liquid nitrogen. The flask was then connected to the chromatograph. The peaks obtained were compared with those on calibration chromatograms. The calibration chromatograms were run from a known pressure of oxygen (0.50 ± 0.02 cm) in a flow-through sample flask of known volume (85.9 cm^3).

Absorption spectra were taken on a Cary 14 spectrophotometer, Serial 244. Quartz absorption cells of 1- and 0.1-cm lengths were employed.

Acknowledgment.—The author is most grateful to Mr. Joseph H. Johnson for the analyses obtained with the mass spectrometer and vapor-phase chromatograph and to Dr. Carl A. Heller and Mrs. Helen R. Young for advice and assistance with the mass spectrometric work.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
REVELLE COLLEGE, UNIVERSITY OF CALIFORNIA, SAN DIEGO,
LA JOLLA, CALIFORNIA 92037

The Rate and Stereochemistry of the Aquation of *trans*-Dichlorotetraamminecobalt(III)

BY R. G. LINCK

Received October 16, 1968

Studies of the rate and stereochemistry of the spontaneous aquation of Co(III) complexes continue to be an area of active research. Recently it was argued that all aquations in complexes of the type $Co(en)_2ACl^{n+}$ proceed by an activation process that is principally bond breaking in nature.[1] A recent analysis by Tobe[2] has supported this point of view and has correlated the value of the entropy of activation with stereochemical change. This correlation was primarily for complexes of the type $Co(en)_2ACl^{n+}$, although complexes in which the two ethylenediamine groups were replaced by 1,4,8,11-tetraazacyclotetradecane, 1,4,7,10-tetraazadecane, or 1,4,8,11-tetraazaundecane also fit the correlation. There exist in the literature sufficient data[3–8] to apply the correlation to one complex in which four ammonias replace the two ethylenediamines—$Co(NH_3)_5Cl^{2+}$. Although this complex satisfactorily fits Tobe's correlation,[9] a second example would be more conclusive. In addition, an early paper[10] on the rate of the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ reported the absence of steric change in the first aquation step. Because this result would imply a significant difference between the behavior of the tetraammine and the corresponding bis-ethylenediamine complex,[11] a reinvestigation of the rate and stereochemistry of the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ was undertaken. In that investigation, reported herein, advantage is taken of the systematic variation of rate of reduction of Co(III) complexes by Fe(II) as the nonbridging ligands are varied[12] to analyze the composition of the solutions.

Experimental Section

The solutions of Co(III) complexes and the Fe(II) solutions used were the same as those previously described.[12] In experiments designed to determine the composition of a partially aquated solution of *trans*-$Co(NH_3)_4Cl_2^+$ it was important to remove as much Fe(III) from the ferrous ion solution as possible, for Fe(III) absorbs relatively strongly at the wavelength used. In order to remove the Fe(III), a degassed solution of ferrous perchlorate in perchloric acid was treated with amalgamated Zn until an aliquot showed very little absorption in the region of interest. The solution was then transferred to a vessel free of Zn under an atmosphere of N_2. The concentration of Zn^{2+} introduced into the solution by this process was negligible, because only a small fraction of the total Fe in the solution was initially Fe(III) and little H_2 evolution took place in the reduction step.

All kinetic runs were followed spectrophotometrically on a Cary Model 14 spectrophotometer equipped with a thermostated cell block.

Results and Discussion

Spectral Characteristics.—The aquation of *trans*-$Co(NH_3)_4Cl_2^+$ in 1.0 *N* $HClO_4$ is accompanied by a decrease in absorbance at 2530 Å, a wavelength where the molar extinction coefficient of *trans*-$Co(NH_3)_4Cl_2^+$ is 2.4×10^4 l. mol^{-1} cm^{-1}. However, at shorter wavelengths, the absorbance of the aquation products, *cis*- and *trans*-$Co(NH_3)_4H_2OCl^{2+}$ both absorb more strongly than does *trans*-$Co(NH_3)_4Cl_2^+$—the maximum for an equilibrium mixture of *cis*- and *trans*-$Co(NH_3)_4H_2OCl^{2+}$ is found at 2330 Å with ϵ 1.57×10^4 l. mol^{-1} cm^{-1}. The feature of these spectral characteristics that is of the most pertinence here is the observation that the absorbance near 2400 Å (depending on temperature) remains constant within ±1.0% during the time necessary to allow the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ to proceed for 10 half-lives. As will be shown below, this is a time during which there is a substantial change in the concentrations of both the *cis*- and *trans*-chloroaquo species. Therefore, within experimental error, the extinction coefficients of the three species are equal at 2400 Å (ϵ 1.40×10^4 l. mol^{-1} cm^{-1}).

The Aquation of *trans*-$Co(NH_3)_4Cl_2^+$.—This process can be studied easily at a number of wavelengths because of the spectral similarity of the *cis*- and *trans*-chloroaquo species. The change in absorbance is largest at 2530 Å, and hence this wavelength was chosen for most extensive study. That both the products absorb approximately equally at this wavelength is established from the quality of the first-order plots—these plots

---

(1) C. Bifano and R. G. Linck, *Inorg. Chem.*, **7**, 908 (1968).

(2) M. L. Tobe, *ibid.*, **7**, 1260 (1968).

(3) F. J. Garrick, *Trans. Faraday Soc.*, **33**, 386 (1937).

(4) B. Adell, *Z. Anorg. Allgem. Chem.*, **246**, 303 (1941).

(5) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

(6) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

(7) C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, **89**, 3141 (1967).

(8) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Australian J. Chem.*, **20**, 597 (1967).

(9) From the various sources,[3–7] a value of $\Delta H^{\ddagger} = 23.5 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6 \pm 3$ cal mol^{-1} deg^{-1} can be calculated. The fit of this negative $\Delta S^{\ddagger}$ to Tobe's correlation depends upon the assumption that the stereochemical consequences of the aquation of $Co(NH_3)_5Cl^{2+}$ are the same as those of $Co(NH_3)_5Br^{2+}$—see ref 8 for the experiments on the latter complex.

(10) R. Tsuchida, *Bull. Chem. Soc. Japan*, **11**, 721 (1936).

(11) M. E. Baldwin, S. C. Chan, and M. C. Tobe, *J. Chem. Soc.*, 4637 (1961).

(12) R. G. Linck, *Inorg. Chem.*, **7**, 2394 (1968).

TABLE I

THE RATE OF AQUATION OF *trans*-$Co(NH_3)_4Cl_2^+$

10^5[Co(III)], *M*	Temp, °C	I^a	n^b	10^3k_1, sec^{-1}
7.1–8.5	34.3	1.0	3	5.10 ± 0.02
7.1		0.10	1	7.00
7.1		0.010	1	7.16
1.1–7.9	25.0	1.0	7	1.48 ± 0.04
7.1		1.0^c	3	1.53 ± 0.05
7.1		0.50	1	1.81
7.1		0.25	1	1.91
5.3–9.7		0.05	4	2.10 ± 0.03
5.3		0.01	3	2.02 ± 0.03
7.1	15.8	1.0	8	0.437 ± 0.08
7.1		0.10	1	0.62
7.1		0.010	1	0.64
6.4	11.1	0.050	1	0.242
7.5		0.010	1	0.246
7.9	6.3	0.050	1	0.119
9.2		0.037	1	0.116
7.9		0.010	1	0.120

[a] Ionic strength, controlled by $HClO_4$. [b] Number of experiments. [c] These three experiments had $[H^+] = 0.074$, 0.381, and 0.670 *M;* Na^+ was used to control the ionic strength.

were linear for 4–5 half-lives. The rate of the aquation was investigated under a number of conditions and temperatures; the results of these investigations are presented in Table I. First, over the range of $[H^+]$ specified, the experiments at 25° demonstrate that there is no dependence of the rate on $[H^+]$. Second, from the data at 25°, there is an increase in rate as the ionic strength of the medium is decreased from 1.0, although the effect levels off after an ionic strength of about 0.1 is reached. The temperature dependence of the rate of aquation of *trans*-$Co(NH_3)_4Cl_2^+$ can be specified by the activation parameters: $\Delta H^{\ddagger} = 22.0 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2.7 \pm 2$ cal mol^{-1} deg^{-1} at unit ionic strength; $\Delta H^{\ddagger} = 23.6 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 8.6 \pm 2$ cal mol^{-1} deg^{-1} at low ionic strength.[13] The results at 25° are in satisfactory agreement with the previous report of Pearson, *et al.*,[6] but the agreement with Tsuchida[10] is less satisfying.

The Reaction of Fe(II) with an Equilibrated Solution of *cis*-$Co(NH_3)_4H_2OCl^{2+}$.—When the solid of analytical composition $[Co(NH_3)_4H_2OCl]SO_4 \cdot 0.5H_2O$ is dissolved in 1 *N* acid, there is no detectable change in spectrum with time in the ultraviolet region. Yet when this solution is treated with Fe(II) solution, there is, as previously established,[12] a rapid change in absorbance, followed by a slower change. The analytical data, the lack of ultraviolet spectral change upon solution, the demonstration of a term in the rate of reduction of *cis*-$Co(NH_3)_4H_2OCl^{2+}$ by Fe(II) that is interpretable as *cis* to *trans* isomerization,[12] and analogy with the bis-ethylenediamine system all argue that the two components are the *cis*- and *trans*-chloroaquo species. On the basis of the similarity of the visible absorption spectrum of the dissolved complex with *cis*-$Co(en)_2H_2OCl^{2+}$,[14] it is concluded that the dominant species in solution is *cis*-$Co(NH_3)_4H_2OCl^{2+}$. Hence the rapidly reduced component, which accounts for the smaller change in absorbance at 2400 Å, is *trans*-$Co(NH_3)_4H_2OCl^{2+}$. That fraction of the total absorbance change that results from the rapid reduction then gives a measure of the fraction of the solution that is the *trans* isomer.

In practice, because the difference in the rate of the two steps is large, the observation of the fraction of the total absorbance change due to the fast step was accomplished by a linear extrapolation[15] of the slow portion after the fast portion was 98% complete. The difference between this linear extrapolation and the observed curve at short times was plotted as log $(A_t - A_{\text{extrap}})$ *vs.* time. Extrapolation of this function to zero time gave the absorbance at zero time (including that due to Fe(II)); the value of the absorbance change due to the *cis* isomer was calculated by extrapolating the linear portion of the slow step to zero time and subtracting from this value the value of the absorbance at the completion of the slow step.

The result of the experiments to determine the fraction of *trans*-$Co(NH_3)_4H_2OCl^{2+}$ in an equilibrated solution[16] of the chloroaquo complexes is that 0.094 ± 0.010 of the total Co(III) is in the form of the *trans* complex. This value is based on 16 experiments at 15.8° in 1 *N* $HClO_4$. In addition, three experiments were performed to establish that the rapidly reacting fraction of the mixture was not a sensitive function of $[Cl^-]$. In experiments with $[Co(III)] \cong 6 \times 10^{-5}$ *M* and $[Cl^-] = 6.4 \times 10^{-4}$, 1.59×10^{-3}, and 3.12×10^{-3} *M*, the values for the rapidly reacting fraction were 0.102, 0.095, and 0.087, respectively. These results with chloride present establish that the rapidly reacting component of the mixture is not *trans*-$Co(NH_3)_4Cl_2^+$ in equilibrium with *cis*-$Co(NH_3)_4H_2OCl^{2+}$ and Cl^-, a result consistent with the different values of the rate constant for reduction reported previously.[12]

Several experiments at 25 and 11.1° indicated that the temperature dependence of the fraction of Co(III) in the form of *trans*-$Co(NH_3)_4H_2OCl^{2+}$ is small, a result in agreement with the earlier experiments on the $Co(en)_2H_2OCl^{2+}$ system.[11]

Determination of the Composition of a Solution of Partially Aquated *trans*-$Co(NH_3)_4Cl_2^+$.—These experiments were carried out essentially as those described above. At 2400 Å, the three components absorb equally, and hence a measure of the fraction of the solution that reacts slowly with Fe(II) gives a measure of the fraction of the solution in the *cis*-chloroaquo

---

(13) "Low ionic strength" refers to the region below about 0.05 *M* where k_1 becomes constant with a change in ionic strength (within experimental error).

(14) The two bands in the visible spectrum occur at 5310 Å (ϵ 52.5) and 3715 Å (ϵ 47) in an equilibrated solution of $[Co(NH_3)_4H_2OCl]SO_4 \cdot 0.5H_2O$ compared to 5185 and 3770 Å in *cis*-$Co(en)_2H_2OCl^{2+}$.[1] There is no evidence of a third band characteristic of the *trans*-chloroaquo configuration.[11]

(15) For typical values of the [Fe(II)], the percentage of the slow reaction that has taken place after the fast step is 95% complete is the order of 2%. This justifies the approximation of A_0e^{-kt} as equal to $A_0(1 - kt)$.

(16) During the time necessary to carry out this equilibration, aquation to $Co(NH_3)_4(H_2O)_2^{3+}$ was negligible: J. N. Brønsted, *Z. Physik. Chem.*, **122,** 383 (1926).

TABLE II

FRACTION OF Co(III) IN THE FORM OF *cis*- AND *trans*-$Co(NH_3)_4H_2OCl^{2+}$ AS A FUNCTION OF TIME AT 15.8° AND 1 *N* $HClO_4$

Time,[a] sec	Fraction of *cis*	Fraction of *trans*, β
201	0.06	0.02
218	0.06	0.03
405	0.10	0.06
440	0.12	0.06
595	0.14	0.19
848	0.22	0.09
865	0.17	0.14
990	0.23	0.12
1443	0.35	0.13
1752	0.34	0.20
1792	0.34	0.20
1970	0.40	0.18
2485	0.52	0.15
2793	0.52	0.18
2918	0.55	0.17
3402	0.55	0.22
3910	0.68	0.14
3986	0.71	0.12
4831	0.69	0.19
5705	0.84	0.07

[a] The time elapsed between the initiation of the aquation and the quenching of it by Fe(II).

form. Since the rate constant for the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ is known,[17] the fraction of the total Co(III) in this form can be calculated; by difference, then, the fraction of Co(III) in the form of *trans*-$Co(NH_3)_4H_2OCl^{2+}$ can be obtained. The results of these experiments are listed in Table II.

Stereochemistry of the Aquation of *trans*-$Co(NH_3)_4Cl_2^+$.—If it is assumed that the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ can be represented by the equations

$$trans\text{-}Co(NH_3)_4Cl_2^+ \xrightarrow{k_1} x(trans\text{-}Co(NH_3)_4H_2OCl^{2+}) + (1 - x)(cis\text{-}Co(NH_3)_4H_2OCl^{2+}) \quad (1)$$

$$trans\text{-}Co(NH_3)_4H_2OCl^{2+} \underset{k_3}{\overset{k_2}{\rightleftarrows}} cis\text{-}Co(NH_3)_4H_2OCl^{2+} \quad (2)$$

then the pertinent differential equations can be integrated to yield

$$\beta = \left[\frac{k_1x - k_3}{k_2 + k_3 - k_1}\right]e^{-k_1t} + \left[\frac{k_3}{k_2 + k_3}\right] - \left[\frac{k_1(k_2x + k_3x - k_3)}{(k_2 + k_3)(k_2 + k_3 - k_1)}\right]e^{-(k_2+k_3)t} \quad (3)$$

where β is the fraction of the total Co(III) in the form of *trans*-$Co(NH_3)_4H_2OCl^{2+}$. Of the terms in eq 3, all can be obtained from the data reported above except x: k_1 is found in Table I; k_3 is obtainable from the Fe(II)-independent term in the reduction of *cis*-$Co(NH_3)_4H_2OCl^{2+}$;[12] k_2 results from the equilibrium constant of reaction 2, 9.6, and the value of k_3; and β as a function of time is given in Table II. Therefore, a plot of β *vs.* time for various values of x can be compared with the experimental data listed in Table II. Figure 1 contains a plot of the data and the theoretical curves for two values of x. Although the precision of the data is not good, it is clear that a value of x other than unity is required to fit the experimental points. The best value for x appears to be 0.45 ± 0.10 at 15.8° in 1 *N* $HClO_4$. This result disagrees with the original report of Tsuchida,[10] although it is not apparent that his data are incompatible with the result.

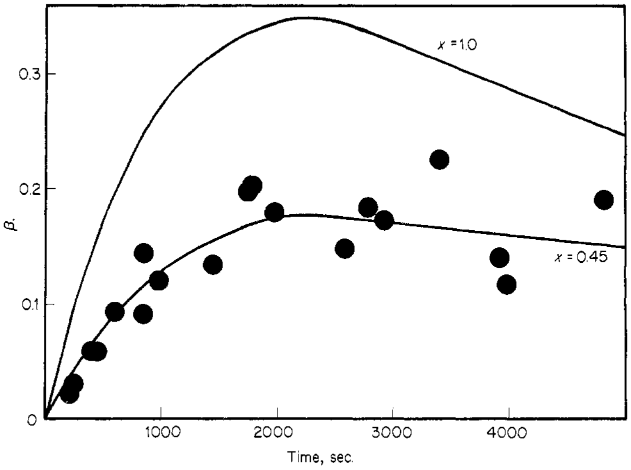

Figure 1.—The fraction of Co(III) in the form of *trans*-$Co(NH_3)_4H_2OCl^{2+}$, β, as a function of time, compared with theoretical curves for x = 1.0 and x = 0.45.

What the stereochemical consequences of the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ demonstrate is that the ethylenediamine rings in the corresponding chelated cobalt(III) tetraammines[11] do not have a dominating effect upon the stereochemistry of aquation reactions. Further, the activation parameters for the aquation of *trans*-$Co(NH_3)_4Cl_2^+$ fit Tobe's correlation:[2] positive values of the entropy of activation are associated with a change in stereochemical configuration. What is still puzzling is why the free energy of activation varies as it does with a change in the coordination sphere of the Co(III) center.

Acknowledgment.—This work was supported in part by a grant from the National Institutes of Health (GM-14830).

CONTRIBUTION FROM THE NATIONAL INSTITUTE OF
ARTHRITIS AND METABOLIC DISEASES,
NATIONAL INSTITUTES OF HEALTH,
BETHESDA, MARYLAND 20014

Low-Temperature Raman Spectra of Solid Osmium Tetroxide and Ruthenium Tetroxide

BY IRA W. LEVIN

Received October 17, 1968

Several recent discussions of the Raman spectra of osmium tetroxide and ruthenium tetroxide report similar multiplet features for both species in the solid

---

[17] The concentration of Fe(II) added was sufficient to react with the *trans*-$Co(NH_3)_4Cl_2^+$ present rapidly enough so as to ensure negligible aquation during the reduction.