by Y^{n-} [equation (2)]. This observation clearly supports a dissociative mechanism[12,13] for the aquation and hence all ligand-substitution reactions of ruthenium(III) amine complexes.

$$trans\text{-}[RuL^1Cl_2]^+ + H_2O \xrightarrow[\text{slow}]{k} trans\text{-}[RuL^1(OH_2)Cl]^{2+} + Cl^- \quad (1)$$

$$trans\text{-}[RuL^1(OH_2)Cl]^{2+} + Y^{n-} \xrightarrow{\text{fast}} trans\text{-}[RuL^1(Cl)Y]^{(2-n)+} + H_2O \quad (2)$$

The relative effects of bromide *versus* chloride as labilizing ligands as measured by k_{BrX}/k_{ClX}, or as leaving groups, measured by k_{ABr}/k_{ACl}, in the substitution reactions of some related ruthenium(III), ruthenium(II), cobalt(III), and rhodium(III) complexes are collected in Table 3. In the evaluation of the leaving-group effects, only those labilizing ligands A with similar electronic displacement property, *i.e.* π-donating property, are included for the comparative study. To take into account the statistical factor of 2 for the reactions of disubstituted *trans*-$[MLX_2]^+$ (X = Cl or Br) complexes, the rate constants have been halved in the calculation of the kinetic ratios. Several trends of behaviour become obvious in Table 3: (1) for analogous L^1 complexes, k_{ABr}/k_{ACl} decrease in the order $Co^{III} > Ru^{III} \approx Ru^{II} > Rh^{III}$; (2) for analogous L^1 complexes, k_{BrX}/k_{ClX} decreases marginally in the order $Rh^{III} > Co^{III} \geqslant Ru^{III} \approx Ru^{II}$; (3) for cobalt(III) complexes, with the exception of *trans*-$[CoL^{10}Br_2]^+$, k_{ABr}/k_{ACl} decreases with additional unsaturation in the tetra-amine macrocycles, but k_{BrX}/k_{ClX} remains similar. Since the activation parameters (Table 2) for a given M and L do not vary much, it is reasonable to assume that the above trends are approximately maintained over a range of temperatures not too far from 25 °C. Following previous arguments,[13,14] it is clear that observation (1) suggests an increasing ' softness ' of the metal ions in the order $Co^{III} < Ru^{III} \approx Ru^{II} < Rh^{III}$, and also that observation (3) supports the earlier deliberation[9,13,14] of increasing ' softness ' of the cobalt(III) ion with unsaturation in the amine macrocycles. Observation (2) indicates that bromide and chloride are very similar in their labilizing effects in the reactions of cobalt(III), ruthenium(III), and ruthenium(II) complexes. The exceptionally higher values of k_{Br_2}/k_{ClBr} and k_{Br_2}/k_{BrCl} compared with the general trend for the cobalt(III)–L^{10} system probably arise from an exceptionally greater kinetic reactivity of *trans*-$[CoL^{10}Br_2]^+$ relative to its dichloro- and bromochloro-analogues, but the reason behind this is unknown. From the above observations, it is clear that the ruthenium(II) (d^6) system behaves more like ruthenium(III) (d^5) than cobalt(III) (d^6) and rhodium(III) (d^6).

A comparison of the aquation rate constants between *trans*-$[RuL^9Cl_2]$ and *trans*-$[RuL^7Cl_2]$ clearly demonstrates steric acceleration, by a factor of *ca.* 2×10^2, and hence

Table 3. The relative effects of bromide *versus* chloride as labilizing (k_{BrX}/k_{ClX}) or leaving groups (k_{ABr}/k_{ACl}) in the substitution reactions of some tetra-amine complexes of the type *trans*-[ML(A)X]$^{n+}$ (M = Ru^{III}, Ru^{II}, Co^{III}, or Rh^{III}; A = π-donating labilizing groups such as Cl, Br, NCS, or OH; and X = Cl or Br) in aqueous acidic solutions at 25.0 °C

		k_{BrX}/k_{ClX} [a]		k_{ABr}/k_{ACl} [a]			
M	L	X = Br	X = Cl	A = Br	A = Cl	A = NCS	A = OH
Ru^{III}	L^1	1.6	1.0	1.3	0.8		
Ru^{II}	L^1	0.9	1.4	0.9	1.4		
Co^{III}	L^1	1.9 [b,c]	2.1 [b,c]	4.7 [b,c]	5.2 [b,c]	5.2 [d]	5.9 [c,e]
	L^7	0.9	2.9	6.9	22	12 [f,g]	
	L^9	1.5	2.6	16	28	8.7 [f,h]	
	L^{10}	16	3.4	10	2.2	1.3 [g]	
	L^{11}					1.2 [g]	
Rh^{III}	L^1	11 [i]	6.3 [i]	0.5 [i]	0.3 [i]		

[a] In the evaluation of the kinetic ratios the observed rate constants for *trans*-[MLX$_2$]$^+$ (X = Cl or Br) have been halved to allow for the statistical factor of 2. [b] W. G. Jackson and C. M. Begbie, *Inorg. Chim. Acta*, 1982, **61**, 167. [c] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 5700. [d] $k_{NCSBr} = 2.4 \times 10^{-7}$ and $k_{NCSCl} = 4.6 \times 10^{-8}$ s^{-1} were extrapolated from published data (C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1956, 1691). [e] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 1961, 4637. [f] W. K. Chau, W. K. Lee, and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 1974, 2419. [g] C. K. Poon and C. L. Wong, *Inorg. Chem.*, 1976, **15**, 1573. [h] Ref. 13. [i] H. L. Bott, E. J. Bounsall, and A. J. Poë, *J. Chem. Soc. A*, 1966, 1275.

supports the previously assigned [7] dissociative mechanism for the aquation of these ruthenium(II) amine complexes.

Within the narrow range of most open-chain amine complexes, it has been suggested [15] that complexes with six-membered chelate rings are more reactive than those with five-membered chelate rings unless they form part of an aromatic system, since the metal chelate bond angle of 90° differs more from the natural bond angle formed by a six-membered ring than by a five-membered ring. The release of one group from the octahedron with the concomitant expansion of appropriate bond angles may relieve part of the strain energy in the transition state, probably more so for complexes with six-membered than with five-membered rings. A comparison of the rate constants for *trans*-[RuL^{2}Cl$_2$] and *trans*-[RuL^{1}Cl$_2$] shows that the former is only 1.5 times as reactive as the latter. This effect, however, is prominent for the corresponding cobalt(III) complexes with the L^2 complex being more reactive than the L^1 complex by a factor of *ca.* 10^3.[15] For open-chain tetra-amine complexes, molecular models suggest that complexes with alternate five- and six-membered rings, *i.e.* L^4 and L^5 complexes, appear more strain-free than those having only six-membered rings, *i.e.* L^6 complexes. This effect, although small, is observed in the reactions of ruthenium(II) complexes, where *trans*-[RuL^{6}Cl$_2$] is about four times more reactive than the corresponding L^4 and L^5 complexes. The effect of strain energy is best examined by comparing the reactivities of analogous complexes containing saturated quadridentate macrocyclic amines of different ring size. Hung and Busch [16] have shown that *trans*-[CoL^{8}Cl$_2$]$^+$ is more reactive than the corresponding L^7 complex by a factor of *ca.* 10^3. However, the corresponding *trans*-[RuL^{8}Cl$_2$] is only three times more reactive than *trans*-[RuL^{7}Cl$_2$]. Based on these limited data, it may be concluded that the aquation of ruthenium(II) amine complexes is much less sensitive to strain-energy effects than are the corresponding cobalt(III) analogues.

The aquation rate of *trans*-[RuL^{3}Cl$_2$] is slower than that of *trans*-[RuL^{1}Cl$_2$] by a factor of *ca.* 5, which is similar to the factor of *ca.* 2 for the corresponding cobalt(III) complexes.[15] These small reduction factors mean that steric effects arising from the *N*-methyl groups are unimportant in the aquation of both ruthenium(II) and cobalt(III) amine complexes.

Finally, it should be pointed out that the rate data and activation parameters of the cobalt(III) complexes reported here have been published by C. L. Wong in his Ph.D. Thesis.[17] However, some of the data were incorrect, and they have been re-investigated here. Unfortunately, Wong's original data were reproduced in advance of this publication by Endicott and Durham [18] in their recent review article. That article, therefore, unavoidably contains some incorrect data and also the references quoted are incorrect in many places in the section concerning axial-ligand reactivities of cobalt(III) complexes.

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References

1 Part 36, C. K. Poon, T. C. Lau, and C. M. Che, *Inorg. Chem.*, in the press.
2 C. K. Poon and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1980, 756.
3 B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
4 P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, 1966, 867.
5 S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 2893.
6 J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1964, **3**, 826.
7 C. K. Poon, C. M. Che, and Y. P. Kan, *J. Chem. Soc., Dalton Trans.*, 1980, 128.
8 D. P. Rillema, J. F. Endicott, and J. R. Barker, *J. Am. Chem. Soc.*, 1973, **95**, 6987.
9 C. K. Poon and C. L. Wong, *J. Chem. Soc., Dalton Trans.*, 1976, 966.
10 R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
11 R. S. Nicholson, *Anal. Chem.*, 1966, **38**, 1406.
12 C. K. Poon and D. A. Isabirye, *J. Chem. Soc., Dalton Trans.*, 1977, 2115.
13 W. K. Lee and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 1974, 2423.
14 C. K. Poon, *Coord. Chem. Rev.*, 1973, **10**, 1.
15 R. G. Pearson, C. R. Boston, and F. Basolo, *J. Am. Chem. Soc.*, 1953, **75**, 3089.
16 Y. Hung and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 4977.
17 C. L. Wong, Ph.D. Thesis, University of Hong Kong, 1976.
18 J. F. Endicott and B. Durham, 'Coordination Chemistry of Macrocyclic Compounds,' ed. G. A. Melson, Plenum, New York, 1979, ch. 6, p. 393.

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