Structural and Mechanistic Studies of Co-ordination Compounds. Part 31.[1] The Chromium(II) Reduction of Some *trans*-Tetra-aminedichlororuthenium(III) Cations

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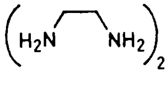
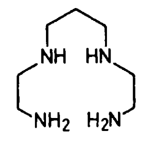
The kinetics of the reduction of *trans*-$[RuLCl_2]^+$ [L = L^1, bis(ethane-1,2-diamine); L^2, 3,7-diazanonane-1,9-diamine; or L^3, 1,4,8,11-tetra-azacyclotetradecane] by chromium(II) have been investigated. These reactions follow the general rate expression $k_{obs.} = (k_1 + k_X[X^-])[Cr^{II}]$, where X^- represents either Cl^- or Br^- added to the reaction solutions. The second-order rate constants, k_1, and activation parameters at $I = 0.50$ mol dm^{-3} are: k_1 = 30.2, 47.3, and 64.4 dm^3 mol^{-1} s^{-1}; $\Delta H^‡$ = 20.3 ± 1.0, 26.6 ± 3.0, and 26.8 ± 1.5 kJ mol^{-1}; and $\Delta S^‡$ = −149 ± 4, −124 ± 12, and −120 ± 6 J K^{-1} mol^{-1} for L = L^1, L^2, and L^3 complexes respectively. These reactions are consistent with an inner-sphere mechanism.

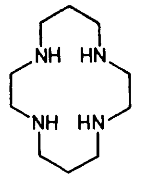
As part of our programme to examine the chemistry of ruthenium(III) amine complexes, we have reported the syntheses of several series of complexes of the types *trans*-$[RuL(A)X]^+$ and *cis*-$[RuLX_2]^+$, where L represents either one quadridentate or two bidentate amines and A and X are uninegative unidentate ligands.[2-6] We have also reported the chelation effects on the acid [7] and base [8] hydrolysis of *trans*-$[RuLCl_2]^+$ and the acid hydrolysis of the corresponding ruthenium(II) species by the method of cyclic voltammetry.[9] Ruthenium(II) complexes are, in general, much more labile than the corresponding ruthenium(III) species, by a factor of *ca.* 10^5. The aim of the present investigation is to examine the chelation effects of L on the chromium(II) reduction of *trans*-$[RuLCl_2]^+$ where L = L^1, bis(ethane-1,2-diamine); L^2, 3,7-diazanonane-1,9-diamine; or L^3, 1,4,8,11-tetra-azacyclotetradecane. The corresponding reduction of *trans*-$[Ru(NH_3)_4Cl_2]^+$ has been reported by Movius and Linck.[10]



L^1



L^2



L^3

EXPERIMENTAL

The complexes *trans*-$[RuL^1Cl_2][ClO_4]$, *trans*-$[Ru\{(R,S)\text{-}L^2\}Cl_2][ClO_4]$, and *trans*-$[RuL^3Cl_2]Cl$ were prepared according to published methods.[2,3,7] Chromium(II) solutions were prepared by reducing a known potassium dichromate solution first to chromium(III), with hydrogen peroxide, and then to chromium(II) with amalgamated zinc.[11] Toluene-*p*-sulphonic acid was used instead of sulphuric acid.[11] Chromium(II) was analysed by oxidizing with deoxygenated iron(III) and determining the resulting iron(II) with acid dichromate. The ionic strength was maintained with sodium toluene-*p*-sulphonate.

Kinetic Measurements.—All kinetics were followed spectrophotometrically *in situ* using an Aminco–Morrow stopped-flow spectrophotometer equipped with an Aminco DASAR (data acquisition, storage, and retrieval) system. Experimental details on data collection, temperature control, and data treatment have been described previously.[12] All operations were carried out under deoxygenated argon. Syringe techniques were used for the transfer of air-sensitive solutions.

RESULTS

When *trans*-$[RuLCl_2]^+$ (L = L^1, L^2, or L^3) was treated with an acidic solution of chromium(II) the absorbance at the maximum of the ruthenium(III) species decreased rapidly with time. The complete disappearance of the intense ligand-to-metal charge-transfer band in the final solution strongly suggests that the d^5 ruthenium(III) centre has been reduced to the d^6 ruthenium(II) counterpart. A stoicheiometric quantity of $[Cr(OH_2)_5Cl]^{2+}$ was detected at the end of the reaction by its absorbance at 605 nm.[10,13] When air was admitted into the final solution and an excess of chloride was added the u.v. spectrum of the solution gradually returned to that of *trans*-$[RuLCl_2]^+$. This is evidence that the reduced species is a monomeric ruthenium(II) complex retaining the amine ligand in the co-ordination sphere.

The semilogarithmic pseudo-first-order rate plots (at λ = 343, 349, and 357 nm for L = L^1, L^2, and L^3 respectively) were linear over the entire range of chromium(II) concentrations (0.96×10^{-3}—4.8×10^{-3} mol dm^{-3}) which were at least 10 times more concentrated than the ruthenium(III) substrates (0.80×10^{-4}—4.3×10^{-4} mol dm^{-3}). These pseudo-first-order rate constants, $k_{obs.}$, are independent of acid (0.030—0.43 mol dm^{-3}) and substrate concentrations, but increase linearly with chromium(II) concentrations. The presence of additional halide X^- (Cl^- or Br^-) enhances the reaction rates according to equation (1). Here, $[Cr(OH_2)_4Cl_2]^+$ was detected spectrophotometrically [10,13] at the end of the reaction when the reduction was carried out in an excess of chloride.

$$k_{obs.} = (k_1 + k_X[X^-])[Cr^{II}] \qquad (1)$$

The effect of ionic strength (over the range I = 0.1—0.6 mol dm^{-3}) on reaction rates is governed by equation (2)

$$\log k_1 = A + B\sqrt{I} \qquad (2)$$

where A and B are two proportionality constants. Most reactions were carried out at I = 0.50 mol dm^{-3}. The rate data are summarized in Table 1.* Second-order rate constants, k_1, at 25.0 °C {extrapolated to $I = 0.010$ mol dm^{-3} for a direct comparison with the published rate data [10] for *trans*-[Ru(NH$_3$)$_4$Cl$_2$]$^+$} and activation parameters (at $I = 0.50$ mol dm^{-3}) are collected in Table 2.

TABLE 1

Rate data for the chromium(II) reduction of some *trans*-[RuLCl$_2$]$^+$ complexes in 0.075 mol dm^{-3} toluene-*p*-sulphonic acid

L	θ_c/°C	I [a]/ mol dm^{-3}	k_1 [b, c]/ dm^3 mol^{-1} s^{-1}	k_X [b, d]/ dm^6 mol^{-2} s^{-1}
L^1	8.5	0.50	17.7	
	13.0	0.50	20.7	
	20.0	0.50	26.0	
	25.0	0.13	19.5	
		0.30	26.0	
		0.50	30.2	58.4 [e]
				45.0 [f]
		0.60	34.5	
L^2	8.5	0.50	23.4	
	13.0	0.50	29.3	
	20.0	0.50	37.7	
	25.0	0.13	27.9	
		0.30	39.5	
		0.50	47.3	99.5 [e]
				71.2 [f]
		0.60	52.0	
L^3	8.5	0.50	32.7	
	13.0	0.50	39.6	
	20.0	0.50	55.0	
	25.0	0.13	40.0	
		0.30	53.9	
		0.50	64.6	214 [e]
				196 [f]
		0.60	71.4	

[a] Ionic strength was maintained with sodium toluene-*p*-sulphonate. [b] $k_{obs.} = (k_1 + k_X[X^-])[Cr^{II}]$; $k_{obs.}$ has been found to be independent of [RuLCl$_2$$^+$] ($0.8 \times 10^{-4}$—$4.3 \times 10^{-4}$ mol dm^{-3}) and [H$^+$] (0.030—0.43 mol dm^{-3}). [c] The kinetic data were obtained from the slopes of the least-squares plots of $k_{obs.}$ *vs.* [Cr^{II}] (over the range 0.96×10^{-3}—4.8×10^{-3} mol dm^{-3}) at $[X^-] = 0$. [d] The kinetic data were obtained from the slopes of the least-squares plots of $k_{obs.}/[Cr^{II}]$ *vs.* [X$^-$] (over the range 0—0.40 mol dm^{-3}) at $[Cr^{II}] = 4.81 \times 10^{-3}$ mol dm^{-3}. [e] X = Cl. [f] X = Br.

TABLE 2

Second-order rate constants, k_1, at 25.0 °C and activation parameters for the chromium(II) reduction of *trans*-[RuLCl$_2$]$^+$ in 0.075 mol dm^{-3} toluene-*p*-sulphonic acid and at $I = 0.10$ mol dm^{-3}

L	k_1 [a]/ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$ [b]/ kJ mol^{-1}	$\Delta S^\ddagger$ [b]/ J K^{-1} mol^{-1}
(NH$_3$)$_4$	126 [c]		
L^1	18.5	20.3 ± 1.0	-149 ± 4
L^2	27.6	26.6 ± 3.0	-124 ± 12
L^3	38.2	26.8 ± 1.5	-120 ± 6

[a] Values at $I = 0.10$ mol dm^{-3} for L = L^1, L^2, and L^3 were obtained by extrapolation of data in Table 1. [b] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated for rate constants at $I = 0.50$ mol dm^{-3}. [c] In 0.10 mol dm^{-3} toluene-*p*-sulphonic acid, ref. 10.

DISCUSSION

The kinetic behaviour of the chromium(II) reduction of *trans*-[RuLCl$_2$]$^+$ is consistent with the following inner-sphere mechanism, equations (3) and (4). Movius and Linck [10] suggested a rapid and reversible electron transfer occurring in the chloro-bridged intermediate, *i.e.* $\{Cr^{II}\text{–}Cl\text{–}Ru^{III}\} \xrightleftharpoons{\text{fast}} \{Cr^{III}\text{–}Cl\text{–}Ru^{II}\}$. The {Cr^{II}–Cl–Ru^{III}} state rapidly dissociates back to the starting substrates, whereas the {Cr^{III}–Cl–Ru^{II}} state is responsible for the ultimate dissociation into the final products.

$$[Cr(OH_2)_6]^{2+} + [ClRuLCl]^+ \xrightleftharpoons{K} [(H_2O)_5Cr\text{–}Cl\text{–}RuLCl]^{3+} \quad (3)$$

$$[(H_2O)_5Cr\text{–}Cl\text{–}RuLCl]^{3+} \xrightarrow{k} [Cr(OH_2)_5Cl]^{2+} + [RuLCl(OH_2)]^+ \quad (4)$$

Since chromium(II) is much more labile than ruthenium(II), it is, therefore, reasonable to assume that reaction (3) is in pseudo-equilibrium while reaction (4) is rate-determining. The kinetic behaviour also requires that the concentration of the chloro-bridged intermediate is negligibly small. This is confirmed by the observation that the extrapolation of the kinetic plots back to zero time gave the absorbance of the starting ruthenium(III) complex. According to this mechanism, the second-order rate constant, k_1, is approximately given by equation (5). However, it is not possible from the present investigation to determine separately the values of k and K.

$$k_{obs.} = k_1[Cr^{II}] = kK[Cr^{II}] \quad (5)$$

With the exception of *trans*-[Ru(NH$_3$)$_4$Cl$_2$]$^+$, it is clear from Table 2 that the reduction rate constant, k_1, increases slightly with increased chelation of L. Since it has been shown [9] that the acid-hydrolysis rate constants for the release of Cl$^-$ from *trans*-[Ru^{II}LCl$_2$] decrease with increased chelation of L [L = (NH$_3$)$_4$, 1.0; L^1, 3.5×10^{-1}; L^2, 6.6×10^{-2}; and L^3, 2.3×10^{-2} s^{-1}], it seems reasonable to assume that the rate constants for the release of [Cr(OH$_2$)$_5$Cl]$^{2+}$, *i.e.* k, would also decrease with increased chelation. Movius and Linck [10] have estimated that the release of X from *cis*-[Ru^{II}(NH$_3$)$_4$ClX]$^{n+}$ is *ca.* 10 times faster for X = Cr(OH$_2$)$_5$Cl^{2+} than for X = Cl$^-$. Assuming that this reactivity ratio is about the same for our system, it seems reasonable to assume the following values of k for the chloro-bridged intermediates: L = (NH$_3$)$_4$, *ca.* 10; L^1, *ca.* 4; L^2, *ca.* 7×10^{-1}; and L^3, *ca.* 2×10^{-1} s^{-1}. Therefore, the net observed increase in k_1 for $L^1 < L^2 < L^3$ means that the values of K must increase, by a greater ratio, in the reversed order of L [*i.e.* L = (NH$_3$)$_4$, *ca.* 13; L^1, *ca.* 5; L^2, *ca.* 40, L^3, *ca.* 190 dm^3 mol^{-1}].

The variation of K with increased chelation is probably associated with solvation and steric effects. The association of two charged species into a charged dimer is probably accompanied by a decrease in solvation energy. The larger is the starting *trans*-[RuLCl$_2$]$^+$ the smaller is its own solvation energy. Accordingly, the smaller will be its loss in solvation energy in forming the dimer, and hence the greater is the value of K. On the other hand, the increased steric constraints of *trans*-[RuLCl$_2$]$^+$ with increased chelation could reduce the value of K.

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* A fuller version of this Table is available as Supplementary Publication No. SUP 23159 (7 pp.). For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

The interplay of these two opposite effects might explain the variation of K in the following order of L: $(NH_3)_4 > L^1 < L^2 < L^3$.

The enhanced reducing effect caused by the addition of halide X^- (Cl^- or Br^-) means that $[Cr(OH_2)_5X]^+$ is a better reducing agent than $[Cr(OH_2)_6]^{2+}$ for these ruthenium(III) complexes [14] according to equations (6)—(8).

$$[Cr(OH_2)_6]^{2+} + X^- \xrightleftharpoons{K_X} [Cr(OH_2)_5X]^+ \quad (6)$$

$$[Cr(OH_2)_5X]^+ + [ClRuLCl]^+ \xrightleftharpoons{K_{X'}} [X(H_2O)_4Cr{-}Cl{-}RuLCl]^{2+} \quad (7)$$

$$[X(H_2O)_4Cr{-}Cl{-}RuLCl]^{2+} \xrightarrow{k_{X'}} [Cr(OH_2)_4XCl]^+ + [RuLCl(OH_2)]^+ \quad (8)$$

The observed third-order rate constant, k_X, is therefore related to K_X, $K_{X'}$, and $k_{X'}$ according to equation (9). However, in the absence of reliable values of K_X at

$$k_X = k_{X'}K_XK_{X'} \quad (9)$$

$I = 0.50$ mol dm^{-3}, we cannot compare the effectiveness $(k'K')$ of $[Cr(OH_2)_5X]^+$ with that of $[Cr(OH_2)_6]^{2+}$ in the reduction of these ruthenium(III) complexes.

An accelerating effect of ionic strength on second-order rate constants is expected for reactions between two reactants of the same charge type. Although the plots of log k_1 *vs.* $\sqrt{I}$ are linear, the slopes (L^1, 0.58; L^2, 0.61; L^3, 0.59) are much smaller than that expected (6.10) from the Brönsted–Debye–Hückel equation [15] for reactions of charge product six. It should be noted that the theoretical equation is derived for reactions in nearly ideal solutions. In the present investigation, reactions were carried out at relatively high ionic strengths (I 0.1—0.6 mol dm^{-3}) and, therefore, the rate constants would be expected to lie in the tailing off regions of the log k_1 *vs.* $\sqrt{I}$ plots. Accordingly, the extrapolation of these plots to zero ionic strength does not yield the true values of k_1 at infinite dilution.

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