Structural and Mechanistic Studies of Co-ordination Compounds. Part 24.[1] Application of Cyclic Voltammetry to Study the Chelation Effect on Acid Hydrolysis of Some *cis*- and *trans*-Ruthenium(II) Amine Complexes

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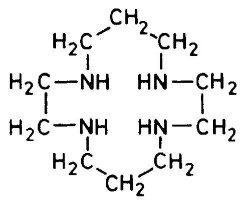
Formal reduction potentials E_f of a series of tetramine ruthenium(III) complexes of the type *cis*- and *trans*-$[RuL(A)X]^{n+}$ have been determined by cyclic voltammetry (c.v.) in aqueous solution. In general, for a given pair of unidentate ligands A and X, the E_f values increase with increased chelation of L: $(NH_3)_4$ < $(en)_2$ (en = $H_2NCH_2CH_2NH_2$) < 2,3,2-tet(3,7-diazanonane-1,9-diamine, *RS* isomer) < cyclam (1,4,8,11-tetra-azacyclotetradecane). On the other hand, for a given tetramine L, the E_f values vary with the nature of A and X in the following manner: dihalogeno- < aquahalogeno- < diaqua-couples, and chloro- < bromo- < isothiocyanato-couples. The E_f values of *cis* isomers are greater than those of the *trans* counterparts. The kinetics of aquation of some ruthenium(II) complexes of the type *trans*-$[RuLX_2]$ (X = Cl or Br) have also been followed over a range of temperature by the c.v. technique. These reactions are stereoretentive with negative entropies of activation, the first-order rate constants, k_1, decrease with increased chelation, and the complexes are less labile than the corresponding *cis* isomers, similar features to those of the corresponding cobalt(III) and ruthenium(III) complexes. A dissociative mechanism with a square-pyramidal intermediate is assumed for these reactions. The importance of solvation, nephelauxetic, and σ-*trans* effects has been invoked to explain the above thermodynamic and kinetic behaviour of these ruthenium complexes.

THE mechanistic study of ruthenium(II) complexes has aroused considerable interest in recent years.[2-7] However, direct syntheses of stable ruthenium(II) amine complexes is, in most cases, quite difficult. Nearly all such complexes have been generated electrolytically in solution from the corresponding stable ruthenium(III) counterparts. Anson and co-workers[8] first noted qualitatively that the rate of aquation of $[Ru(NH_3)_5X]^+$ varied with X in the order Br > Cl > [NCS]. The kinetics of aquation of these halogenopenta-ammine complexes were later reported by Kuempel and co-workers[3] but no definite mechanistic conclusion was drawn. Taube and co-workers[6,9] and Allen and Ford[4,10] independently followed the anation of $[Ru(NH_3)_5(OH_2)]^{2+}$ and *cis*- and *trans*-$[Ru(NH_3)_4(OH_2)_2]^{2+}$ by a variety of π-unsaturated nucleophiles and they suggested a dissociative mechanism. Very recently, Ford and co-workers[7] reported that the aquation rates of *cis*- and *trans*-$[Ru(NH_3)_4A(X)]^+$ are relatively independent of the identity of X^- (X^- = Cl^-, Br^-, or I^-), but are strongly dependent on the character and stereochemistry of the neutral ligand A, in the order acn (acetonitrile) < isna (isonicotinamide) < py (pyridine) < NH_3 for the *trans* series and isna ≈ acn < py < NH_3 for the *cis* series. Again, a dissociative mechanism was suggested to explain these reactions.

As part of our programme to extend the kinetic and mechanistic studies of substitution reactions of cobalt(III) amine complexes to other metal systems, we have reported the chelation effect on the acid[11] and base[12] hydrolysis of some ruthenium(III) complexes of the type *trans*-$[RuLCl_2]^+$, [L = $(NH_3)_4$; $(en)_2$ (en = ethylenediamine); 2,3,2-tet(3,7-diazanonane-1,9-diamine, *RS* isomer), and cyclam (1,4,8,11-tetra-azacyclotetradecane)]. It is also of interest to study the aquation of the corresponding ruthenium(II) complexes to see how the difference in electronic structure[2] of the central metal ion will alter the kinetic and mechanistic behaviour of the *cis*- and *trans*-$[RuLCl_2]$ complexes relative to their ruthenium(III) counterparts [ruthenium(II) is an electron donor (electron-rich centre) whereas ruthenium(III) is an electron acceptor (electron-deficient centre)[2]]. Furthermore, a comparison of the kinetic behaviour of the ruthenium(II) complexes with that of the corresponding cobalt(III) complexes, both of low-spin d^6 configuration, may be of great mechanistic value. Attempts to prepare crystalline samples of *cis*- and *trans*-$[RuLX_2]$ (X = Cl or Br) were unsuccessful. We report here the application of cyclic voltammetry (c.v.) on the species *trans*-$[RuLX_2]^+$ (X = Cl or Br) and *cis*-$[Ru(en)_2Cl_2]^+$ as a means of following the aquation of the corresponding ruthenium(II) complexes. Since the base hydrolysis of the parent ruthenium(III) complex and the background aquation of the reduced ruthenium(II) species are both rather fast, it is not possible to follow the base hydrolysis of these ruthenium(II) complexes by the c.v. technique.



cyclam

EXPERIMENTAL

The compounds *cis*-$[Ru(en)_2Cl_2]^+$,[13] *trans*-$[Ru(NH_3)_4Cl_2]^+$,[14,15] and *trans*-$[RuLX_2]^+$ [11,16,17] [L = $(en)_2$, 2,3,2-tet(*RS* isomer), or cyclam; X = Cl or Br] were prepared by the literature methods. Recrystallized-toluene-*p*-sulphonic acid (Hpts) and potassium toluene-*p*-sulphonate (K[pts]) were used as supporting electrolytes. Doubly redistilled water was used in all electrochemical studies.

Apparatus.—Cyclic voltammograms were obtained with 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 2 000 X–Y recorder at slow scan rates (< 1 V s^{-1}) and with a Tektronix model 5 103N storage oscilloscope at high scan rates (> 1 V s^{-1}). Controlled-potential coulometric electrolysis was carried out with a PAR model 9 610 coulometric cell system which was supplied with a PAR model 377 synchronous stirring motor. All reaction solutions were deaerated before the c.v. scans and during the constant-potential electrolyses processes.

Kinetics.—Thermostatted solutions containing *ca.* 0.001 mol dm^{-3} of the complexes, 0.01 mol dm^{-3} Hpts, and 0.19 mol dm^{-3} K[pts] were subjected to cyclic-voltammetric scans between 0.2 and −0.6 V against a saturated calomel reference electrode (s.c.e.). Scan rates were chosen to be compatible with reaction rates. With our PAR instruments, we could only select scan rates at fixed intervals, such as 10, 20, 50 mV s^{-1}, *etc.* A device having a variable scan rate, with which a much wider range of kinetic data could have been obtained, was not available. However, rate constants reported here represent average values determined from two to four different scan rates. Reactions were followed over a range of temperature, complex concentration, acid concentration, and ionic strength.

RESULTS

The electrochemical behaviour of *trans*-$[Ru(en)_2Cl_2]^+$ in 0.01 mol dm^{-3} Hpts with $I = 0.2$ mol dm^{-3} using K[pts] can be taken as representative of that of all ruthenium(III) complexes under the present investigation (Figure 1). At a relatively fast scan rate (0.5 V s^{-1}) at 12 °C, the cyclic voltammogram is typical of that for a reversible one-electron redox system. One peak is observed in both the forward cathodic [reduction of ruthenium(III) to ruthenium(II)] and the reverse anodic (re-oxidation process) waves with a peak separation of 63 ± 6 mV which is independent of scan rate. At a slower scan rate (200 mV s^{-1}) at 20 °C, a second anodic peak appears at a more positive potential in the first reverse scan while a small second cathodic peak also appears at a more positive potential during the second forward scan. A third set of peaks finally appears at even more positive potentials in subsequent cycles at slower scan rates. A peak separation of *ca.* 60 mV, being independent of scan rate, remains a constant feature in these two subsequent sets of peaks. The presence of these three sets of peaks can be better illustrated by first allowing a solution of the complex to undergo a one-electron constant-potential electrolysis to *ca.* $33\frac{1}{3}$% completion, then recording the cyclic voltammogram at a scan rate which is slightly slower than the aquation rate of the complex. The complete hydrolysis of the ruthenium(II) species after the partial electrolysis enables the third set of peaks to appear during the first few cycles of the c.v. scan of the remaining ruthenium(III) species (Figure 2). The behaviour of the voltammogram is consistent with the Scheme. The formal reduction potential E_f for each set of couples has been taken to be the average value of the corresponding anodic (E_{ap}) and cathodic (E_{cp}) peak potentials. These data at 25.0 °C, after being corrected for the E_f of s.c.e. (+241 mV *vs.* standard hydrogen electrode [18]), are collected in Table 1. The proposed reaction Scheme is supported by some independent observations. First, all complexes studied give the same c.v. pattern. The E_f of the third set of peaks is independent of the nature of X^- ($X^- = Cl^-$ or Br^-) and is identical with that determined independently for the *trans*-$[RuL(OH_2)_2]^{3+,2+}$ couple. Secondly, a solution of known concentration of *trans*-$[RuLCl_2]^+$ was subjected to a one-electron controlled-potential electrolysis. The solution was then air-oxidized and excess of NaCl was added. The course of the reaction, traced by electronic spectroscopy, was identical with the stepwise quantitative anation of *trans*-$[RuL(OH_2)_2]^{3+}$ by Cl^- back to *trans*-$[RuLCl_2]^+$.[11,19]

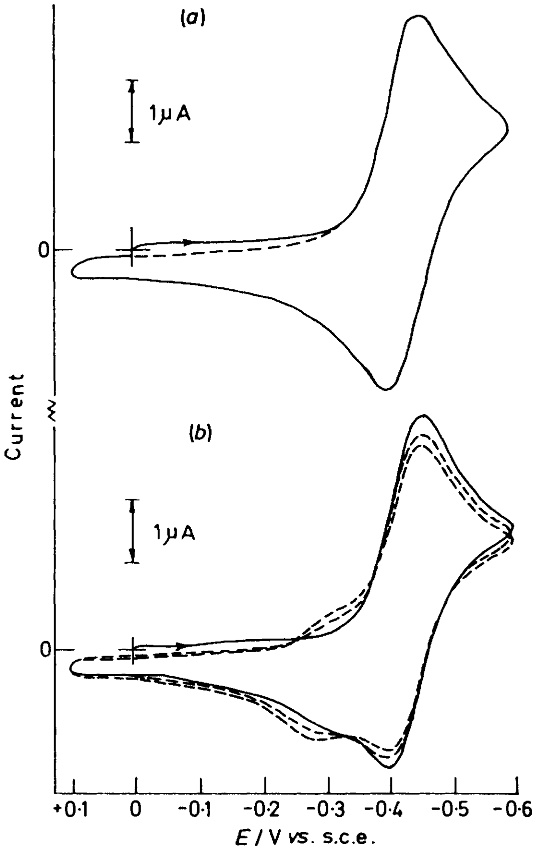
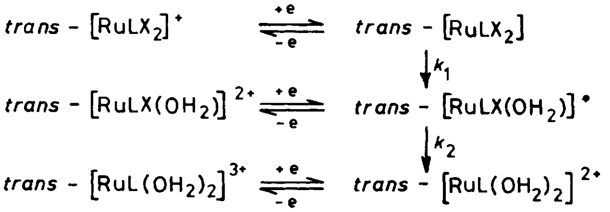


FIGURE 1 Cyclic voltammograms of *trans*-$[Ru(en)_2Cl_2]^+$ (0.001 mol dm^{-3}) in 0.01 mol dm^{-3} Hpts and 0.19 mol dm^{-3} K[pts] at different scan rates: (*a*) at 0.5 V s^{-1} at 12 °C, (*b*) at 0.2 V s^{-1} at 20 °C

First-order rate constants k_1 for the aquation of *trans*-$[RuLX_2]$ (X = Cl or Br) following a reversible electron-transfer process at the h.m.d.e. were determined by the method of Nicholson and Shain.[20,21] For a given cyclic



SCHEME

voltammogram, the ratio of the observed anodic to cathodic peak currents for the first set of peaks, $(i_{ap})_{obs.} : (i_{cp})_{obs.}$ (corrected for residual currents [22]), was converted into the theoretical ratio $(i_{ap}) : (i_{cp})$, with the appropriate theoretical base lines according to the equation,[21] where $(i_{sp})_{obs.}$ represents the observed switching potential current. The

$$\frac{(i_{ap})}{(i_{cp})} = \frac{(i_{ap})_{obs.}}{(i_{cp})_{obs.}} + \frac{0.485(i_{sp})_{obs.}}{(i_{cp})_{obs.}} + 0.086$$

$(i_{ap}) : (i_{cp})$ ratio was then related to the parameter, $k_1\tau$, where τ is the elapsed time from the corresponding polarographic half-wave potential $E_{\frac{1}{2}}$ ($E_{\frac{1}{2}} = 0.851\,7\ E_{cp}$ [21]) to the switching potential E_{sp}. Since τ can be calculated for each scan rate, the observed first-order rate constant k_1 can be determined. For a reproducible and accurate determination, the scan rate should be chosen such that the $(i_{ap}) : (i_{cp})$ ratio lies between 0.6 and 0.9 : 1. The rate constants so determined suffer a normal uncertainty of *ca.* 15—20%. Reactions were repeated as many times, and over as many possible scan rates, as required (usually 8 to 10 runs), at a single temperature in order to obtain a more reliable average value. These rate constants, being independent of scan rate, complex concentration, acid concentration (0.01—0.10 mol dm^{-3}), and ionic strength (0.10—0.20 mol dm^{-3}), are collected in Table 2. Activation parameters were obtained by the least-squares method from the Eyring plot of ln (k_1/T) against $1/T$ where T represents the temperature on the absolute scale. The aquation of *trans*-$[Ru(NH_3)_4Cl_2]$ has been studied independently at 25.0 °C by Elson *et al.*[5] and Ford and co-workers [7] but a large discrepancy exists. We have now followed the aquation of this complex in greater detail and over a range of temper-

TABLE 1

Formal reduction potentials E_f of some tetramineruthenium couples in aqueous solution [a]

Redox couples	E_f / mV *vs.* s.h.e.
trans-$[Ru(NH_3)_4Cl_2]^{+,0}$	−164, −180,[b] −166,[c] −160 [d]
trans-$[Ru(en)_2Cl_2]^{+,0}$	−188
trans-$[Ru(RS\text{-}2,3,2\text{-}tet)Cl_2]^{+,0}$	−168
trans-$[Ru(cyclam)Cl_2]^{+,0}$	−144
trans-$[Ru(en)_2Br_2]^{+,0}$	−162
trans-$[Ru(RS\text{-}2,3,2\text{-}tet)Br_2]^{+,0}$	−124
trans-$[Ru(en)_2(NCS)_2]^{+,0}$	+122 [e]
trans-$[Ru(NH_3)_4Cl(OH_2)]^{2+,+}$	−70, −50 [c,d]
trans-$[Ru(en)_2Cl(OH_2)]^{2+,+}$	−66
trans-$[Ru(RS\text{-}2,3,2\text{-}tet)Cl(OH_2)]^{2+,+}$	−27
trans-$[Ru(cyclam)Cl(OH_2)]^{2+,+}$	−19
trans-$[Ru(en)_2Br(OH_2)]^{2+,+}$	−53
trans-$[Ru(RS\text{-}2,3,2\text{-}tet)Br(OH_2)]^{2+,+}$	−23
trans-$[Ru(NH_3)_4(OH_2)_2]^{3+,2+}$	+46, +20,[b] +40,[c] +80 [f]
trans-$[Ru(en)_2(OH_2)_2]^{3+,2+}$	+92
trans-$[Ru(RS\text{-}2,3,2\text{-}tet)(OH_2)_2]^{3+,2+}$	+117
trans-$[Ru(cyclam)(OH_2)_2]^{3+,2+}$	+145
cis-$[Ru(NH_3)_4Cl_2]^{+,0}$	−100,[b] −82,[c] −110 [d]
cis-$[Ru(en)_2Cl_2]^{+,0}$	−90
cis-$[Ru(NH_3)_4Cl(OH_2)]^{2+,+}$	+30,[c] 0 [d]
cis-$[Ru(en)_2Cl(OH_2)]^{2+,+}$	+151
cis-$[Ru(NH_3)_4(OH_2)_2]^{3+,2+}$	+100 [b,c,f]

[a] By c.v. technique, unless otherwise specified, using a h.m.d.e. at 25 °C. Supporting electrolytes: 0.01 mol dm^{-3} Hpts + 0.19 mol dm^{-3} K[pts]. E_f values of diaqua-complexes were obtained on solutions after a complete one-electron controlled-potential coulometric electrolysis. Values are accurate to ±10 mV and each entry represents an average of 6 to 8 measurements. s.h.e. = standard hydrogen electrode. [b] Ref. 8 in 0.2 mol dm^{-3} $Na[O_2CCF_3]$ using a h.m.d.e. [c] Ref. 5, in 0.3 mol dm^{-3} $Na[O_3SMe]$ adjusted to pH 2.0 using a h.m.d.e. [d] Ref. 7, in 0.1 mol dm^{-3} Hpts and 0.1 mol dm^{-3} K[pts]. Electrode not specified; either a platinum-ball electrode or a dropping mercury electrode (d.m.e.). [e] C. M. Che, unpublished work. [f] Ref. 6, in 0.1 mol dm^{-3} HBF_4 using a platinum button electrode.

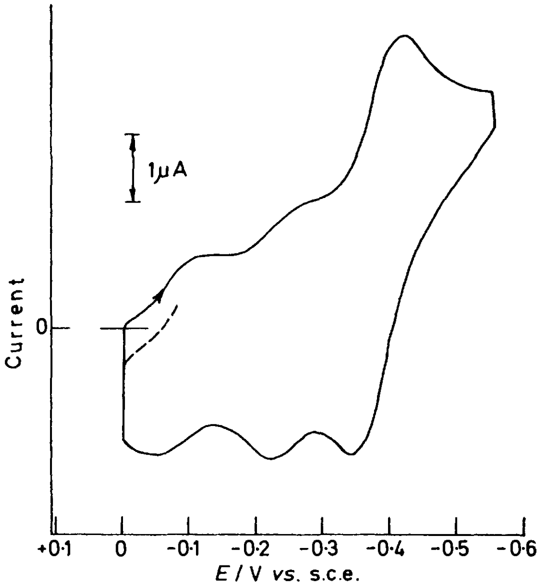


FIGURE 2 Cyclic voltammogram of *trans*-$[Ru(cyclam)Cl_2]^+$ in 0.10 mol dm^{-3} Hpts and 0.10 mol dm^{-3} K[pts] showing the presence of three sets of redox couples (see text)

TABLE 2

First-order aquation rate constants k_1 of some ruthenium(II) complexes of the type *trans*-$[RuLX_2]$ in aqueous solution at pH = 2 (Hpts) and I = 0.2 mol dm^{-3} (K[pts])

L	X	θ_C/°C	k_1/s^{-1}
$(NH_3)_4$	Cl	13.3	0.30 ± 0.060
		18.3	0.47 ± 0.060
		24.3	0.97 ± 0.065
		28.5	1.5 ± 0.10
		32.8	2.05 ± 0.20
$(en)_2$	Cl	15.1	0.12 ± 0.20
		20.2	0.22 ± 0.040
		25.0	0.34 ± 0.060
		30.0	0.57 ± 0.10
		40.0	1.5 ± 0.15
RS-2,3,2-tet	Cl	15.4	0.022 ± 0.004
		24.6	0.063 ± 0.010
		25.3	0.072 ± 0.012
		30.2	0.11 ± 0.014
		34.7	0.18 ± 0.030
		39.6	0.32 ± 0.060
		49.8	0.80 ± 0.15
cyclam	Cl	15.1	0.0079 ± 0.0014
		20.3	0.014 ± 0.0020
		25.1	0.021 ± 0.0030
		30.0	0.040 ± 0.0050
		35.1	0.071 ± 0.014
		45.0	0.17 ± 0.025
		49.7	0.29 ± 0.040
$(en)_2$	Br	14.6	0.14 ± 0.030
		24.2	0.42 ± 0.080
		29.2	0.72 ± 0.13
		34.1	1.1 ± 0.15
RS-2,3,2-tet	Br	21.3	0.069 ± 0.013
		25.1	0.084 ± 0.014
		29.6	0.15 ± 0.018
		34.3	0.23 ± 0.040
		39.1	0.37 ± 0.040

ature. Our result agrees well with that of Ford (Table 3). All these rate constants, extrapolated to 25.0 °C, and activation parameters are collected in Tables 1 and 3.

DISCUSSION

In general, several trends of behaviour are apparent for the data in Tables 1 and 3. Thermodynamically, E_f values increase with increased chelation. This effect is more prominent for the diaqua- and aquahalogeno-series while the variation in the dihalogeno-series is only marginal. E_f values of *cis* couples are greater than those of the *trans* counterparts. They also vary with the nature of the monoaniono-ligands: chloro- < bromo- < isothiocyanato-couples; and dihalogeno- < aquahalogeno- < diaqua-couples. Kinetically, the aquation of these ruthenium(II) complexes *cis*- or *trans*-[$RuLX_2$] (X = Cl or Br) are stereoretentive with negative entropies of activation. *cis* Complexes are more reactive than their *trans* isomers and the reactivities of *trans* complexes, in general, decrease with increased chelation. Finally, all these ruthenium(II) complexes are much more reactive than the corresponding ruthenium(III) and cobalt(III) analogues.

TABLE 3

Some first-order aquation rate constants, k_M/s^{-1}, at 25.0 °C and activation parameters for the aquation of some complexes of the type *cis*- and *trans*-[MLX_2]$^+$ [a]

L	X	Configuration	$k_{Ru(II)}$/s^{-1}	$\Delta H_{Ru(II)}^{\ddagger}$/kJ mol^{-1}	$\Delta S_{Ru(II)}^{\ddagger}$/J K^{-1} mol^{-1}	$k_{Ru(III)}$/s^{-1}	$k_{Co(III)}$/s^{-1}
$(NH_3)_4$	Cl	*trans*	1.0 9×10^{-1} [d] 4.4 [e]	72.1 ± 2.9	-3 ± 10	1.7×10^{-6} [b]	1.8×10^{-3} [c]
$(en)_2$	Cl	*trans*	3.5×10^{-1}	73.0 ± 1.5	-9 ± 4	4.2×10^{-6} [b]	3.5×10^{-5} [f]
RS-2,3,2-tet	Cl	*trans*	6.6×10^{-2}	78.6 ± 1.5	-4 ± 4	4.8×10^{-7} [b]	1.5×10^{-5} [g]
cyclam	Cl	*trans*	2.3×10^{-2}	78.1 ± 1.8	-14 ± 6	very slow [h]	1.1×10^{-6} [i]
$(en)_2$	Br	*trans*	4.4×10^{-1}	74.5 ± 4.0	-2 ± 10		1.4×10^{-4} [j]
RS-2,3,2-tet	Br	*trans*	9.4×10^{-2}	72.0 ± 4.5	-23 ± 15		
$(NH_3)_4$	Cl	*cis*	*ca.* 3.2×10 [d] *ca.* 7.3×10 [e]			8.8×10^{-5} [k]	fast [l]
$(en)_2$	Cl	*cis*	*ca.* 3.8×10			3.7×10^{-4} [k]	2.4×10^{-4} [f]

[a] This work unless otherwise indicated. [b] Ref. 11. [c] R. G. Linck, *Inorg. Chem.*, 1969, **8**, 1016. [d] Ref. 7. [e] Ref. 5. [f] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 1961, 4637. [g] R. Niththyanathan and M. L. Tobe, *Inorg. Chem.*, 1969, **8**, 1589. [h] 3×10^{-7} at 102 °C by isotopic chloride-exchange reaction; ref. 11. [i] C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1967, 2069. [j] F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 4883; S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 5700. [k] J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, 1968, **7**, 2519. [l] With respect to conventional methods of following the kinetics with a lower limit of *ca.* 10^{-1} s^{-1}; R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, 1955, **59**, 304.

In discussing the chemistry of ruthenium(II), especially in relation to that of ruthenium(III) complexes, much attention is drawn to the contrasting behaviour of the metal ion in these two different oxidation states with regard to metal–ligand π bonding.[2] In the present case, π-bonding effects cannot explain all the observations outlined above, and some other effects, such as solvation, nephelauxetic, and σ-*trans* effects, have to be evoked to account for the behaviour more satisfactorily.

Thermodynamically, the dependence of E_f on the nature of the monoaniono-ligands is in accordance with the π-bonding effect. The much higher E_f value for the isothiocyanato-couple might arise from the π-accepting capability [8] of the co-ordinated isothiocyanato-ligand which could preferentially stabilize the electron-rich ruthenium(II) centre, while π-donating halide ligands would relatively stabilize the electron-deficient ruthenium(III) complexes. The relative insensitivity of E_f towards the nature of the halide (Cl^- or Br^-) seems to indicate that π bonding may not play an important role in the overall metal–halide bonding for these complexes.[7] Switching to chelation effect, the variation of E_f with the nature of the tetramine ligands L cannot be due primarily to π-bonding effects since L cannot participate directly in the π-bonding system. It was suggested [23] that the major effect associated with increased chelation might be solvation. As chelation increases, the number of peripheral acidic hydrogens (amine hydrogens) gradually decreases with a corresponding increase in the size of the molecules, hence leading to less efficient solvation, more so for the higher charged ruthenium(III) than for the ruthenium(II) complexes. In other words, ruthenium(II) complexes are less destabilized relative to ruthenium(III) complexes with increased chelation. It was also pointed out that, for octahedral amine complexes, increased chelation was accompanied by an increased nephelauxetic effect [11,12,24,25] of the amine ligand. This leads to a greater expansion of the *d*-electron cloud away from the central metal ion, hence causing the metal ion to experience a greater demand for electrons and making it easier to be reduced. Both solvation and nephelauxetic effects work in the same direction but the relative importance of each individual effect is difficult to assess. As observed, both effects are expected to be more pronounced for the more highly charged aqua-series than for the corresponding halogeno-complexes. This, to some extent, is reminiscent of the increasing acidity of *trans*-[$CoL(OH_2)_2$]$^{3+}$ with increased chelation,[25] with the chelation effect on the first pK_a values being more prominent. Of course, the gradual increase in E_f values when anionic halide ligands (Cl^- or Br^-) are replaced by the neutral ligand H_2O could simply be due to electrostatic interactions between the metal ion and the ligands.[8] Anionic ligands would relatively stabilize ruthenium(III) while neutral ligands stabilize ruthenium(II). Naturally, it is reasonable to assume that all these effects work together co-operatively to affect the E_f values of these complexes. The reason for the greater E_f values for the *cis* isomers is not immediately clear. It might have been thought that *cis* complexes being much more effectively solvated than the *trans* isomers might have lower E_f values since the ruthenium(III) state would have been more susceptible to this effect than the ruthenium(II) state. So, neither solvation nor π-bonding effects are primarily responsible for the E_f values of *cis* isomers. The variation of nephelauxetic effect with stereochemistry has not been evaluated. However, it seems reasonable to assume that the *d*-electron cloud would diffuse away from the metal ion much more effectively in the *cis* complex, to the side opposite that of the two unidentate aniono-ligands, than in the *trans* isomer, where the two unidentate ligands occupy opposite sides.

The kinetic behaviour of the ruthenium(II) complexes, *trans*-[RuLX_2] (X = Cl or Br), with regard to chelation is very similar to that of the analogous series of cobalt(III) [24,26] and ruthenium(III) [11] complexes. A dissociative mechanism, which has been established [11,26,27] for the latter two systems, seems also to be operative in the ruthenium(II) system. For aquation of *trans*-[Co(en)$_2$A(X)]$^+$ (X = Cl or Br), it has been shown [27] that π labilization, from π-donating orienting ligands A, invariably leads to stereochemical change through the symmetry requirement that the π-donating ligands A must occupy an equatorial position in a trigonal-bipyramidal intermediate. In the present study, the absence of any stereochemical change suggests that trigonal bipyramidal intermediates with the remaining halide in the trigonal plane are not formed. In fact, the negative entropies of activation strongly indicate that these reactions proceed through square-pyramidal intermediates.[28] This implies that π labilization from a *trans*-π-donating halide is not the primary factor responsible for the reactivity of these complexes. Nevertheless, the kinetic behaviour can be explained in much the same way as the thermodynamic behaviour, in terms of combined solvation, nephelauxatic, and σ-*trans* effects. The kinetic lability of a complex depends on the free-energy difference between the ground and transition states. Therefore, a decrease in solvation, more so for the transition state which has one positive charge more than the ground state, would lead to a decrease in lability with increased chelation. As far as nephelauxetic effect is concerned, the increasing electronic demand of the central metal ion (through a greater expansion of the *d*-electron cloud with increased chelation) would reduce its tendency to expel a leaving halide (to gain a greater delocalization of the *d* electrons into the vacated orbital and thereby release the ground-state electronic repulsion in the transition state). Therefore, the reaction rate constants gradually decrease. Hence, both solvation and nephelauxetic effects work together to give rise to the observed kinetic chelation effect. It might be expected that the smaller and more highly charged cobalt(III) ion would be more susceptible to the chelation effect than the ruthenium(II) ion, both with a filled t_{2g}^6 configuration of an octahedral parentage. It is indeed observed (Table 3) that the chelation effect is more pronounced in the cobalt(III) system, as reflected by a much wider spread of the *k* ratio, cyclam : 2,3,2-tet : (en)$_2$: (NH$_3$)$_4$ = 1 : 14 : 32 : 1 600 for cobalt(III) and 1 : 3 : 15 : 39 for ruthenium(II). The enhanced kinetic lability of ruthenium(II) complexes over the corresponding ruthenium(III) and cobalt(III) complexes (*ca.* 10^5 and 10^3—10^4 times more labile respectively) cannot be accounted for by the charge effect alone. The loss of one positive charge from the central metal ion, in general, only accounts for a factor of *ca.* 10—10^2 in the increase in reactivity.[27] Recently, attention was drawn to the importance of the σ-*trans* effect of non-labile ligands on the kinetic lability of complexes.[11,12,29–32] Obviously, the relatively electron-rich ruthenium(II), which is known to be an electron donor, is much more effective at transmitting this electronic effect than the ' harder ' (*i.e.* less polarizable) cobalt(III), and even more so than the electron-deficient ruthenium(III) centres. The observation that *cis* complexes are more reactive than the *trans* isomers strongly supports this view. In the *cis* complexes, the leaving halide lies *trans* to an amine nitrogen while in the *trans* complexes the leaving halide is *trans* to another halide. Since nitrogen has a greater σ-*trans*-labilizing effect than halide, it is reasonable to expect *cis* complexes to be more reactive than their *trans* counterparts.

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