Structural and Mechanistic Studies of Co-ordination Compounds. Part 33.[1] Inner-sphere *vs.* Outer-sphere Mechanisms in the Reductions of Some *trans*-Dianiono(tetramine)ruthenium(III) Cations by Chromium(II) and Vanadium(II)

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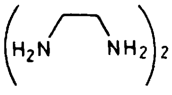
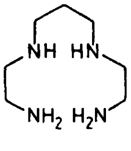
The kinetics of the reduction of *trans*-$[RuL^1AX]^+$ [L^1 = bis(ethane-1,2-diamine); AX = Cl_2, Br_2, I_2, or BrCl] and *trans*-$[RuLCl_2]^+$ [L = L^2 (3,7-diazanonane-1,9-diamine), L^3 (1,4,8,11-tetra-azacyclotetradecane), L^4 (1,4,8,12-tetra-azacyclopentadecane), L^5 or L^6 (*C-meso* or *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane respectively)] by chromium(II) and vanadium(II) have been studied at 25.0 °C in aqueous acidic solutions of ionic strength 0.50 mol dm^{-3}. The chromium(II) reductions have been shown to proceed by an inner-sphere mechanism *via* the bridging ligand X^-. These reactions are very sensitive to steric effects with *trans*-$[RuL^5Cl_2]^+$ and *trans*-$[RuL^6Cl_2]^+$ more reactive than the corresponding steric-free L^3 complex by a factor of 76.5 and 58.0 respectively. For *trans*-$[RuL^1AX]^+$ complexes, the second-order rate constants drop systematically in the following order of AX: $I_2 > Br_2 \geqslant ClBr \geqslant BrCl > Cl_2$ (148, 38, 37, 31, and 15 $dm^3\ mol^{-1}\ s^{-1}$ respectively, after a statistical factor of two has been applied to the dihalogeno-complexes). For vanadium(II) reductions, the second-order rate constants, ranging from 1.21×10^3 $dm^3\ mol^{-1}\ s^{-1}$ for *trans*-$[RuL^1Cl_2]^+$ to 1.27×10^4 $dm^3\ mol^{-1}\ s^{-1}$ for *trans*-$[RuL^1I_2]^+$, are much greater than the ligation rates of vanadium(II). This, together with the observation that steric factors have relatively little effect on the reactivity, strongly supports an outer-sphere mechanism for these vanadium(II) reductions.

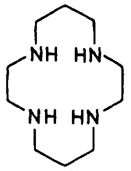
THE study of reductions of ruthenium(III) amine complexes has so far been confined to ammine systems, such as $[Ru(NH_3)_6]^{3+}$,[2] $[Ru(NH_3)_5X]^{n+}$ (X = halide, H_2O, or carboxylate),[3] and *cis*- and *trans*-$[Ru(NH_3)_4ClX]^{n+}$ (X = Cl or H_2O).[4] We have recently reported[5-7] the syntheses of extensive series of amine complexes of the type *trans*-$[RuLAX]^+$, where L represents either two bidentate or one quadridentate amine and A and X are unidentate ligands, and have also reported[8] the chelation effects of L on chromium(II) 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].



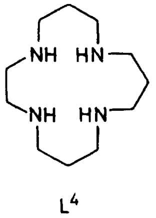
L^1



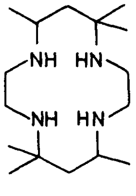
L^2



L^3



L^4



L^5 (*C-meso*)
or
L^6 (*C-rac*)

These reactions have been shown to proceed by an inner-sphere mechanism.[8] In this paper, we have extended the study to a much wider range of complexes, *trans*-$[RuL^1AX]^+$ (AX = Br_2, I_2, or ClBr) and *trans*-$[RuLCl_2]^+$ (L = L^4, 1,4,8,12-tetra-azacyclopentadecane, L^5 or L^6, *C-meso* or *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane respectively), in order to understand steric and ring-size effects and the effects of co-ordinated halides on these reduction reactions.

Reductions by vanadium(II) give rise to both inner- and outer-sphere reactions.[2-4,9,10] It was, therefore, also the intention of this work to investigate the vanadium(II) reduction mechanisms of the above series of *trans*-tetramineruthenium(III) and *trans*-$[RuLCl_2]^+$ (L = L^1 L^2, or L^3) complexes.

EXPERIMENTAL

The complexes *trans*-$[RuL^1AX][ClO_4]$[6] (AX = Cl_2, Br_2, or BrCl), *trans*-$[RuL^1I_2]I$,[6] *trans*-$[RuL^2Cl_2][ClO_4]$,[11] *trans*-$[RuL^3Cl_2]Cl$,[5,6] and *trans*-$[RuLCl_2][ClO_4]$[7] (L = L^4, L^5, or L^6) were prepared according to published methods. Chromium(II) solutions were prepared by reducing potassium dichromate solutions first to chromium(III) with hydrogen peroxide and then to chromium(II) with amalgamated zinc.[12a] Chromium(II) was analysed by oxidizing with deoxygenated iron(III) and determining the reduced iron(II) with acid dichromate. Vanadium(II) solutions were prepared by reduction of solutions of vanadium(V) oxide in toluene-*p*-sulphonic acid with amalgamated zinc under an atmosphere of argon and were used immediately after standardization with iron(III) in the presence of excess of thiocyanate.[12b] 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.[13] All operations were carried out under deoxygenated argon. Syringe techniques were used for the transfer of air-sensitive solutions.

RESULTS

The spectrophotometric changes for both chromium(II) and vanadium(II) reductions in toluene-*p*-sulphonic acid (Hpts, 0.1 mol dm^{-3}) are characterized by a gradual disappearance of the intense ligand-to-metal charge-transfer bands of the complexes, thus confirming the conversion of d^5 ruthenium(III) centre into the d^6 ruthenium(II) counterpart. For inner-sphere chromium(II) reductions,[8] the nature of the bridging ligand in the reaction of *trans*-$[RuL^1ClBr]^+$ is not trivial. It was determined by the following method. An acidic solution (0.1 mol dm^{-3} Hpts) of *trans*-$[RuL^1ClBr]^+$ at 25.0 °C was treated with a suitable quantity of chromium(II) for 1.5 min. Air was immediately admitted to re-oxidize the ruthenium(II) instantaneously back to the inert ruthenium(III) species. The u.v. spectrum of this solution, labelled A, showed that it was a mixture of *trans*-$[RuL^1Cl(OH_2)]^{2+}$ and *trans*-$[RuL^1Br(OH_2)]^{2+}$ indicating that both Cl^- and Br^- are functioning as bridging ligands in a competitive manner. To determine this competition ratio quantitatively, solution A was equally divided into two portions, A1 and A2. Portion A1 was treated with an excess of NaCl and the solution warmed to *ca.* 40 °C for *ca.* 20 min. This gave a mixture of *trans*-$[RuL^1ClBr]^+$ and *trans*-$[RuL^1Cl_2]^+$, the exact concentrations of which were determined from the known molar absorption coefficients[6] of these species at $\lambda_{max.}$ (343 nm) of the latter. In a typical run, the concentrations of the chlorobromo- and dichloro-complexes were found to be $c_{ClBr} = 8.2 \times 10^{-5}$ and $c_{Cl_2} = 9.6 \times 10^{-5}$ mol dm^{-3} respectively. Similarly, solution A2 was treated with excess of NaBr and the final solution, as determined from the absorbances at 409 nm, corresponded to a mixture of *trans*-$[RuL^1ClBr]^+$ ($c_{ClBr} = 9.8 \times 10^{-5}$ mol dm^{-3}) and *trans*-$[RuL^1Br_2]^+$ ($c_{Br_2} = 8.0 \times 10^{-5}$ mol dm^{-3}).

Assuming the following competitive reductions of *trans*-$[RuL^1ClBr]^+$ by chromium(II) [equations (1) and (2)], where

$$trans\text{-}[RuL^1ClBr]^+ + [Cr(OH_2)_6]^{2+} \xrightarrow{k_{ClBr}} trans\text{-}[RuL^1Cl(OH_2)]^+ + [Cr(OH_2)_5Br]^{2+} \quad (1)$$

$$trans\text{-}[RuL^1ClBr]^+ + [Cr(OH_2)_6]^{2+} \xrightarrow{k_{BrCl}} trans\text{-}[RuL^1Br(OH_2)]^+ + [Cr(OH_2)_5Cl]^{2+} \quad (2)$$

k_{AX} represents the appropriate second-order rate constant for the bridging pathway (X = Cl or Br), it is obvious that the competition ratio of k_{ClBr}/k_{BrCl} is given by the concentration ratio of $[RuL^1Cl(OH_2)^+]/[RuL^1Br(OH_2)^+]$. In solution A1, c_{Cl_2} and c_{ClBr}, in fact, corresponded to the concentrations of *trans*-$[RuL^1Cl(OH_2)]^+$ and *trans*-$[RuL^1Br(OH_2)]^+$ respectively of the mother solution A, and hence give the competition ratio $k_{ClBr}/k_{BrCl} = 1.17$. This agrees very well with the independently determined competition ratio of 1.23 from solution A2 where c_{ClBr} and c_{Br_2} denote the concentrations of *trans*-$[RuL^1Cl(OH_2)]^+$ and *trans*-$[RuL^1Br(OH_2)]^+$ respectively. The consistency of these two ratios further indicates that the extent of aquation of the reduced species, *trans*-$[RuL^1A(OH_2)]^+$ (A = Cl or Br), is insignificant within the time scale of the experiment. However, when the experiments were repeated with an extended reduction time, it was found that this competition ratio for solution A1 gradually increased but that for solution A2 decreased with the reduction time. This observation is consistent with the aquation of the reduced species thus generating some *trans*-$[RuL^1(OH_2)_2]^{2+}$ in solution A which eventually gives a higher estimate of dihalogeno-complexes over *trans*-$[RuL^1ClBr]^+$ on reaction with excess of halide.

The kinetics of the redox reactions at 25.0 °C were followed spectrophotometrically at the absorption maxima of the ruthenium(III) complexes. Concentrations of the reductants, either chromium(II) or vanadium(II), were kept at least 20-fold (1.0×10^{-3}—1.0×10^{-2} mol dm^{-3}) greater than those of the oxidants (0.80×10^{-4}—4.3×10^{-4} mol dm^{-3}).

Second-order rate constants at 25.0 °C for chromium(II) and vanadium(II) reductions of some *trans*-$[RuLAX]^+$ complexes in 0.10 mol dm^{-3} toluene-*p*-sulphonic acid and at $I = 0.50$ mol dm^{-3} (sodium toluene-*p*-sulphonate)[a]

Complex			$10^{-1}k_{Cr}$ / $dm^3\ mol^{-1}\ s^{-1}$	$10^{-3}k_V$ / $dm^3\ mol^{-1}\ s^{-1}$
L	A	X		
$(NH_3)_4$	Cl	Cl	12.6[b]	0.83[b]
L^1	Cl	Cl	3.02[c]	1.21
L^1	Br	Cl	3.1	2.25
L^1	Cl	Br	3.7	2.25
L^1	Br	Br	7.63	3.07
L^1	I	I	29.5	12.7
L^2[d]	Cl	Cl	4.73[c]	2.03
L^3	Cl	Cl	6.46[c]	3.48
L^4	Cl	Cl	11.6	3.56
L^5	Cl	Cl	494[e]	7.28
L^6	Cl	Cl	375[e]	7.69

[a] Second-order rate constants, being independent of acid (0.05—0.50 mol dm^{-3}), are obtained from the slopes of the least-squares plots of $k_{obs.}$ *vs.* [reductant] over the range $1.0 \times 10^{-3}-1.0 \times 10^{-2}$ mol dm^{-3}. In the case of chromium(II) reactions, X^- represents the bridging ligand. [b] Ref. 4, $I = 0.10$ mol dm^{-3}. [c] Ref. 8. [d] *R,S*-isomer. [e] These two complexes are unstable in very dilute acids. Rate constants are independent of acid in the range 0.20—0.45 mol dm^{-3}.

The ionic strength of the reaction solutions was maintained at 0.50 mol dm^{-3}. Semi-logarithmic plots of $\log(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ represent absorbances at time *t* and at infinity (10 half-lives) respectively, were linear over at least three half-lives. The pseudo-first-order rate constants, $k_{obs.}$, are independent of the wavelengths of measurement, acid (0.05—0.50 mol dm^{-3} for L^{1-4} complexes and 0.20—0.45 mol dm^{-3} for L^5 and L^6 complexes), and substrate concentrations, but increase linearly with reductant concentrations. For each substrate, experiments were repeated for at least five different concentrations of the reductants. Second-order rate constants, k_{Cr} or k_V, were obtained from the slopes of the appropriate linear plots of $k_{obs.}$ *vs.* [reductant] by the method of least squares.

The rate constants for the bromide-bridged and chloride-bridged paths, k_{ClBr} and k_{BrCl} respectively, of *trans*-$[RuL^1ClBr]^+$ were determined from the competition ratio (average $k_{ClBr}/k_{BrCl} = 1.20$) and equation (3), where k_1 is

$$k_1 = k_{BrCl} + k_{ClBr} \quad (3)$$

the observed second-order rate constant for the disappearance of *trans*-$[RuL^1ClBr]^+$ in the chromium(II) reduction reactions.

All these kinetic data are collected in the Table.

DISCUSSION

It has been shown[8] unambiguously that chromium(II) reductions of *trans*-$[RuLCl_2]^+$ ($L = L^{1-3}$) proceed by an inner-sphere mechanism according to the general equations (4) and (5), with the second-order rate constants k_{Cr} given by equation (6). The present observation of steric acceleration (*trans*-$[\mathrm{RuL^5Cl_2}]^+$ and

$$[\mathrm{ALRuX}]^+ + [\mathrm{Cr(OH_2)_6}]^{2+} \overset{K}{\rightleftharpoons} [\mathrm{ALRu{-}X{-}Cr(OH_2)_5}]^{3+} \quad (4)$$

$$[\mathrm{ALRu{-}X{-}Cr(OH_2)_5}]^{3+} \xrightarrow{k} [\mathrm{RuLA(OH_2)}]^+ + [\mathrm{Cr(OH_2)_5X}]^{2+} \quad (5)$$

$$k_{\mathrm{Cr}} = kK \quad (6)$$

trans-$[\mathrm{RuL^6Cl_2}]^+$ are more reactive than *trans*-$[\mathrm{RuL^3Cl_2}]^+$ by a factor of 76.5 and 58.0 respectively) is fully consistent with this mechanism. It is well known that steric effects accelerate the dissociation of a leaving group. The acid hydrolysis of *trans*-$[\mathrm{CoLCl_2}]^+$ ($\mathrm{L} = \mathrm{L}^{5,6}$) has been shown to be faster than that of *trans*-$[\mathrm{CoL^3Cl_2}]^+$ by a factor of *ca.* 10^3.[14,15] This steric effect is even more pronounced for the corresponding ruthenium(III) system.[16] It seems reasonable to expect that the values of k in equation (5) for the L^5 and L^6 chloride-bridged intermediates are greater than that of the corresponding L^3 intermediate by at least a factor of *ca.* 10^3. The presence of $[\mathrm{Cr(OH_2)_5Cl}]^{2+}$ as a leaving group, which is larger than Cl^-, would only serve to enhance the steric acceleration on k. The variation of K in equation (4) with additional methyl groups in the macrocycle L is probably associated with solvation and non-bonding steric crowding effects. The association of two charged species into a charged dimer is probably accompanied by a decrease in solvation energy. The larger starting complex *trans*-$[\mathrm{RuLCl_2}]^+$ ($\mathrm{L} = \mathrm{L}^{5,6}$) would suffer a smaller relative loss in solvation energy by desolvation than *trans*-$[\mathrm{RuL^3Cl_2}]^+$, and hence would assume a greater value of K. On the other hand, the increased non-bonding steric crowding of *trans*-$[\mathrm{RuLCl_2}]^+$ with additional methyl groups would reduce the value of K. The interplay of these two opposing effects, with the latter probably more important for L^5 and L^6 systems, might lead to an overall decrease in the value of K, although to a much less extent as k increases with steric effects. The combination of k and K, *i.e.* k_{Cr}, is therefore expected to increase with steric effects. The observed steric ratios of 76.5 and 58.0 are consistent with this inner-sphere mechanism.

As far as ring-size effect is concerned, the observation that *trans*-$[\mathrm{RuL^4Cl_2}]^+$ is slightly more reactive than *trans*-$[\mathrm{RuL^3Cl_2}]^+$, by a factor of 1.8, is also consistent with the inner-sphere mechanism. This effect, which has the same magnitude as the chelation effect (*trans*-$[\mathrm{RuL^3Cl_2}]^+$ is more reactive than *trans*-$[\mathrm{RuL^2Cl_2}]^+$ by a factor of 1.4), probably arises from the same solvation effects and steric constraints.[8]

A comparison of k_{Cr} for various *trans*-$[\mathrm{RuL^1AX}]^+$ complexes, after correcting for the statistical factor of two for dihalogeno-complexes, shows that the second-order rate constants decrease systematically with the nature of $\mathrm{AX}: \mathrm{I_2} > \mathrm{Br_2} \geqslant \mathrm{ClBr} \geqslant \mathrm{BrCl} > \mathrm{Cl_2}$ (**148, 38, 37, 31,** and **15** $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ respectively). It is worth noting, even based on the limited number of experimental data, that the bridging efficiencies of the halides depend on the nature of the *trans*-activating ligands. Thus, with chloride as the *trans*-activating ligand, bromide functions as a better bridge than chloride ($k_{\mathrm{ClBr}}/k_{\mathrm{Cl_2}} = 2.5$), whereas for *trans*-bromo-complexes the bridging efficiencies of bromide and chloride are virtually identical ($k_{\mathrm{Br_2}}/k_{\mathrm{BrCl}} = 1.2$). On the other hand, the *trans*-activating efficiencies of the halides also depend on the nature of the bridging ligands. With chloride as the bridging ligand, bromide has a greater *trans*-activating effect than chloride ($k_{\mathrm{BrCl}}/k_{\mathrm{Cl_2}} = 2.1$) but this superiority disappears when bromide becomes the bridging ligand ($k_{\mathrm{Br_2}}/k_{\mathrm{ClBr}} = 1.0$). It thus appears that the order of bridging or *trans*-activating efficiencies of halides for one ruthenium(III) system may not be the same for another, even though very similar, and care must be exercised in discussing these efficiencies. The much greater reactivity of *trans*-$[\mathrm{RuL^1I_2}]^+$ relative to other L^1 halogeno-complexes reported here could then be due to either a greater *trans*-activating effect or bridging effect of iodide or both. The present experimental results do not allow us to draw a conclusion on the relative merits of these effects.

The behaviour of vanadium(II) reductions of these tetramineruthenium(III) complexes appears to be quite different to that of the chromium(II) reductions discussed above. The fact that all the second-order rate constants, k_{V}, are much greater than the ligation rates of vanadium(II) * clearly indicate an outer-sphere mechanism for these reactions. The lack of ring-size and significant steric effects in contrast to those observed for inner-sphere chromium(II) reactions further supports this mechanism. That the bulkier *trans*-$[\mathrm{RuLCl_2}]^+$ ($\mathrm{L} = \mathrm{L}^{5,6}$) complexes are slightly more reactive than *trans*-$[\mathrm{RuL^3Cl_2}]^+$ by a factor of *ca.* 2.1 is probably a solvation effect.

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* An upper limit of *ca.* 40 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ for vanadium(II) inner-sphere reactions has been estimated by Sutin.[17]

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