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Mechanism and Steric Course of Octahedral Aquation. XIII.[1] The Kinetics and Steric Course of the Acid and Base Hydrolysis of *cis*- and *trans*-Dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) Cations

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The acid hydrolysis of *cis*- and *trans*-Cr(cyclam)Cl_2^+ (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been studied as a function of temperature. For the *cis* isomer $k_{25°} = 2.5 \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 22.4 \pm 0.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -5 \pm 2$ cal deg^{-1} mol^{-1}. For the less reactive *trans* isomer, $k_{25°} = 2 \times 10^{-8}$ sec^{-1}, $\Delta H^{\ddagger} = 27 \pm 1$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -2 \pm 4$ cal deg^{-1} mol^{-1}. The base hydrolysis has been studied at or near 25° and a typical second-order rate law observed. The rates are very much less than those of the corresponding cobalt(III) complexes. The upper limits are set for the rates of aquation of *cis*- and *trans*-Cr(cyclam)(OH)Cl^+ and the rates of base hydrolysis are reported. All of the substitution reactions proceed with complete retention of configuration and there is no evidence for any displacement of the amine ligand.

Introduction

Until very recently, systematic studies of the effect of nonparticipating ligands upon the rates, activation parameters, and steric courses of the aquation of octahedral complexes of the transition elements were mainly confined to Werner-type complexes of cobalt(III). Data for analogous complexes of Rh(III), Ir(III), and Ru(III) are now starting to appear and for many years Garner[2] and his coworkers have been reporting upon the behavior of the Cr(III) analogs. In general, apart from the Co(III) complexes and certain of the Cr(III) complexes, substitution takes place with strict retention of configuration and it was of interest to us to concentrate upon those areas where stereochemical change was not uncommon. When this work was started, the amount of information on the aquation of Cr(III) complexes of the type $Cr(en)_2AX^{n+}$ was strictly limited (although recently Fee, *et al.*,[3] have prepared a wide range of such complexes) and there was evidence that, in some cases, the studies were complicated by loss of ethylenediamine from the complex.[4-6]

It seemed worthwhile, therefore, to examine the substitution reactions of the analogous Cr(III) complexes of the cyclic quadridentate secondary amine 1,4,8,11-tetraazacyclotetradecane (cyclam) since here the chances of displacing the amine ligand were considerably reduced. In addition, it was considered desirable to compare the behavior of analogous Cr(III) and Co(III) complexes, especially toward base hydrolysis.

Experimental Section

The preparation and analysis of the compounds used in this study are described elsewhere.[7] Other chemicals were reagent grade materials.

Kinetics.—Solutions, generally 10^{-2} *M* (for titrimetric runs) and (2–5) $\times 10^{-3}$ *M* (for spectrophotometric runs) were prepared by dissolving a weighed amount of complex in dilute nitric acid in a volumetric flask. The reaction mixture was placed in a thermostat, and once thermal equilibrium was reached, samples (5.00 or 10.00 ml) were withdrawn and rapidly cooled. For titrimetric measurements they were then passed down a 2-in. column of strong cation-exchange resin in the acid form and the chloride in the effluent and washings was determined potentiometrically with silver nitrate. The spectrophotometric measurements were made on similar aliquots using a Unicam SP 800 recording spectrophotometer. Usually the wavelength range 700–350 nm was scanned. The thermostat baths contained water dyed with Nigrosine black to avoid photocatalytic effects and the temperature of the reaction was controlled to ±0.05°. Because of the small amount of material available the spectrophotometric kinetics of *trans*-Cr(cyclam)Cl_2^+ were followed *in situ* in the spectrophotometer cell. Here 10.00 ml of 0.01 *M* HNO_3 previously brought to the reaction temperature was added by pipet to a weighed amount of complex in the silica cell. This was shaken and replaced in the spectrophotometer in an electrically heated housing which held the temperature to ±0.2°.

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[1] Part XII: R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).

[2] The relevant papers are referenced individually in the course of the discussion.

[3] W. W. Fee, personal communication, 1969.

[4] Hunt, *et al.*,[5] did not report any serious complication due to loss of NH_3 in the aquation of *trans*-Cr$(NH_3)_4Cl_2^+$ and recent work in these laboratories[6] suggests that the loss of ethylenediamine from *trans*-Cr(en)$_2Cl_2^+$ is less serious than was previously believed.

[5] D. W. Hoppenjans, J. B. Hunt, and C. R. Gregoire, *Inorg. Chem.*, **7**, 2506 (1968).

[6] E. Campi and M. L. Tobe, to be submitted for publication.

[7] J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, **4**, 109 (1970).

The temperature was measured by inserting a thermometer at the end of the reaction.

The base hydrolysis was studied in two ways. (i) The reactions in buffer solution were followed by allowing a known volume (8–9 ml) of an aqueous solution of the complex and potassium nitrate at the appropriate concentrations to reach thermal equilibrium in the spectrophotometric cell and the reaction was started by adding a known volume (1–2 ml) of the buffer (NaOH–H_3BO_3) solution, previously warmed to the same temperature, by means of a syringe. The solution was thoroughly stirred by a small platinum foil stirrer which was fitted through the stopper of the cell and which could be withdrawn from the light path when measurements were made. Optical densities were recorded as a function of time at a single wavelength. The pH was measured at the end of the reaction. The reaction mixture was thermostated by water circulating through the cell holder and the temperatures recorded are those measured by inserting a thermometer in the reaction mixture (±0.1°).

(ii) The reactions at higher pH were carried out in a standard fast-mixing and sampling apparatus immersed in a water thermostat. The reaction was stopped by pouring the sample into an excess of dilute nitric acid, and after adjusting the total volume to a known amount, the spectrum of the "killed" solution was measured.

Results

(1) Acid Hydrolysis of *cis*-[Cr(cyclam)Cl$_2$]Cl.—

The spectrum of a solution of *cis*-[Cr(cyclam)Cl$_2$]Cl in 0.01 M HNO_3 changes with time in a way that is consistent with a two-stage reaction, the second, characterized by isosbestic points at 497, 428, and 375 nm, being some 10 times slower than the first (with isosbestic points at 520, 444, and 389 nm). The spectrum of pure *cis*-$Cr(cyclam)(H_2O)_2^{3+}$ passed through all the isosbestic points of the second stage and addition of sodium chloride in 10–100-fold molar excess leads to an anation represented by a series of spectra also passing through these points. Independent titrimetric determination of the amount of chloride released in the course of the aquation also confirms the conclusion that these two stages represent the stepwise aquation of the complex

$$cis\text{-}Cr(cyclam)Cl_2^+ + H_2O \xrightarrow{k_1} cis\text{-}Cr(cyclam)(H_2O)Cl^{2+} + Cl^-$$

$$cis\text{-}Cr(cyclam)(H_2O)Cl^{2+} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} cis\text{-}Cr(cyclam)(H_2O)_2^{3+} + Cl^-$$

The kinetics of the first reaction were followed by the change in optical density at 497 nm, where the second reaction does not interfere, and the first-order rate constants were determined from the slope of the plot of log $(D_t - D_\infty)$ against time (D_t and D_∞ are the optical densities at time t and at the isosbestic point). Direct titrimetric determination gave rate constants in agreement with those obtained spectrophotometrically. The rate constants are collected in Table I.

(2) Acid Hydrolysis of *trans*-[Cr(cyclam)Cl$_2$]Cl.—

A spectrophotometric study of the reactions of an acid solution of *trans*-[Cr(cyclam)Cl$_2$]Cl suggests that the reaction is more complicated than a simple aquation. The isosbestic points at 547 and 442 nm which characterize the conversion of *trans*-$Cr(cyclam)Cl_2^+$ to *trans*-$Cr(cyclam)(H_2O)Cl^{2+}$ are observed for the first part of the reaction but at later stages there is a general increase in absorbance. The first change is closely paralleled by the release of one chloride but the second does not correspond to the solvolysis of the other chloride, nor does it represent any *trans* ⇄ *cis* isomerization.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF *cis*- AND *trans*-$Cr(cyclam)Cl_2^+$ IN DILUTE NITRIC ACID SOLUTION

cis complex			*trans* complex		
Temp, °C	[H$^+$], M	10^4k_1, sec^{-1}	Temp, °C	[H$^+$], M	10^4k_1, sec^{-1}
35.0	0.010	0.63	72.5	0.010	0.16
35.0	0.010	0.66[a]	75.0	0.010	0.19
50.0	0.010	3.4	80.0	0.010	0.40
55.0	0.010	6.8	84.9	0.010	0.77
65.0	0.010	18.0	88.2	0.010	0.85[a]
65.0	0.100	20.0	88.2	0.010	0.95
			90.5	0.010	0.89
			92.5	0.010	1.5

[a] Determined titrimetrically.

It apparently possesses a high activation energy and interference therefore is most serious at the highest temperatures. Thus, it was not possible to follow the aquation spectrophotometrically at temperatures above 93°, whereas at the lowest temperature used there was no significant interference until the first stage was essentially complete. The first-order rate constants for the aquation were determined by Guggenheim's method using data gathered in the period when the isosbestic points were observed. These constants are collected in Table I. The scatter of the data allows only approximate values for the activation parameters.

(3) The Base Hydrolysis of *cis*- and *trans*-[Cr(cyclam)Cl$_2$$^+$.—

The changes in spectra of basic solutions of the *cis*- or the *trans*-$Cr(cyclam)Cl_2^+$ complexes are consistent with two consecutive reactions, the first stage being characterized by isosbestic points at 538, 449, and 380 nm for the *cis* isomer and 552 nm for the *trans* isomer. The second stage showed isosbestic points at 410 nm for the *cis* isomer and 493 and 440 nm for the *trans* isomer and, in both cases, was considerably slower than the first. Although it has not been possible to isolate and characterize the intermediate *cis*- and *trans*-$Cr(cyclam)(OH)Cl^+$ cations (or their aquochloro conjugate acids), it can be demonstrated that all the base hydrolyses proceed with complete retention of configuration within the limits of experimental error. Thus, the acidified product of the complete base hydrolysis of the *cis*-dichloro complex has a spectrum identical in every respect with that of the independently prepared and characterized *cis*-$Cr(cyclam)(H_2O)_2^{3+}$ cation. The product of the base hydrolysis of *trans*-$Cr(cyclam)Cl_2^+$ has a spectrum that is completely different from that derived from the *cis* isomer and the extinction coefficient at 600 nm is so small (1.9 M^{-1} cm^{-1}) compared to that of the *cis* isomer (53.3 M^{-1} cm^{-1}) that no more than 4% of the latter can possibly be present. Such an observation at the end of the second-stage reaction can be accounted for only if the replacement of the first chlorine also takes place with retention of configuration. The first stage of the reaction was carried out under first-order conditions by using boric acid–borate buffers to maintain constant pH. The hydroxide concentration was varied by altering the buffer ratio and determined from the pH of the solution, measured at the end of the reaction, using the appropriate value for the ionic product of water. The slower second reaction stages were studied in the presence of excess sodium hydroxide. Ionic strength was held constant in each set of reactions. The kinetics were followed spectrophotometrically and the derived first-order rate constants, k_{obsd}, were independent of the wavelength used.

The values of k_{obsd} are reported in Table II. In all four reactions a plot of k_{obsd} against $[OH^-]$ is essentially linear at constant ionic strength. For the two *cis* substrates there is a finite intercept at $[OH^-] = 0$, so that $k_{obsd} = k_1 + k_{OH}[OH^-]$. k_1 corresponds to the rate constant for aquation in the absence of base and, in the case of *cis*-$Cr(cyclam)Cl_2^+$, k_1 (3×10^{-5} sec^{-1} at 26.3°, $\mu = 0.74$) corresponds closely to the value extrapolated from data measured at higher temperatures (2.5×10^{-5} sec^{-1} at 25°, $\mu = 0.01$). Values of k_{OH} ($= (k_{obsd} - k_1)/[OH^-]$) are also listed in Table II.

TABLE II

RATE CONSTANTS FOR THE BASE HYDROLYSIS OF SOME Cr(III) COMPLEXES

	Temp, °C	μ, M	$10^3[OH^-]$, M	10^4k_{obsd}, sec^{-1}	$(k - k_1)/[OH^-]$, M^{-1} sec^{-1}
cis-$Cr(cyclam)Cl_2^+$	26.3	0.74	0.033	3.0	8.2
	26.3	0.74	0.051	4.9	9.0
	26.3	0.74	0.078	7.0	8.6
trans-$Cr(cyclam)Cl_2^+$	26.3	0.10	0.065	1.0	1.5
	26.3	0.10	0.110	1.8	1.6
	26.3	0.10	0.162	2.7	1.7
cis-$Cr(cyclam)(OH)Cl^+$	20.7	0.36	69	14.7	0.021
	20.7	0.36	142	26	0.018
	20.7	0.36	214	41	0.019
	20.7	0.36	287	59	0.021
	20.7	0.36	360	70	0.019
	25.5	0.03	27	21	0.078
	25.5	0.055	54	37	0.068
	25.5	0.090	88	56	0.064
	25.5	0.18	178	82	0.046
	25.5	0.36	360	149	0.041
trans-$[Cr(cyclam)(OH)Cl]^+$	26.3	0.10	34	3.3	0.010
	26.3	0.10	54	6.4	0.012
	26.3	0.10	74	8.3	0.011
	26.3	0.10	94	11.2	0.012

Discussion

Comparisons of the rates, steric courses, and activation parameters for aquation and base hydrolysis of analogous complexes of Co(III) and Cr(III) have been made on a number of occasions in the past.[8-11] The general conclusion has been that, in the acid hydrolysis reactions, provided the M–N bond remained intact, there was a considerable similarity between the rates of reactions of analogous Co(III) and Cr(III) complexes. On the other hand, the Co(III) complexes were very much more sensitive to base hydrolysis than those of Cr(III). Tables III and IV are further compilations of data,[12-23] including now the data with the cyclic tetramine ligand cyclam which indicate quite clearly that the simple correlation certainly does not hold in all cases. For example, the relatively small difference (factor of 7) between the rate constants for the aquation of *cis*- and *trans*-$Co(en)_2Cl_2^+$ cations is comparable with the slightly large ratio (15) for the corresponding Cr(III) complexes. On changing from

TABLE III

A COMPARISON OF THE RATES AND ACTIVATION PARAMETERS FOR THE AQUATION OF DICHLORO- AND HYDROXOCHLOROAMINE COMPLEXES OF Co(III) AND Cr(III)

	$k_{25°}$, sec^{-1}	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	Ref
trans-$Co(NH_3)_4Cl_2^+$	2.0×10^{-3}	23.6	+8	12
trans-$Cr(NH_3)_4Cl_2^+$	4.5×10^{-5}	21.6	−6	5
trans-$Co(en)_2Cl_2^+$	3.5×10^{-5}	26.2	+14	13
trans-$Cr(en)_2Cl_2^+$	2.2×10^{-5}	22.7	−5	14
trans-$Co(cyclam)Cl_2^+$	1.1×10^{-6}	24.6	−3	15
trans-$Cr(cyclam)Cl_2^+$	$\sim 2 \times 10^{-8}$	27	−2	This work
cis-$Co(en)_2Cl_2^+$	2.4×10^{-4}	21.5	−5	16
cis-$Cr(en)_2Cl_2^+$	3.3×10^{-4}	20.5	−6	17
α-*cis*-$Co(trien)Cl_2^+$	1.5×10^{-4}	21.5	−6	18
α-*cis*-$Cr(trien)Cl_2^+$	1.9×10^{-4}	20.7	−6	11
cis-$Co(cyclam)Cl_2^+$	1.6×10^{-2}	18.3	−6	19
cis-$Cr(cyclam)Cl_2^+$,	2.5×10^{-5}	22.4	−5	This work
trans-$Co(en)_2(OH)Cl^+$	1.6×10^{-3}	25.9	+20	20
trans-$Cr(en)_2(OH)Cl^+$	4.6×10^{-3}	...	...	10
cis-$Co(en)_2(OH)Cl^+$	1.2×10^{-2}	23.0	+10	20
cis-$Cr(en)_2(OH)Cl^+$	3.3×10^{-3}	...	...	10
cis-$Cr(cyclam)(OH)Cl^+$	2.0×10^{-4}	...	...	This work

[a] The enthalpies of activation quoted are generally reliable to better than ±0.5 kcal/mol and the entropies of activation to better than ±1.5 cal deg^{-1} mol^{-1}.

TABLE IV

SECOND-ORDER RATE CONSTANTS FOR THE BASE HYDROLYSIS OF SOME DICHLORO- AND HYDROXOCHLOROAMINE COMPLEXES OF COBALT(III) AND CHROMIUM(III), IN AQUEOUS SOLUTION (VARIED IONIC STRENGTH) AT 25° (M^{-1} SEC^{-1})

	Cr	Co	Ref
trans-$M(cyclam)Cl_2^+$	1.3	67,000	This work, 21
trans-$M(en)_2Cl^+$	0.037	3,100	8, 22, 23
trans-$M(cyclam)(OH)Cl^+$	0.009	4.5	This work, 21
trans-$M(en)_2(OH)Cl^+$	0.3	0.56	10, 23
cis-$M(cyclam)Cl_2^+$	7.2	...	This work
cis-$M(en)_2Cl_2^+$	0.027	710	8, 22, 23
cis-$M(cyclam)(OH)Cl^+$	0.041	...	This work
cis-$M(en)_2(OH)Cl^+$	2.2	11.9	10, 23

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ethylenediamine to cyclam these factors change to 15,000 for Co(III) and 1000 for Cr(III). However the similarity of the rate constants for the aquation of the $Co(en)_2Cl_2^+$ cations hides the very marked differences between the enthalpies and entropies of activation, whereas the similarity of rate constants for the two analogous Cr(III) isomers is found in the activation parameters as well.

Insofar as the finer points of the mechanism are concerned, the aquation of *trans*-$Co(en)_2Cl_2^+$ (and the very similar *trans*-$Co(NH_3)_4Cl_2^+$) differs from that of the other complexes listed in Table III and we therefore should not expect these to conform in any pattern of similarities or differences. It has been suggested[24] that the high entropies of activation and the accompanying stereochemical change indicate a trigonal-bipyramidal intermediate for their dissociative reaction whereas the others generate a square-pyramidal, stereoretentive five-coordinate intermediate.[25] The effect of replacing ethylenediamine by cyclam leads to a marked increase (factor of 70) in the reactivity of the *cis*-dichlorocobalt(III) complex whereas in the Cr(III) case such a change reduces the rate by a factor of 13. All of these reactions have very similar entropies of activation.

The lack of the relevent data rules out a similar comparison for the hydroxochloro complexes. It is difficult to see the cause of these differences. Replacement of ethylenediamine by triethylenetetramine does not lead to such a difference in behavior in the α-*cis*-M(trien)Cl^{2+} cations[11,18] so that it cannot be an effect associated with secondary nitrogen atoms. It would only be possible to account for this behavior in terms of steric effects (*i.e.*, interligand repulsion and ring strain differences) if the configurations adopted in the macrocycle differ from cobalt(III) to chromium(III). Kuroya, *et al.*,[26] have shown that not only is *trans*-$[Cr(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ isomorphous with the corresponding Co(III) complex, but the M–Cl and M–N bond lengths for M = Co and M = Cr are equal within experimental error. Whether or not this is true for the *cis*-bisethylenediamine and the cyclam complexes will not be known until such time as full structural determinations are carried out.

In general, the behavior of the dichloro complexes toward base hydrolysis is as expected. The Cr(III) complexes are very much less sensitive than those of Co(III) and the greater reactivity of the cyclic amine complexes, compared to those with ethylenediamine, is found in all cases. For the $Co(en)_2(A)Cl^+$ series, the replacement of A = Cl by A = OH leads to a very marked reduction of rate (factors of 5500 and 60, respectively, for the *trans* and *cis* isomers). Much of the reduction is due to a decrease in the entropy of activation.[23] A similar decrease of reactivity is noted in both the Cr– and the Co–cyclam complexes although the *cis* Cr(III) complex is very much more affected than the *trans*. It is therefore rather puzzling to find that the *cis*-$Cr(en)_2(OH)Cl^+$ cation is some 10^2 times more reactive than the corresponding dichloro complex. Indeed, even though much has been made of the big reactivity difference between complexes of Co(III) and Cr(III) toward base hydrolysis, no one has commented on the fact that the rate constants for the *cis*-$M(en)_2(OH)Cl^+$ complexes (M = Co, Cr) are so similar.

Acknowledgment.—We wish to thank the Science Research Council for financial assistance.

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