Proton Exchange and Base-catalysed Hydrolysis of some *trans*- and *cis*-Dichloro(1,4,8,11-tetra-azacyclotetradecane) Complexes of Chromium(III), Ruthenium(III), and Rhodium(III)

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The ratio of the rate constants for the solvolysis (k_2) and reprotonation (k_{-1}) of the amido-conjugate base of *trans*-[M{*RSSR*-cyclam}Cl$_2$]$^+$ (M = Cr, Ru, or Rh) and *cis*-[M{*RRRR*(*SSSS*)-cyclam}Cl$_2$]$^+$ (M = Cr or Rh) (cyclam = 1,4,8,11-tetra-azacyclotetradecane) have been estimated from the proton exchange (k_1) and base hydrolysis (k_{OH}) rate constants. All complexes are considerably less reactive towards base hydrolysis than the analogous Co^{III} species. The lower reactivity of Cr^{III} is due to a lowering of k_1 and k_2/k_{-1} by similar amounts, while that of Rh^{III} arises mainly from a large reduction of k_2/k_{-1} in the *cis* isomer. A similar reduction of k_2/k_1 coupled with a big decrease in k_1 accounts for the extremely low reactivity of the *trans* isomer. The considerable reduction in k_2/k_{-1} for the *trans* Ru^{III} complex is compensated by a large increase in k_1.

The enormous sensitivity of cobalt(III) amine complexes towards base-catalysed substitution processes stands in marked contrast to the much weaker effects observed with other reaction centres.[1,2] Only in the case of Ru^{III} is there a similar sensitivity,[3-6] but, in that system, it is often difficult to separate the single act of base-catalysed substitution from the other subsequent or parallel processes that lead to the complete destruction of the complex. The result is that Ru^{III} as a reaction centre has yet to be studied in depth.

The base-catalysed substitution process requires deprotonation of a suitably located amine group, either rapidly and reversibly or, in certain circumstances, rate limiting,[7-9] to give an amido-species that is substitutionally labile. It has been a matter of some interest to know which of these factors is responsible for the differences in the behaviour patterns of the various reaction centres. Early work[10] suggested that the high reactivity of Ru^{III} substrates arose from the high lability of the amine protons, whereas Cr^{III}, Co^{III}, and Rh^{III} complexes had similar proton lability and therefore it was thought that any explanation of the undue sensitivity of the Co^{III} complexes must relate to the way in which the metal interacted with the amido-group. Recent work,[11-13] however, suggests that the rate constants for proton exchange in amine(aniono)chromium(III) complexes can be very much less than those for analogous Co^{III} species and this can account for a significant part of the differences in the reactivity of the two systems with respect to base hydrolysis.

Another way in which Co^{III} and Cr^{III} on the one hand, and Ru^{III} and Rh^{III} on the other differ from one another has been the relationship between the labilizing power of the amido-group and its position with respect to the leaving group. In Co^{III} complexes the evidence suggests that the amido-group is much more labilizing when it is *cis* to the leaving group[2,14,15] and the Cr^{III} species seem to parallel Co^{III} in this respect, while Rh^{III} and Ru^{III} complexes without an amine group *trans* to the leaving group are far less sensitive to base catalysis than those with.[3,4,16-18]

Most of the systems available have many amine protons and major problems can arise in the identification of the sites of the labilizing amido-group. As part of our study of the relationship between proton transfer and base-catalysed hydrolysis we have chosen to examine complexes of the type *trans*- and *cis*-[M(cyclam)Cl$_2$]$^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane). Although there is still considerable scope for isomerism arising from the possible combinations of configuration of the nitrogen atoms,[19] the isomers studied have been characterized and the sites of the labilizing amido-groups identified. The results for M = Co^{III} have already been published[9] and those for M = Cr^{III}, Ru^{III}, and Rh^{III} are reported in this paper.

Experimental

Preparations and Reagents.—trans-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*chromium*(III) *Chloride.* Anhydrous CrCl$_3$ (0.25 g) was placed in the filter thimble of a Soxhlet extractor together with Zn/Hg amalgam (1 cm^3), and a solution of cyclam (0.37 g) in dry (molecular sieve) ethanol (70 cm^3) was added to the reservoir flask. The apparatus was flushed with dry oxygen-free nitrogen for 10 min before the ethanol was refluxed. The chromium chloride was extracted as a deep green solution and reacted immediately with the cyclam to produce a deep purple solution. When all the CrCl$_3$ had been extracted (after 1 h) the vessel was opened to the air and the pinkish-purple precipitate (0.15 g) filtered off. The deep purple filtrate was treated with a small amount of LiCl, allowed to stand at room temperature for 20 min, and a second crop of complex that formed was filtered off (0.087 g). Concentration of the filtrate and further treatment with LiCl yielded a third crop. The combined crops were extracted with methanol, leaving a white residue, the solution was evaporated to dryness and the solid recrystallized from hydrochloric acid (1 mol dm^{-3}). The needle crystals were filtered off, washed with acetone and diethyl ether, and dried (Found: C, 33.5; H, 6.75; N, 15.4. $C_{10}H_{24}Cl_3CrN_4$ requires C, 33.5; H, 6.75; N, 15.6%). The u.v.—visible spectrum agrees well with published values.[20]

The *perchlorate* was obtained by adding dilute perchloric acid to a filtered aqueous solution of the chloride. The crystals were filtered off, washed with perchloric acid (0.1 mol dm^{-3}), water, acetone and diethyl ether, and air dried. The compound was identical to that prepared by Poon and Pun[20] by a less convenient method.

trans-*Dichloro*{[$^2H_4$]-1,4,8,11-*tetra-azacyclotetradecane*}-*chromium*(III) *chloride*. *trans*-[Cr(cyclam)Cl$_2$]Cl was dissolved in the minimum amount of D_2O (99.8%) at room temperature and a solution of LiOD (prepared from the metal) in D_2O added until the solution was alkaline. The mixture was allowed to stand overnight and then acidified with concentrated hydrochloric acid. The deuteriated chloride precipitated slowly and was filtered off, washed with a small amount of cold ethanol, acetone and diethyl ether, and dried. The process was repeated until the i.r. spectrum indicated that the ν(N–H) peak at 3 240 cm^{-1} was absent and replaced by a new peak [ν(N–D)] at 2 400 cm^{-1}.

The *perchlorate* was obtained from the chloride in the same manner as described above.

cis-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*chromium*(III) *chloride*. This complex was prepared by the method of Ferguson and Tobe[21] (Found: C, 33.3; H, 6.80; N, 15.6. $C_{10}H_{24}Cl_3CrN_4$ requires C, 33.5; H, 6.75; N, 15.6%).

The *perchlorate* was prepared by adding dilute perchloric acid to a concentrated aqueous solution of the chloride, freezing the solution in a solid CO_2–acetone bath and allowing it to melt slowly. The crystals were filtered off, washed with ice-cold perchloric acid (0.3 mol dm^{-3}), methanol and diethyl ether, and air dried.

cis-*Dichloro*{[$^2H_4$]-1,4,8,11-*tetra-azacyclotetradecane*}-*chromium*(III) *chloride*. *cis*-[Cr(cyclam)Cl_2]Cl was dissolved in the minimum amount of D_2O (99.8%) and the solution evaporated to dryness on a steam-bath. The process was repeated three times, the extent of deuteriation being monitored by the i.r. spectrum (Found: C, 32.5; N, 15.1. $C_{10}H_{20}Cl_3CrD_4N_4$ requires C, 33.1; N, 15.4%).

The *perchlorate* was prepared as above.

trans-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*rhodium*-(III) *chloride*. This complex was prepared by the method of Bounsall and Koprich[22] (Found: C, 29.3; H, 5.6; N, 13.6. $C_{10}H_{24}Cl_3N_4Rh$ requires C, 29.3; H, 5.9; N, 13.7%).

The insoluble *perchlorate* was obtained by adding dilute perchloric acid to a solution of the chloride.

cis-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*rhodium*(III) *chloride*. This complex was prepared by the method of Bounsall and Koprich[22] (Found: C, 29.3; H, 5.6; N, 13.6. $C_{10}H_{24}Cl_3N_4Rh$ requires C, 29.3; H, 5.9; N, 13.7%).

The *perchlorate* was prepared as above.

trans-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*ruthenium*-(III) *chloride*. This complex was prepared by the method of Poon and Che.[23] However, it was found that, after two recrystallizations, the colour was yellow and not pale brown as reported (Found: C, 29.5; H, 5.85; N, 13.9. $C_{10}H_{24}Cl_3N_4Ru$ requires C, 29.4; H, 5.95; N, 13.5%).

The *perchlorate* was prepared as above.

cis-*Dichloro*(1,4,8,11-*tetra-azacyclotetradecane*)*ruthenium*(III) *chloride*. This complex was prepared by the method of Poon and Che[24] (Found: C, 29.6; H, 5.95; N, 13.75. $C_{10}H_{24}Cl_3N_4Ru$ requires C, 29.4; H, 5.95; N, 13.75%).

Kinetics.—(a) *Base hydrolysis*. The reactions were followed spectrophotometrically using a Pye-Unicam 1750 or a Perkin-Elmer 554 spectrophotometer with the reaction cell thermostatted by circulating water in the first case and electrically (making use of the Peltier effect) in the second. Temperatures were kept within ±0.1 °C and measured with a platinum resistance thermometer placed within the cell housing. After preliminary spectral scanning experiments to characterize the reaction and identify the most suitable wavelengths, the progress of the reaction was determined from the plot of absorbance against time. All reagents, except the complex, were brought to the reaction temperature in the thermostatted cell compartment and the reaction was initiated by adding a small known amount of the finely powdered complex which dissolved rapidly. Rate constants were determined from the slopes of the plots of ln $|A_t - A_\infty|$ against time, t, (A_t and A_∞ being the absorbances at time t and at the end of the reaction respectively).

(b) *Proton exchange: diamagnetic complexes*. These reactions were followed by ^{1}H n.m.r. using a Varian XL 200 spectrometer. Solutions of the complex in D_2O in the presence of a deuteriated buffer were kept at the reaction temperature in the n.m.r. tube and the spectrum was measured at appropriate times. The areas under the amine proton peaks were integrated and compared to areas under the appropriate non-exchanging methine proton peaks.

(c) *Proton exchange: paramagnetic complexes*. These reactions were followed by i.r. spectroscopy. The method developed by Basolo *et al.*,[25] who monitored the change in the absorbance of the peak at 1.65 µm, assigned to an HOD stretching overtone, could not be used in this case because the concentration of complex required to get a strong enough signal was too large. Instead, a semi-quantitative method was developed in which the relative heights of the peaks assigned to ν(N–H) and ν(N–D) in the hexachlorobutadiene mull spectra were measured and calibrated against the spectra of the corresponding Co^{III} complexes whose isotopic composition was determined by ^{1}H n.m.r. The examination of the *trans* complex was straightforward. The four N–H protons in the Co^{III} complex are magnetically equivalent and the evidence strongly favours the assignment of the *trans-RSSR* configuration to this species. Hexachlorobutadiene mulls of *trans*-[M(cyclam)Cl_2]ClO_4 are very similar with a sharp peak at 3 225, 3 225, or 3 210 cm^{-1} assigned to ν(N–H) for M = Co^{III}, Cr^{III}, or Ru^{III} respectively, and another sharp peak at 2 395, 2 400, or 2 395 cm^{-1} assigned to ν(N–D). Partly exchanged samples showed both peaks. A series of partly exchanged Co^{III} complexes was prepared by precipitating the insoluble perchlorates from a slightly basic solution of *trans*-[Co(cyclam)Cl_2]Cl in D_2O (or the N-deuteriated complex in H_2O). The average number of protons attached to N, N_H, was determined from the ^{1}H n.m.r. spectrum of the perchlorate in [$^2H_6$]dimethyl sulphoxide by comparing the area under the N–H peak at δ 6.40 with that under the 4 H methine multiplet within the range δ 1.6—2.2. From the i.r. spectrum of a hexachlorobutadiene mull of the same perchlorate sample the % transmission of the ν(N–H) peak (T_H), the baseline nearby (T_0), the ν(N–D) peak (T_D) and the baseline nearby (T'_0) were read off and the apparent fraction of complex in the protio-form, F_H, estimated using the relationship, $F_H = \log(T_0/T_H)/[\log(T_0/T_H) + \log(T'_0/T_D)]$. A number of different mulls of the same sample were prepared and, although the % transmission values varied considerably, the values of F_H were in good agreement. However, there is not a linear relationship between F_H and N_H for the same sample and so a calibration curve of N_H *versus* F_H was constructed. By assuming that the i.r. properties of the analogous Co^{III}, Cr^{III}, and Ru^{III} complexes were similar, the values of N_H corresponding to the value of F_H calculated from the i.r. spectrum of a sample of the exchanging perchlorate precipitated after time, t, were read off from the calibration curve. The rate constant for the exchange was obtained from the slope of the plot of $\ln(4 - N_H)$ [or $\ln(N_H)$ when starting from the protium complex in D_2O] against t.

The i.r. spectra of the *cis*-[M(cyclam)Cl_2]ClO_4 mulls are very similar for M = Co and Cr and it is known that both have the *RRRR*(*SSSS*) ligand configuration.[19,26] The two amine proton peaks in the ^{1}H n.m.r. spectrum of the perchlorate in [$^2H_6$]dimethyl sulphoxide have been assigned[9] for the Co^{III} complex and only those *trans* to Cl (δ 5.74) exchange. The i.r. spectra of hexachlorobutadiene mulls of the perchlorates have two peaks assigned to ν(N–H) at 3 145 and 3 205 cm^{-1} which are replaced by a pair of ν(N–D) peaks at 2 325 and 2 385 cm^{-1}. If the protium complex is partly deuteriated only the peak at 2 325 cm^{-1} appears and only the peak at 3 145 cm^{-1} diminishes. In this way these two vibrations are identified with the N–H (N–D) stretch *trans* to Cl. The i.r. spectra of the Cr^{III} complex behave in a very similar way [peaks at 3 168 and 3 220 cm^{-1} for ν(N–H) and 2 340 and 2 400 cm^{-1} for ν(N–D); only those at 3 168 and 2 340 cm^{-1} changing]. The number of N–H present *trans* to Cl (N_H, maximum 2) was obtained from the ratio of the

Table 1. Rate constants for the base hydrolysis of *cis*- and *trans*-$[Cr(cyclam)Cl_2]^+$ in 0.01 mol dm^{-3} NaOH[a]

	trans[b,c]		*cis*[d,e]	
T/°C	$10^2k_{obs.}$/s^{-1}	k_{OH}/dm^3 mol^{-1} s^{-1}	$10^2k_{obs.}$/s^{-1}	10^2k_{OH}/dm^3 mol^{-1} s^{-1}
0.0			0.22	0.22
5.0			0.36	0.36
5.4	0.0814	0.0814		
10.0			0.76	0.76
10.4	0.20	0.20		
15.0			1.34	1.34
15.4	0.41	0.41		
20.0			2.8	2.8
20.4	1.11	1.11		
30.4	3.8	3.8		
	$\Delta H^\ddagger = 25.1 \pm 0.7$ kcal mol^{-1}		$\Delta H^\ddagger = 19.8 \pm 1.0$ kcal mol^{-1}	
	$\Delta S^\ddagger = 27 \pm 2.9$ cal K^{-1} mol^{-1}		$\Delta S^\ddagger = 11 \pm 4$ cal K^{-1} mol^{-1}	

[a] [complex] = 1×10^{-3} mol dm^{-3}. [b] Rate constant for uncatalysed aquation = *ca.* 2×10^{-8} s^{-1} at 25 °C.[30] [c] I = 0.01 mol dm^{-3}. [d] Rate constant for uncatalysed aquation = 2.5×10^{-5} s^{-1} at 25 °C.[30] [e] I = 0.1 mol dm^{-3} ($NaNO_3$).

area under the δ 5.74 peak and the δ 3.15—3.45 (4 H) multiplet peaks of the $[^2H_6]$dimethyl sulphoxide solution of the perchlorate and F_H was determined from the mull i.r. spectrum of the same sample in the way described above using the peaks at 3 145 and 2 325 cm^{-1}. The data for the Co^{III} complex were used to construct a calibration curve for the Cr^{III} complex, F_H being obtained from the peaks at 3 168 and 2 340 cm^{-1}, and the rate constant for the exchange was obtained from the slope of the plot of $\ln(2 - N_H)$ against time.

Buffers.—Borax ($Na_2B_4O_7{\cdot}10H_2O$) buffers (pH 8.23—9.23) could be used for the Cr^{III} complexes without interference and 2,4,6-trimethylpyridine (pH 7.2—8.8) was also used for short reaction times at 0 °C. Acetic acid—sodium acetate (pH 3.76—5.76), borax, and phenol–sodium phenoxide (pH 9.0—10.0) were used without interference for the Rh^{III} reactions and the acetic acid–sodium acetate buffer was used for Ru^{III}.

Buffers were prepared by dissolving the required base in water and adding the appropriate acid until the desired pH was approached. The buffer was then treated with the required amount of $NaNO_3$ and diluted to its final concentration. The pH was measured with a calibrated Radiometer PHM 26 meter using a glass electrode and a calomel reference electrode. The concentration of hydroxide was calculated using the relationship, $[OH^-] = 10^{(\log K_{H_2O}{}^{I,T} + pH)}$, where $K_{H_2O}{}^{I,T}$, the ionic product of water at ionic strength, I, and the temperature, T, of the buffer was obtained from literature values of the ionic product at zero ionic strength at the appropriate temperature[27] using the appropriate activity coefficients.[27] For the deuteriated buffers, the bases were dissolved in D_2O and treated with standard DCl until the 'pH' reading had reached the desired value. Ionic strengths were adjusted as before and the pD of the reaction solution was obtained from the empirical relationship, pD = 'pH meter reading' + 0.400.[28] $[OD^-]$ was calculated as above using literature values for the ionic product of D_2O at zero ionic strength[29] and the activity coefficients for H_2O (it was assumed that the isotope effect would be small).

Results

Base Hydrolysis of cis- and trans-$[Cr(cyclam)Cl_2]^+$.—A study of the kinetics of the base hydrolysis has been made at 25 °C[30] and measurements have now been extended over a range of temperatures in order to obtain activation parameters. In 0.01 mol dm^{-3} NaOH the base hydrolysis was very much faster than the uncatalysed solvolysis reaction but still slow enough to be followed by classical spectrophotometry. The *trans* complex shows isosbestic points at 427, 436, and 545 nm while hydrolysis of the *cis* isomer is characterized by isosbestic points at 371, 440, 484, and 533 nm. These changes correspond to the stereospecific loss of one chloride and are not affected by the subsequent, much slower, loss of the second chlorine. The kinetics of the first step were followed by the change in absorbance at 492 nm for the *trans* isomer and 404 nm for the *cis*. These wavelengths are quite close to the isosbestic points for the second steps. First-order rate constants and the derived second-order rate constants are collected in Table 1.

Proton Exchange in the cis- and trans-$[Cr(cyclam)Cl_2]^+$ *Cations.*—The reactions were started by dissolving the desired amount of the fully N-deuteriated complex chloride in either sodium tetraborate (borax) buffer for the *trans* isomer or $2,6Me_2$-py–HNO_3 ($2,6Me_2$-py = 2,6-dimethylpyridine) buffer for the *cis* isomer, previously brought to the reaction temperature (0 °C). After the required time, the reaction was stopped by adding excess perchloric acid. The *trans*-$[Cr(cyclam)Cl_2]ClO_4$ precipitates immediately, while the *cis* isomer requires its solution to be frozen before it will crystallize out. There was no significant solvolysis during the exchange experiments. The extent of exchange was determined from the i.r. spectrum of a hexachlorobutadiene mull of the precipitated perchlorate. The four protons in the *trans* isomer are equivalent with respect to exchange while only two of the four amine protons in the *cis* isomer exchange within reasonable time. From a comparison of the i.r. spectra of the partially exchanged Co^{III} and Cr^{III} complexes it can be concluded that the rapidly exchanging protons are on nitrogens *trans* to Cl. No attempt was made to measure the rate of exchange of the less labile amine protons because a suitable calibration curve could not be constructed (the Co^{III} complex is fully solvolysed before any exchange of the protons in question can occur). The data and the derived rate constants are in Table 2.

Proton Exchange in cis- and trans-$[Rh(cyclam)Cl_2]^+$ *Cations.*—The ^1H n.m.r. spectrum of the chloride of the *trans* complex in D_2O is characterized by multiplets at δ 1.34—2.2 (4 H) assigned to the methine protons on the central carbons of the six membered rings, another set of multiplets in the region δ 2.4—3.4 (16 H) assigned to methine protons adjacent to N, and a broad peak at δ 5.46 (4 H) assigned to the four equivalent amine protons. The general form is similar to that of *trans*-$[Co(\textit{RSSR}\text{-cyclam})Cl_2]ClO_4$ in $[^2H_6]$dimethyl sulphoxide and

Table 2. Rate constants for proton exchange in complexes of the type $[M(cyclam)Cl_2]^+$

M	Cr	Cr	Rh	Rh	Rh	Ru
Configuration	*cis-RRRR(SSSS)*	*trans-RSSR*	*cis-RRRR(SSSS)*	*cis-RRRR(SSSS)*	*trans-RSSR*	*trans-RSSR*
Protons	*trans* to Cl	all	*trans* to Cl	*trans* to NH	all	all
Label*	$^2H_4$ in H_2O	$^2H_4$ in H_2O	$^1H_4$ in D_2O	$^1H_4$ in D_2O	$^1H_4$ in D_2O	$^1H_4$ in D_2O
Buffer	$2,6Me_2py$–HNO_3	boric acid–borax	CH_3CO_2D–$CH_3CO_2^-$	NaOH	C_6H_5OD–C_6H_5O–	CH_3CO_2D–CH_3CO_2–
pH	7.29	9.46	4.87 (pD)	—	10.38 (pD)	5.01 (pD)
T/°C	0.0	0.0	20.0	20.0	23.3	0.0
I/mol dm^{-3}	0.10	0.03	0.05	0.05	0.05	0.10
$10^{15}K_w$/mol dm^{-3}	1.86	1.56	1.35	—	1.05	0.231
$[OH^-]$ (or $[OD^-]$)/mol dm^{-3}	3.62×10^{-8}	4.5×10^{-6}	1.00×10^{-10}	3.0×10^{-4}	2.49×10^{-5}	2.36×10^{-11}
$k_{obs.}$/s^{-1}	$(3.9 \pm 0.4) \times 10^{-4}$	$(4.4 \pm 0.3) \times 10^{-5}$	$(9.6 \pm 0.7) \times 10^{-5}$	$(1.4 \pm 0.1) \times 10^{-3}$	$(1.6 \pm 3) \times 10^{-4}$	$(3.1 \pm 0.3) \times 10^{-4}$
k_1/dm^3 mol^{-1} s^{-1}	$(8.2 \pm 1.1) \times 10^3$	9.8 ± 0.8	$(9.6 \pm 0.7) \times 10^5$	4.5 ± 0.3	6.5 ± 1.3	$(1.3 \pm 0.1) \times 10^7$

* Isotopic form of amine H and solvent indicated.

a similar ligand configuration is indicated. Since solvolysis (catalyzed or otherwise) does not take place fast enough to interfere, proton exchange was studied *in situ* using the normal complex in deuteriated buffer (phenol–sodium phenoxide). The reaction was followed at 23 °C in the n.m.r. tube, spectra were measured from time to time and the amount of exchange determined from the decrease in the area under the amine proton peak. The results are collected in Table 2.

The ^1H n.m.r. spectrum of the chloride of the *cis* complex in D_2O at pD 4.87 remains unchanged long enough for it to be recorded and consists of multiplets between δ 1.58 and 2.26 (12 H) and between δ 2.92 and 3.38 (4 H). The amine protons appear as two broad peaks at δ 5.98 (2 H) and δ 6.20 (2 H). That at δ 5.98 is shifted in the presence of sufficient chloride. In 0.38 mol dm^{-3} DCl the two signals merge into a single peak, while in 1.9 mol dm^{-3} DCl there are two peaks at δ 6.16 and δ 6.36. In [$^2H_6$]dimethyl sulphoxide the perchlorate salt has two amine proton peaks at δ 6.16 and 6.52. These peaks appear at δ 6.52 and 7.62 when the chloride salt is studied and addition of extra LiCl shifts the 'mobile' peak further downfield to δ 8.1. This is very similar to the behaviour of the Co^{III} complex[9] and, as in that case, is ascribed to ion association. The chloride sensitive signal is assigned to the protons on the nitrogen *trans* to Cl and they must be in equivalent environments. Since the sensitivity to ion association is large and comparable to that observed in the Co^{III} case, these protons must be *anti* with respect to the adjacent Co–Cl bond {the big difference between *syn* and *anti* protons is discussed in connection with the *cis*-$[Co(cyclen)Cl_2]^+$ complex (cyclen = 1,4,7,10-tetra-azacyclododecane), which has one of each[31]}. The Rh^{III} complex must therefore have the same *RRRR(SSSS)* configuration as the Co^{III} species. Because the solvolytic lability is low it was possible to examine the exchange of these protons (δ 5.98) at pD 4.87 at 20 °C in CH_3CO_2D–$CH_3CO_2^-$ buffer and, in addition, examine the exchange of the much less labile protons (δ 6.20) in freshly prepared 0.000 30 mol dm^{-3} NaOD using the technique described for the *trans* isomer. The data are collected in Table 2.

Proton Exchange in trans-$[Ru(cyclam)Cl_2]^+$.—The *cis*- and *trans*-$[Ru(cyclam)Cl_2]^+$ complexes are only stable in reasonably strong acid solution and the *cis* isomer could not be studied because of the accompanying decomposition. For the same reason the *trans* isomer could not be fully deuteriated. Consequently, the reaction was followed by adding *trans*-$[Ru(cyclam)Cl_2]Cl$ to a buffered D_2O solution (CH_3CO_2D–$CH_3CO_2^-$, pD 5.01 at 0.0 °C), stopping the reaction by adding excess perchloric acid and measuring the amount of exchange in the recovered unreacted material using the method described for the analogous Cr^{III} complex. The data and rate constants are reported in Table 2.

Discussion

It is now generally accepted that the base catalysis of the substitution reactions of octahedral amine complexes arises from the generation of a substitutionally labile amido-complex by the removal, by hydroxide (or other base), of a suitably placed amine proton, *e.g.*,[2] equations (i)—(iii), where L_4 represents any combination of four donor atoms. This leads to the simple second-order rate law that is observed, *i.e.*, $-d[M(L_4)(HNR_2)X^{n+}]/dt = k_{OH}[M(L_4)(HNR_2)X^{n+}][OH^-]$, provided the intermediate species remain at very low concentration, with $k_{OH} = k_1k_2/(k_{-1} + k_2)$. Since the complexes used contain more than one set of n_i equivalent protons, the relationship is more completely expressed as $k_{OH} = \Sigma n_i k^i_1 k^i_2/(k^i_{-1} + k^i_2)$ although it is not necessary that every possible deprotonation pathway contributes to the act of base hydrolysis.

$$[M(L_4)(HNR_2)X]^{n+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M(L_4)(NR_2)X]^{(n-1)+} + H_2O \quad \text{(i)}$$

$$[M(L_4)(NR_2)X]^{(n-1)+} \xrightarrow{k_2} [M(L_4)(NR_2)]^{n+} + X^- \quad \text{(ii)}$$

$$[M(L_4)(NR_2)]^{n+} + H_2O \xrightarrow{\text{fast}} [M(L_4)(HNR_2)(OH)]^{n+} \quad \text{(iii)}$$

It has long been known that amine(aniono)cobalt(III) complexes are frequently much more labile towards base-catalysed hydrolysis than equivalent complexes of other transition metals, *e.g.*, Cr^{III}, Rh^{III}, Ir^{III}, and Pt^{IV}. Basolo and Pearson discuss this at length in their classic textbook[1] and recognise the importance of separating the contributions from the deprotonation of the substrate and those from the dissociation of the conjugate base. It was thought at the time that reprotonation of the conjugate base was diffusion controlled so that the deprotonation rate constant, k_1, could be used as a measure of the acidity. Discussion centred upon the base hydrolysis of $[M(NH_3)_5Cl]^{2+}$, where the reactivity sequence is M = Ru^{III} (13 000)[32] > Co^{III} (3 900)[33] > Cr^{III} (19)[34] > Rh^{III} (1).[35] [The values in parentheses are the rate constants relative to that for Rh^{III} = 1 at 25.0 °C and I = 0.0.] In this sequence, Co^{III} gives up its leading position to Ru^{III} but the Co^{III} penta-ammine complexes are unusually unreactive and the value of k_2/k_{-1} (= $k_{OH}/12k_1$) = 4×10^{-7} is unusually small. (It is assumed that the labilising amido-group will be *cis* to the leaving group,[14] hence $n = 12$.) The corresponding ratios for the other chloropenta-ammine complexes are not known.

The dichloro(tetra-amine) complexes present a different picture and the Co^{III} complexes are generally much more labile than the others and demonstrate a marked sensitivity to minor variations in the nature of the tetra-amine ligands. Such complexes frequently exist in *cis* and *trans* geometric forms and there is considerable scope for further isomerism arising from the various skeletal arrangements of the multidentate ligands as well as the chirality of the secondary nitrogens.

The choice of the $[M(cyclam)Cl_2]^+$ system allows the comparison of the base hydrolysis and proton exchange to be carried out with minimum ambiguity. Apart from the Co^{III} system, where the *trans-RRRR*(*SSSS*) isomer is also known,[36] all *trans* isomers have the *R*(*3*)*S*(*2*)*S*(*3*)*R* configuration (the numbers in parentheses being the number of carbon atoms linking the nitrogens whose chirality is indicated), and all the *cis* isomers have the *RRRR*(*SSSS*) configuration. The amine protons are all equivalent in the *trans* isomers and the site of deprotonation in the *cis* isomers (the nitrogens *trans* to Cl) is well established.

The Co^{III} system has already been reported[9] and it was found that, for the *trans* isomer, the ratio k_2/k_{-1} was < 1 below, and > 1 above, 3 °C. The *cis* complex was much more labile but this lability came from a 2×10^3-fold increase in k_1, the effect of which was reduced by a 20-fold reduction in k_2/k_{-1}. The dependence of k_1 upon the nature of the ligand *trans* to the exchanging proton is well known[37] and weak σ donors, such as Cl, are particularly effective. [A feature of the *cis*-dichloro(tetra-amine)cobalt(III) complexes is that one of the chlorides serves to increase k_1 for the protons on the nitrogen *trans* to itself which, on deprotonation, labilises the other, mutually *cis* chloride.]

In the Cr^{III} complexes, the reactivity is very much less (k_{OH} is some 5 to 6 orders of magnitude smaller than that for Co^{III}) but otherwise the pattern of behaviour is much the same. The observation, made many years ago, that k_1 for $[M(NH_3)_6]^{3+}$ and $[M(en)_3]^{3+}$ (en = $NH_2CH_2CH_2NH_2$) were virtually the same for M = Cr and Co[38] had led to the conclusion that the difference between Co^{III} and Cr^{III} must lie in the labilities of their amido-conjugate bases.

House and Nor[13] have already shown that, in *trans*-$[Cr(L_4)X_2]^+$ [L_4 = 3,2,3-tet (1,10-diamino-4,7-diazadecane), X = Cl or Br; L_4 = tet-a (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane), X = Cl] the values of k_1 are considerably smaller than those for the analogous Co^{III} complexes and that it is this decrease that makes the major contribution to the lowering of k_{OH}. For example, for L_4 = *RR*(*SS*)-3,2,3-tet, $k_1 = 1.0 \times 10^3$ dm³ mol⁻¹ s⁻¹ and $k_{OH} = 0.58$ dm³ mol⁻¹ s⁻¹ at 25 °C so that $k_2/k_{-1} = 0.58/(2 \times 1.0 \times 10^3) = 2.9 \times 10^{-4}$ (it is assumed that one of the two secondary amine protons is removed). The behaviour of the complex where L_4 = tet-a is even more extreme; $k_1 = 3.5 \times 10^2$ dm³ mol⁻¹ s⁻¹ and $k_{OH} = 145$ dm³ mol⁻¹ s⁻¹ at 25 °C so that $k_2/k_{-1} = 145/(4 \times 3.5 \times 10^2 + 145) = 0.094$. (No attempt has been made to apply any isotope effect correction to this calculation which, if it were the same as in a typical Co^{III} system, would halve this number.) Although the analogous Co^{III}–tet-a system has not been analysed in this way, it is unlikely that the ratio would be more than one to two orders of magnitude greater. The *trans-RSSR* cyclam case falls into this pattern and it also appears that the *cis-RRRR*(*SSSS*) isomer is not greatly different from the *trans* species. It is therefore necessary to account for the lower sensitivity of Cr^{III} complexes towards base-catalysed substitution by explaining the lower proton lability as well as finding a reason for the reduced labilising ability of the amido-group.

The relative *cis*- and *trans*-effects in the Co^{III} and Cr^{III} cases are remarkably similar. The value of k_2/k_{-1} for the *cis* complex divided by that for the *trans* complex for the $[M(cyclam)Cl_2]^+$ system is much the same for M = Cr^{III} ($1.4 \times 10^{-5}/3.8 \times 10^{-4} = 0.036$) and M = Co^{III} ($4.1 \times 10^{-2}/7.9 \times 10^{-1} = 0.052$).

It has long been known that Rh^{III} complexes are far less sensitive towards base hydrolysis than their Co^{III} analogues[39] and that the reactivity pattern also varies considerably. In the $[M(L_4)Cl_2]^+$ system, *cis* Rh^{III} isomers are some 5—6 orders of magnitude less reactive than their Co^{III} counterparts, while the effect is even more marked in the case of the *trans* isomers (11—12 orders of magnitude[2]). The enormous difference in isomer reactivity can be seen from the ratio $k_{OH}{}^{cis}/k_{OH}{}^{trans} = 2.2 \times 10^5$ (refs. 17, 39) and 1.3×10^6 (refs. 16, 18), respectively for M = Rh^{III} and L_4 = $(en)_2$ or cyclam.

In the *cis*-$[Rh(cyclam)Cl_2]^+$ isomer it is not possible to test which of the two sets of equivalent nitrogens provides the labilizing amido-group (or even how to apportion the reactivity between them) because both exchange their protons far faster than the complex undergoes base hydrolysis. If we assume that, as in the case of Co^{III}, it is the nitrogens that are *trans* to (and also *cis* to) Cl, it follows that the reactivity difference between the two metals resides in the difference in the ratio, k_2/k_{-1}, the values of k_1 for these protons differing by less than one order of magnitude. (If for some reason in Rh^{III} it was the other nitrogens that provided the labilization, the value calculated for k_2/k_{-1}, 4.7×10^{-3}, would be much closer to that for Co^{III} and the reactivity difference would lie in the change of k_1.) Although it is dangerous to assume that the nitrogen with the most labile protons will form the main pathway for the base hydrolysis,[40] there is, in this case, no reason to believe that it will not, but, until the Rh^{III} system has been examined in adequate detail, this must remain a plausible assumption.

Assuming, once again, that the labilization comes from the same nitrogens as in Co^{III}, the 10^6-fold reduction in reactivity on going from the *cis* to the *trans* isomer of the Rh^{III} complex is caused mainly by a 10^5-fold reduction in k_1. The ratio, k_2/k_{-1} is only reduced by one order of magnitude.

For the same reason that it is wrong to assume that proton-exchange lability (k_1) provides a measure of proton acidity (k_1/k_{-1}), it is equally wrong to assume that the ratio k_2/k_{-1} provides a measure of the lability of the conjugate base (k_2). Before such assumptions are made it would be necessary to reason that k_{-1} is insensitive to the changes in the nature of the substrate. It has not yet been possible to measure K_a for these systems and, until such time as this is done, this problem will remain. Nevertheless, it is known that the pK_a (water deprotonation) of the complex *trans*-$[Co(L_4)(A)(H_2O)]^{n+}$ is very sensitive to the nature of the *trans* ligand A,[41] and, to a first approximation, the variation follows the same *trans* effect sequence as proton exchange in $[Co(NH_3)_5A]^{n+}$,[37] *i.e.*, the stronger the influence of A, the less acid is the aqua group and the less labile is the *trans* ammine proton. If the aqua and ammine ligands can be equated in this way, it would be reasonable to assume that k_{-1} varies far less than k_1 and k_2 and so the ratio k_2/k_{-1} *can* be taken as a crude measure of the relative labilities of the conjugate bases. Consequently, it must be concluded that the big difference in the labilities of the *cis* and *trans* dichloro-complexes arises from the very large difference in the effect of NHR_2 and Cl upon the rate constant for the deprotonation of amine group *trans* to themselves. There is no need to invoke a change from *cis* labilisation from $-\ddot{N}R_2$ in Co^{III} to *trans* labilisation in Rh^{III} complexes.

The absence of information about the base hydrolysis of *cis*-$[Ru(cyclam)Cl_2]^+$ leaves this part of the study incomplete. The high reactivity of the *trans* complex is due to the great lability of the amine protons, which is sufficient to overcome a much smaller lability of the amido-conjugate base. Even in the s of k_2/k_{-1} for the base hydrolysis of $[\mathrm{M(cyclam)Cl_2}]^{+\,a}$

M	Configuration	Proton exchanging	T/°C	k_{OH}/ dm^3 mol^{-1} s^{-1}	k_1/ dm^3 mol^{-1} s^{-1}	k_2/k_{-1}
Co	*cis-RRRR(SSSS)*	*trans* to Cl	0.0	$4.5 \times 10^{5\,b}$	$5.8 \times 10^{6\,b}$	$4.1 \times 10^{-2\,b}$
Co	*trans-RSSR*	*cis* to Cl	0.0	$4.1 \times 10^{3\,b}$	$2.5 \times 10^{3\,b}$	$7.9 \times 10^{-1\,b}$
Cr	*cis-RRRR(SSSS)*	*trans* to Cl	0.0	2.2×10^{-1}	8.2×10^{3}	1.4×10^{-5}
Cr	*trans-RSSR*	*cis* to Cl	0.0	1.2×10^{-2}	9.8	3.8×10^{-4}
Rh	*cis-RRRR(SSSS)*	*trans* to Cl	23.0	$4.2 \times 10^{-2\,c}$	9.6×10^{5}	2.1×10^{-8}
Rh	*trans-RSSR*	*cis* to Cl	20.0	$3.8 \times 10^{-8\,d}$	6.5	1.5×10^{-9}
Ru	*trans-RSSR*	*cis* to Cl	0.0	2.3^{e}	1.3×10^{7}	4.3×10^{-8}

All k_{OH} values are determined in the absence of ^{2}H; all k_1 values are obtained by exchange of ^{1}H with ^{2}H. Except for the *trans* Co^{III} complex no attempt has been made to correct for isotopic effects. This would serve to decrease k_2/k_{-1} by a factor between 1.5 and 2.0. [b] Data from ref. 9. [c] Ref. 16. [d] Ref. 18. [e] Data from ref. 6 extrapolated to 0.0 °C.

absence of an exchange labilising chloride in the *trans* position, the rate constant for deprotonation, k_1 (1.3×10^7 dm^3 mol^{-1} s^{-1} at 0 °C) is within three orders of magnitude of that for a diffusion-controlled process. If the exchange labilising role of a *trans* chloride was also present in Ru^{III} complexes, the *cis* isomer might be expected to have a diffusion controlled k_1 and it is even possible that there is an alternative proton-transfer pathway in acid solution in which water itself acts as the base, *e.g.* equation (iv), giving $k_{obs.} = 2k'_1k_2/k'_{-1}[\mathrm{H_3O^+}]$ under conditions where

$$\begin{tikzcd} \textit{cis}\text{-}[\mathrm{Ru(cyclam)Cl_2}]^+ + \mathrm{H_2O} \arrow[r, shift left, "k'_1"] & \text{`conjugate base'} + \mathrm{H_3O^+} \arrow[l, shift left, "k'_{-1}"] \arrow[d, "k_2"] \\ & \text{products} \end{tikzcd} \qquad \text{(iv)}$$

$k'_{-1}[\mathrm{H_3O^+}] \gg k_2$. Since $k'_1/k'_{-1} = K_a$ and $k_1/k_{-1} = K_a/[\mathrm{H_3O^+}][\mathrm{OH^-}]$, $2k'_1/k'_{-1}[\mathrm{H_3O^+}] = 2k_1k_2[\mathrm{OH^-}]/k_{-1}$, *i.e.*, $k_{obs.}$ is the same whether the proton is abstracted by OH$^-$ or H_2O. This is, of course, a restatement of the principle of specific base catalysis. If, however, proton transfer was rate determining, general base catalysis would result and the kinetics would be affected. This has been elegantly demonstrated by Balt *et al.*,[42] but in the context of the reaction of *trans*-$[\mathrm{Co(NH_3)_4Cl_2}]^+$ in liquid ammonia. No attempt was made to see if the rate of proton exchange of *trans*-$[\mathrm{Ru(cyclam)Cl_2}]^+$ was pH dependent in the range studied. However, if the system is obeying the rules of specific base catalysis, the number recorded under k_2/k_{-1} in Table 3 represents the partition of the conjugate base between pathways leading to solvolysis and reprotonation irrespective of whether the base–acid system is $\mathrm{OD^-}$–$\mathrm{D_2O}$ or $\mathrm{D_2O}$–$\mathrm{D_3O^+}$. A much more detailed study of the Ru^{III} system is called for but it must await a significant improvement upon the techniques used in this study.

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