

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

The Iron(II) Reduction of Chlorotetraamminecobalt(III) Complexes

By R. G. LINCK

Received February 23, 1968

The rates of the Fe(II) reduction of *trans*-Co(NH₃)₄Cl₂⁺, *cis*-Co(NH₃)₄H₂OCl²⁺, and *trans*-Co(NH₃)₄H₂OCl²⁺ have been investigated. The rate constants for the reduction are 2.21, 3.53 × 10⁻², and about 10 M⁻¹ sec⁻¹, respectively, at 25° and Σ[ClO₄⁻] = 1.0 M. The activation parameters for the reduction of the first two Co(III) complexes are reported. The data are discussed in terms of the σ-bonding model for the rate of reduction of similar Co(III) complexes and a correlation of the available data is presented.

Introduction

A number of workers have been active in the investigation of the effect of nonbridging ligands on the rate of electron-transfer reactions.¹⁻¹⁰ Two systems have held the interest of most of the workers:¹¹ The Fe(II) reduction of Co(en)₂XYⁿ⁺ complexes^{1,8} and the Cr(II)-Cr(III) electron-exchange reaction as the ligands on the Cr(III) center are varied.^{3-7,9,10} These choices have been made in order to have a known configuration of ligands around the oxidant; they reflect the predominant interest in the effect of nonbridging-ligand variation on the rate of inner-sphere reactions¹² (although all of the reductions with Fe(II) have not been proven as proceeding by the inner-sphere mechanism). The purpose of this study is to gain information about the effect on the rate constant for Fe(II) reduction of a Co(III) complex upon changing two ethylenediamine ligands to four ammonia ligands.

Experimental Section

Materials.—[*trans*-Co(NH₃)₄Cl₂]Cl·1.5H₂O was prepared by the method of Jørgenson¹³ as outlined by Brauer.¹⁴ *Anal.* Calcd for Co(NH₃)₄Cl₃·1.5H₂O: Co, 22.63; N, 21.51; H, 5.80. Found: Co, 22.28; N, 21.15; H, 5.52. [*cis*-Co(NH₃)₄H₂OCl]SO₄·0.5H₂O was prepared by the method of Kauffman and Pinnell¹⁵ from the corresponding chloride salt. *Anal.* Calcd for Co(NH₃)₄ClSO₄·1.5H₂O: Co, 20.64; N, 19.62; H, 5.30. Found: Co, 20.80; N, 19.77; H, 5.39. Ferrous perchlorate was obtained by recrystallizing G. F. Smith ferrous perchlorate. All other reagents were of reagent grade and were used without further purification.

Solutions of Fe(II) for the kinetic experiments were prepared by dissolving the recrystallized ferrous perchlorate in perchloric

acid, capping the vessels with serum caps, and then degassing the solution with chromous ion scrubbed nitrogen. The Fe(II) concentrations in the solutions were determined by adding excess Ce(IV) to an aliquot of the Fe(II) solution and titrating the excess Ce(IV) with standard Fe(II) using ferroin as an indicator. Total anion concentration was determined by passing an aliquot of the solution of Fe(II) down a cation-exchange column (Dowex 50-W-X8) in the hydrogen ion form and titrating the liberated acid with standard NaOH solution. Solutions of sodium perchlorate were prepared by treatment of sodium carbonate with an excess of standard perchloric acid, boiling to eliminate CO₂, and diluting to volume. Water was doubly distilled.

Kinetic Techniques.—Because the aquation of *trans*-Co(NH₃)₄Cl₂⁺ is relatively rapid, special techniques were used to store this reagent with as little aquation as possible. A weighed quantity of solid *trans*-[Co(NH₃)₄Cl₂]Cl was dissolved in a predetermined volume of doubly distilled water that had been cooled until crystallization began. The total time for dissolving the *trans*-[Co(NH₃)₄Cl₂]Cl was generally less than 5 min and the temperature of the solution never exceeded 1°. As soon as the solid had completely dissolved, the solution was divided into smaller portions and each of these was frozen at -78° until the experiment was started.

For kinetic runs, the desired quantities of Fe(II) solution, perchloric acid, and water were placed in a spectrophotometric cell and thermostated. After the desired temperature had been reached, one of the aliquots of frozen *trans*-Co(NH₃)₄Cl₂⁺ solution was thawed and brought to approximately the temperature of the reaction vessel, and the desired volume was then added with a syringe (the volume of the *trans*-Co(NH₃)₄Cl₂⁺ solution added was small compared to the volume in the spectrophotometric cell, and thus exact control of the temperature of the Co(III) solution was not necessary). Experiments in which the Co(III) solution was added first, followed by rapid addition of Fe(II) solution, showed identical kinetic behavior.

In experiments with *cis*-Co(NH₃)₄H₂OCl²⁺, the solutions of the complex in 1 N HClO₄ were prepared at room temperature. Aliquots of this solution, water, and perchloric acid were added such that the sum of the concentration of ClO₄⁻ ion after addition of the Fe(II) solution would be 1.0 M. These components were thermostated in a spectrophotometric cell; after the desired temperature had been reached, an aliquot of the Fe(II) solution, also thermostated at the desired temperature, was added with a syringe.

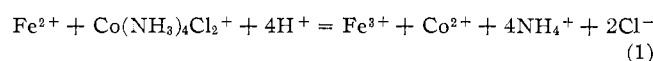
All of the kinetic experiments were followed spectrophotometrically on a Cary Model 14 recording spectrophotometer with a thermostated cell holder. Temperature control was ±0.05°, and accuracy is estimated to be ±0.2°.

Results

The ultraviolet spectrum of a solution of *trans*-Co(NH₃)₄Cl₂⁺ has a maximum at 2530 Å. At this wavelength, the molar extinction coefficients of the various materials are as follows (in units of M⁻¹ cm⁻¹):

- (1) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965), and references therein.
- (2) R. D. Cannon and J. E. Earley, *ibid.*, **87**, 5264 (1965); **88**, 1872 (1966).
- (3) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).
- (4) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 585 (1966).
- (5) D. W. Pennington and A. Haim, *ibid.*, **5**, 1887 (1966).
- (6) J. H. Espenson, and S. G. Slocum, *ibid.*, **6**, 906 (1967).
- (7) A. Adin, J. Doyle, and A. G. Sykes, *J. Chem. Soc., A*, 1504 (1967).
- (8) C. Bifano and R. G. Linck, *J. Am. Chem. Soc.*, **89**, 3945 (1967).
- (9) J. M. DeChant and J. B. Hunt, *ibid.*, **89**, 5988 (1967).
- (10) D. G. Pennington and A. Haim, *Inorg. Chem.*, **6**, 2138 (1967).
- (11) See ref 1 and 2 for other studies.
- (12) It was suggested in ref 1 that outer-sphere reactions might not show a dramatic dependence on ligand variations; that both inner-sphere and outer-sphere reactions would show a dependence was suggested in ref 8. Recent investigations by J. F. Endicott and R. C. Patel (private communication) show that the change in rate constant with variation in ligands on the oxidant can be large for outer-sphere reactions.
- (13) S. M. Jørgenson, *Z. Anorg. Allgem. Chem.*, **14**, 404 (1897).
- (14) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd ed, Academic Press, New York, N. Y., 1965, p 1537.
- (15) G. B. Kauffman and R. P. Pinnell, *Inorg. Syn.*, **6**, 176 (1960).

Fe(III), 3670; Co(II), less than 20; *trans*-Co(NH₃)₄Cl₂⁺, 2.4 × 10⁴,¹⁶ *cis*- and *trans*-Co(NH₃)₄H₂OCl²⁺, which are approximately equal, 6260.¹⁶ From these independently obtained values, the stoichiometry of the Fe(II) reduction of the complexes can be verified. If, as supposed, the stoichiometry is as represented by



then a calculated value of the total absorbance change, under conditions where Fe(II) is in sufficient excess so as to ensure that 99% of the *trans*-Co(NH₃)₄Cl₂⁺ is reduced to Co(II) (rather than aquated), can be obtained. For an experiment in which the initial concentrations of Co(III) and Fe(II) were 6.69 × 10⁻⁵ and 3.08 × 10⁻² M, respectively, the calculated absorbance change was 1.34; the experimental value was 1.39.

When *trans*-Co(NH₃)₄Cl₂⁺ is placed in a solution containing Fe(II), several reactions take place: the complex is reduced and, simultaneously, aquated to a mixture of *cis*- and *trans*-Co(NH₃)₄H₂OCl²⁺, each of which in turn is reduced by Fe(II). As long as the concentration of Fe(II) is sufficiently high and the reaction is monitored at 2530 Å, one can study the rate of the reduction with little interference from the other reactions. This results from the large absorptivity of *trans*-Co(NH₃)₄Cl₂⁺ and the similar absorptivities of Fe(III) and the *cis* and *trans* isomers of the chloroaquo complexes. A plot of the function log (*A_t* - *A_∞*) vs. time, where *A_t* is the absorbance at time *t* and *A_∞* is the absorbance at the completion of the reaction, vs. time, under conditions such that the concentration of Fe(II) is a constant (a condition met in all the experiments reported herein), will yield a slope that is proportional to the pseudo-first-order rate constant for the reduction plus the rate constant for aquation.¹⁸ In all cases, the observed slope was corrected by subtracting the spontaneous aquation rate constant, *k*₁.¹⁶ The second-order rate constants, *k*_A, obtained from the corrected rate constants by division by the [Fe(II)] are listed in Table I. In all cases, the data indicate that the appropriate rate law is

$$\frac{-d[\text{trans-Co}(\text{NH}_3)_4\text{Cl}_2^+]}{dt} = k_A[\text{trans-Co}(\text{NH}_3)_4\text{Cl}_2^+][\text{Fe}(\text{II})]$$

The rate constant reported in the work of Benson and Haim¹ for the Fe(II) reduction of *trans*-Co(en)₂Cl₂⁺ is independent of [H⁺]; thus it was felt that two exper-

(16) The value of the molar extinction coefficient for *trans*-Co(NH₃)₄Cl₂⁺ is obtained by extrapolating the function log (*A_t* - *A_∞*), where *A_t* is the absorbance at time *t* and *A_∞* is that at the end of the first aquation step, to zero time. Values for *A_∞* give the molar extinction coefficient for a mixture of the *cis* and *trans* isomers of Co(NH₃)₄H₂OCl²⁺. Further aquation, to Co(NH₃)₄(H₂O)₂³⁺, is negligible during the length of time to complete the primary aquation.¹⁷ The details of these measurements and the rates of aquation will be reported separately.

(17) J. N. Brønsted, *Z. Physik. Chem.*, **122**, 383 (1926).

(18) Even if as much as 30% of the *trans*-dichloro complex reacted to form chloroaquo species and, further, even if these latter species reacted with Fe(II) only very slowly, the drift in *A_∞* would amount to only 3.5% of the total change in absorbance, *A₀* - *A_∞*. Because some of the chloroaquo complexes are reduced (and their products of reduction are the same as those of the reduction of the *trans*-dichloro compound), the actual drift in *A_∞* is much less. Any reasonable choice of *A_∞* yielded satisfactory straight-line plots. In the majority of experiments, no such drift was observed since the Fe(II) concentration was sufficiently large that the amount of *trans*-dichloro complex that aquated was less than 5%.

TABLE I

RATE OF REDUCTION OF *trans*-Co(NH₃)₄Cl₂⁺ BY Fe(II) WHERE [ClO₄⁻] = 1.0 M^a

10 ² [Fe(II)], M	10 ⁶ [Co(III)], M	Temp, °C	<i>n</i> ^b	<i>k</i> _A , M ⁻¹ sec ⁻¹
1.10-3.50	4.3-9.4	34.3 ^c	5	3.47 ± 0.15
0.17-3.08	1.0-23	25.0 ^d	8	2.21 ± 0.06
2.34-3.08	6.8	15.8 ^e	3	1.34 ± 0.01

^a HClO₄. ^b Number of experiments. ^c *k*₁ = 5.1 × 10⁻³ sec⁻¹. ^d *k*₁ = 1.48 × 10⁻³ sec⁻¹. ^e *k*₁ = 0.44 × 10⁻³ sec⁻¹.

iments would suffice to establish that *k*_A was independent of [H⁺]. At 25.0°, [ClO₄⁻] = 1.0 M and [Co(III)] = 6.3 × 10⁻⁵ M, and, with Na⁺ as the other cation, experiments with [Fe(II)] = 1.82 × 10⁻² M, [H⁺] = 0.097 M and [Fe(II)] = 2.6 × 10⁻² M, [H⁺] = 0.102 M yielded rate constants of 2.20 and 2.22 M⁻¹ sec⁻¹, respectively.

Several experiments were undertaken to determine the dependence of *k*_A on [Cl⁻]. At 25.0°, [H⁺] = 1.0 M, and [Co(III)] = 6.3 × 10⁻⁵ M, the values of [Fe(II)], [Cl⁻], and *k*_A were, respectively, for each experiment: 1.66 × 10⁻² M, 1.28 × 10⁻² M, and 2.42 M⁻¹ sec⁻¹; 2.68 × 10⁻² M, 3.1 × 10⁻³ M, and 2.28 M⁻¹ sec⁻¹; 2.34 × 10⁻² M, 7.9 × 10⁻⁴ M, and 2.31 M⁻¹ sec⁻¹. Thus the chloride ion concentration introduced by the original Co(III) complex and its aquation products has no effect on *k*_A, although there may be a kinetic path in [Cl⁻] at higher [Cl⁻].

The Reduction of *cis*-Co(NH₃)₄H₂OCl²⁺ by Fe(II).—The reaction of *cis*-Co(NH₃)₄H₂OCl²⁺ with Fe(II) is slow relative to that of *trans*-Co(NH₃)₄Cl₂⁺. Hence, experiments could be carried out over a wide range of [Fe(II)]. In all cases, the concentration of Fe(II) was in sufficient excess to ensure that the reaction was pseudo first order in Fe(II). The first-order rate constants were calculated from the normal plot. Data were obtained at 5250 Å for the more concentrated Fe(II) solutions ([Fe(II)] > 0.09 M) and at 2400 Å for the more dilute. The data in Table II illustrate the values of the pseudo-first-order rate constant as a function of Fe(II). It can be seen that the rate is not first order in Fe(II). When the values of the observed pseudo-first-order slope are plotted against the concentration of Fe(II), a straight line with positive intercept results. Thus the rate law for the reduction of *cis*-Co(NH₃)₄H₂OCl²⁺ by Fe(II) takes the form

$$\frac{-d[\text{Co}(\text{III})]}{dt} = \{k_B + k_A[\text{Fe}(\text{II})]\}[\text{Co}(\text{III})]$$

Values of the parameters *k*_B and *k*_A of this equation for the various temperatures at which the reduction of *cis*-Co(NH₃)₄H₂OCl²⁺ was carried out are listed in Table III. Values of the pseudo-first-order rate constant calculated by the parameters in Table III, *k*_{calc}, are listed in Table II in order to demonstrate the fit of this rate law to the experimental data. The parameters in Table III were calculated by neglecting the experiments at high [Fe(II)]. This procedure was used because, although the [ClO₄⁻] was held constant (in order that the rate constants reported herein could be compared to those in ref 1), in experiments at high [Fe(II)], the

TABLE II
RATE CONSTANTS FOR THE Fe(II) REDUCTION OF
cis-Co(NH₃)₄H₂OCl²⁺ WHERE [ClO₄⁻] = 1.0 M

10 ² [Fe- 10 ⁴ k _{obsd} , ^a (II)], M sec ⁻¹			10 ² [Fe- 10 ⁴ k _{obsd} , 10 ⁴ k _{calcd} , ^c (II)], M sec ⁻¹		
T = 34.3°			T = 15.8° ^c		
0.49	13.9	14.5	1.58	3.28 ^c	3.27
0.56	15.5	15.1	1.65	3.32	3.39
0.74	16.8	16.6	1.82	3.67	3.69
1.10	19.6	19.4	1.92	3.50	3.86
1.28	20.0	20.9	2.04	4.05	4.07
1.82	25.5 ^b	25.3	2.14	4.06	4.24
1.89	25.6	25.8	2.20	4.27	4.35
2.67	32.6	32.1	2.34	4.63	4.59
2.79	32.3	33.0	2.44	4.75	4.76
3.79	40.6	41.1	2.73	5.07	5.26
4.01	43.2	42.8	2.98	5.63	5.70
			3.08	5.76	5.87
T = 25.0°			3.80	7.12	7.11
0.92	6.28	6.45	4.04	7.62 ⁱ	7.53
1.10	7.26	7.09	15.0 ^e	27.3	26.5
1.28	7.47	7.73	21.0 ^f	38.8	36.8
1.46	8.44	8.36	24.0 ^g	45.0	42.0
1.82	9.67 ^c	9.63	27.0 ^h	50.4	47.2
2.34	12.0 ^d	11.5	30.0 ⁱ	53.0	52.5
2.68	12.7	12.7			
3.52	14.9	15.6	T = 11.1°		
4.33	18.8	18.5	1.66	1.90	1.91
15.0 ^e	49.1	56.2	2.20	2.42	2.40
21.0 ^f	70.5	77.3	2.73	2.90	2.88
24.0 ^g	72.8	87.9	3.25	3.89	3.34
27.0 ^h	81.0	98.5	4.03	4.03	4.05
30.0 ⁱ	99.5	109.1	9.0 ^b	9.63	8.52
			15.0 ^e	15.5	13.9
T = 15.8°			18.0 ⁱ	19.6	16.6
0.49	1.57	1.38	18.0 ^m	20.4	16.6
0.81	2.02	1.94	18.0 ⁿ	20.0	16.6
0.92	2.21	2.13	21.0 ^f	22.6	19.3
1.12	2.49	2.48	24.0 ^g	25.7°	22.0
1.28	2.80	2.75	27.0 ^h	26.3	24.7
1.39	3.03 ^c	2.94	30.0 ⁱ	31.8	29.0
1.46	3.13	3.07			

^a Calculated from the parameters in Table III. ^b Average of 5 experiments. ^c Average of 3 experiments. ^d Average of 18 experiments. ^e Ionic strength $I = 1.15$; $[H^+] = 0.70 M$. ^f $I = 1.21$; $[H^+] = 0.58 M$. ^g $I = 1.24$; $[H^+] = 0.52 M$. ^h $I = 1.27$; $[H^+] = 0.46 M$. ⁱ $I = 1.30$; $[H^+] = 0.40 M$. ^j Average of 6 experiments. ^k $I = 1.09$; $[H^+] = 0.82 M$. ^l $I = 1.18$; $[H^+] = 0.64 M$; $[HSO_4^-] = 0.0041 M$. ^m $I = 1.17$; $[H^+] = 0.64 M$; $[HSO_4^-] = 0.0102 M$. ⁿ $I = 1.19$; $[H^+] = 0.65 M$; $[HSO_4^-] = 0.0162 M$. ^o Average of 2 experiments.

TABLE III
RATE OF REDUCTION OF *cis*-Co(NH₃)₄H₂OCl²⁺ BY
Fe(II) WHERE [ClO₄⁻] = 1.0 M

10 ² [Fe(II)], M	10 ⁴ [Co(III)], M	Temp, °C	10 ⁴ k _{obsd} , M ⁻¹ sec ⁻¹	10 ⁴ k _B , M ⁻¹ sec ⁻¹
0.49-4.01	5.2-8.5	34.3	10.6	8.05
0.92-4.33	5.2-7.3	25.0	3.21	3.53
0.49-3.80	5.2-8.5	15.8	0.54	1.73
1.66-4.03	6.5-6.75	11.1	0.42	0.90

ionic strength was not constant. Further, the fraction of the ionic strength accounted for by the presence of the dipositive cation Fe(II) is very significant in the experiments at high [Fe(II)]. It is seen that the values of the observed rate constant calculated from the parameters in Table III agree very well with k_{obsd} at low [Fe(II)] and reasonably well with the values at high [Fe(II)]. Since the observed rate constant at high [Fe(II)] is larger than that calculated at 11.1, smaller at 25.0, and nearly equal at 15.8°, it may be that the activation parameters differ in the systems of differing ionic content.

The results at high [Fe(II)] do serve to establish that the rate of the reduction of *cis*-Co(NH₃)₄H₂OCl²⁺ is independent of acid and HSO₄⁻, the counterion of the complex ion.

The Reduction of *trans*-Co(NH₃)₄H₂OCl²⁺ by Fe(II).

—In the experiments described in the previous section, no care was taken to mix the reagents rapidly. In addition, the log ($A_t - A_\infty$) plots reported in the last section, when extrapolated to zero time, gave an A_0 value in disagreement with that observed.

If mixing is done rapidly on a solution of *cis*-Co(NH₃)₄H₂OCl²⁺ that has equilibrated for several minutes, there is observed a rapid decrease in absorbance (at 2400 Å) in addition to the slow change reported in the last section. Extrapolation of a plot of log ($A_t - A_\infty$) for the slow step into the region of the fast process and a plot of the log of the difference $A_{obsd} - (A_t - A_\infty)_{extrap}$ vs. time gave another linear plot. The slope of this plot, divided by the [Fe(II)] demonstrated, to within experimental error, that the fast process was first order in Fe(II) as well as in Co(III). The fastest of these two simultaneous reactions is sufficiently rapid that highly accurate values of the rate constant could not be obtained. However, at 15.8°, a value of sufficient accuracy to allow discussion of the trend in rate constant with a change in nonbridging ligand can be obtained. A summary of the experiments done is found in Table IV.

TABLE IV

RATE OF REDUCTION OF <i>trans</i> -Co(NH ₃) ₄ H ₂ OCl ²⁺ BY Fe(II) AT 1.0 N HClO ₄ , 15.8°, AND [Co(III)] = (3.8-6.6) × 10 ⁻⁶ M			
10 ² [Fe(II)], M	k _o , M ⁻¹ sec ⁻¹	10 ² [Fe(II)], M	k _o , M ⁻¹ sec ⁻¹
0.83	3.9	1.92	3.5 ^b
0.92	5.1	2.14	3.7
1.28	5.3	2.20	3.5
1.38	4.1 ^a	2.44	3.5 ^b
1.46	4.5	2.72	3.1 ^b
1.66	4.5	2.98	2.3
1.82	4.6	4.03	4.6
			3.9 ± 0.8 ^c

^a Average of 4 experiments. ^b Average of 2 experiments. ^c Average of 20 experiments.

Discussion

The rate law for the reduction of *trans*-Co(NH₃)₄Cl₂⁺ is straightforward, but that for the reduction of *cis*-Co(NH₃)₄H₂OCl²⁺ differs from the usual oxidation-reduction rate law. A similar rate law for a similar complex, *cis*-Co(en)₂H₂OCl²⁺, was found in the study by Benson and Haim.¹ They interpreted the two paths as being direct reduction of *cis*-Co(en)₂H₂OCl²⁺ by Fe(II) and isomerization of the *cis* complex to the *trans* complex, with subsequent rapid reduction of the latter. A completely similar interpretation is appropriate in the case of *cis*-Co(NH₃)₄H₂OCl²⁺. The requirement that the reduction of the *trans* isomer be rapid has been independently established herein by experiment on an equilibrium mixture of the isomers. Hence one can take k_3 as a measure of the rate of isomerization of *cis*-Co(NH₃)₄H₂OCl²⁺ to the corresponding *trans* isomer

and k_B as a measure of the rate of the Fe(II) reduction of the *cis* isomer. Table V summarizes the rate constants and their corresponding activation parameters as obtained in this work.

TABLE V
SUMMARY OF RATE PARAMETERS FOR THE Fe(II)
REDUCTION OF COBALT(III)-TETRAAMMINE COMPLEXES

Complex	$k,^a M^{-1} \text{sec}^{-1}$	$\Delta H^\ddagger,$ kcal mol ⁻¹	$\Delta S^\ddagger,$ cal mol ⁻¹ deg ⁻¹
<i>trans</i> -Co(NH ₃) ₄ Cl ₂ ⁺	2.21	8.5 ± 0.7	-29 ± 2
<i>cis</i> -Co(NH ₃) ₄ H ₂ OCl ₂ ⁺	3.53 × 10 ⁻²	14.1 ± 0.5	-18 ± 2
<i>trans</i> -Co(NH ₃) ₄ H ₂ OCl ₂ ⁺ (10) ^{b,c}

^a At 25.0°. ^b Estimated by assuming the temperature dependence of the rate of this reduction is related to that of *cis*-Co(NH₃)₄H₂OCl₂⁺ as *trans*-Co(en)₂H₂OCl₂⁺ is related to *cis*-Co(en)₂H₂OCl₂⁺. The latter data are the unpublished work of C. Bifano and R. G. Linck. ^c The rate at 15.8° is 3.9 M⁻¹ sec⁻¹.

To compare the rate of reduction of cobalt(III)-chloroamine complexes by Fe(II) when two ethylenediamine ligands are changed for four ammonia ligands is the aim of this work. The pertinent data from this study are combined with data in the literature^{1,5,9,19} to give the values shown in Table VI. Considering

TABLE VI
EFFECT ON RATE OF REDUCTION OF THE REPLACEMENT OF TWO
ETHYLENEDIAMINE LIGANDS BY FOUR AMMONIA LIGANDS

Reaction ^a	$k[(\text{NH}_3)_4]/$ $k(\text{en})_2]$	Ref
Fe ²⁺ + <i>trans</i> -CoA ₄ Cl ₂ ⁺	69	1, b
Fe ²⁺ + <i>trans</i> -CoA ₄ NH ₃ Cl ₂ ⁺	20	1, 19
Fe ²⁺ + <i>trans</i> -CoA ₄ H ₂ OCl ₂ ⁺	40	1, b
Fe ²⁺ + <i>cis</i> -CoA ₄ NH ₃ Cl ₂ ⁺	85	1, 19
Fe ²⁺ + <i>cis</i> -CoA ₄ H ₂ OCl ₂ ⁺	75	1, b
Cr ²⁺ + <i>trans</i> -CrA ₄ H ₂ OCl ₂ ⁺	2.7	5, 9
Cr ²⁺ + <i>cis</i> -CrA ₄ H ₂ OCl ₂ ⁺	9.8	5, 9

^a A = NH₃ or 0.5en. ^b This work.

first the data for the Fe(II) reduction of Co(III) complexes, it can be seen from the relative rates that the replacement of two ethylenediamine ligands by four ammonia ligands causes a substantial increase in rate. Further, that increase is approximately independent of the other ligand in the complex, indicating that the effect of the replacement of these nonbridging²⁰ ligands is additive. That the effect should be additive follows from the σ -bonding model presented earlier.⁸ If the rate of the reaction depends on the bond length changes in order to make the energy level of the donor and acceptor orbitals equal,²¹⁻²³ then the higher the energy of the acceptor orbital (one of the e_g orbitals of the Co(III) center under the assumption of octahedral geometry) for a fixed reductant, the more energy must be supplied to equate the energy level of acceptor and donor.

(19) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

(20) The use of the term "nonbridging ligands" implies that the reaction is inner sphere. This has not been proven for all of the systems studied here. The arguments in favor of the inner-sphere classification for Fe(II) reductions of Co(III) complexes of the type under consideration have been summarized before. See ref 1, C. Bifano and R. G. Linck, *Inorg. Chem.*, **7**, 908 (1968), and references therein.

(21) The σ -bonding model is a one-electron approximation to the multi-electron, multinuclear problem. In addition, second coordination sphere effects are assumed constant (see also ref 22).

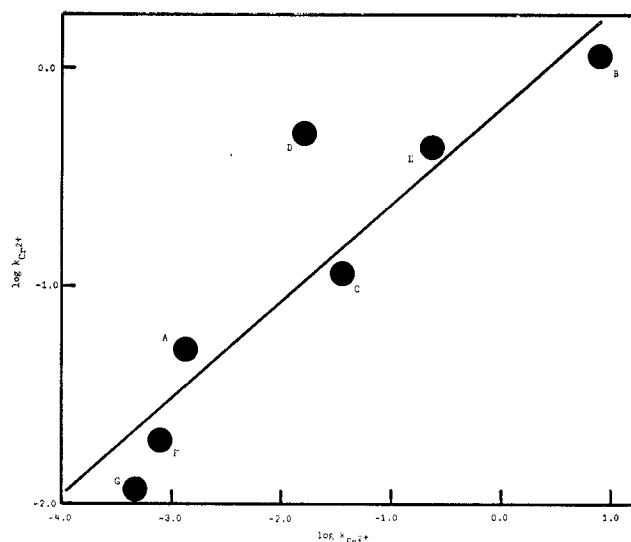
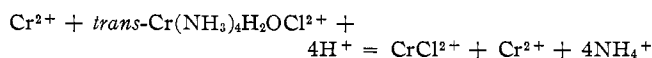


Figure 1.—Log k for Cr²⁺ + CrA₄XClⁿ⁺ vs. log k for Fe²⁺ + CoA₄XClⁿ⁺: A, M(NH₃)₅Cl₂⁺; B, *trans*-M(NH₃)₄H₂OCl₂⁺; C, *cis*-M(NH₃)₄H₂OCl₂⁺; D, *trans*-M(en)₂Cl₂⁺; E, *trans*-M(en)₂H₂OCl₂⁺; F, *cis*-M(en)₂Cl₂⁺; G, *cis*-M(en)₂H₂OCl₂⁺.

Hence, the stronger the σ -bonding ligand,²² the slower the rate. To the extent that the various bonds in the Co(III) complex can be considered to be independent, their effect on the energy level of the acceptor orbital will be additive.²³

It should be noted that the above argument rests not upon which bonds stretch and how much they stretch. Instead of attempting to assess this parameter, the only question asked is how much total energy must be absorbed by the system. The detailed nature of the stretching motions necessary to achieve the activated complex is another question and not one that is readily answered by models. Nonsymmetrical motions of the five nonbridging ligands of the Co(III) center will take place if the transition state for the oxidant is more stable with both ligands along the z axis stretched;²⁴ however, with respect to acceptor energy level, extreme stretching of the bridging ligand and symmetrical stretching of the other five ligands can achieve the same end. Hence, the two isotopic fractionation experiments in the literature^{9,25} can be rationalized if one accepts that the Cr(III) oxidant in the reaction⁹



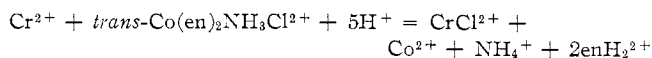
(22) The pertinent Co(III) orbital is antibonding in nature. The ordering of ligands in terms of σ bonding is not simple. In the previous paper,⁸ structurally similar ligands were ordered. As ligands vary more widely, effects of changes in solvent reorganization energies must be taken into account, since these factors will be superimposed upon the σ bonding effect. That an empirical assignment may be useful is indicated by studies to be reported soon; see ref 23.

(23) It is to be noted that nothing in the argument presented demands an inner-sphere activated complex. Indeed, the arguments predict an identical result for an outer-sphere system providing the stereochemical relationship between the oxidant and reductant remains constant with Co(III) complexes of low symmetry. The results of Endicott and Patel¹² indicate that the change in rate constant with a change in nonbridging ligand shows a striking parallel when comparison is made between the reductants Fe(II)¹⁸ and Ru(NH₃)₆²⁺. Similarly, the rate constants for the reduction of various Co(III) complexes with V(II) indicate that these also follow the same trend with a change in nonbridging ligand: P. Guenther and R. G. Linck, unpublished observations.

(24) The Co-Cl (bridging) bond defines the z axis.

(25) M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

prefers to distort tetragonally, while the Co(III) center in the reaction²⁵



prefers to distort toward a square-based pyramid.²⁵

The data in Table VI concerning the two Cr(II)-catalyzed aquations of chlorochromium(III) complexes illustrate the decreased sensitivity to nonbridging ligands that is observed in this system. A further example of this phenomenon is illustrated in Figure 1 where a plot of the logarithm of the rate of Fe(II) reduction of chlorocobalt(III) complexes against the logarithm of the Cr(II)-catalyzed aquation of chloro-

chromium(III) complexes is to be found.^{5,9,26} The observed slope, 0.45, shows that the Cr(II)-catalyzed aquation, the mechanism of which is electron transfer in nature,²⁶ is less than half as sensitive to a change in nonbridging ligands than is the Fe(II) reduction of the chlorocobalt(III) complexes.

Acknowledgments.—This research was supported by the National Institutes of Health (Grant GM-14830). The author thanks Professor John Endicott for helpful discussions and a preprint of the results of reductions with $\text{Ru}(\text{NH}_3)_6^{2+}$.

(26) A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, **80**, 1084 (1958).

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON W.C.1, ENGLAND

Mechanism and Steric Course of Octahedral Aquation. XI.¹ The Mechanism of Isomerization of *cis*-Hydroxoquo(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cations

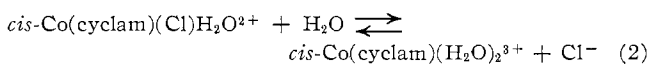
By C. K. POON AND M. L. TOBE

Received March 18, 1968

The *cis* to *trans* isomerization of *cis*-Co(cyclam)Cl₂⁺ (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been shown to go by way of the labile *cis*-Co(cyclam)(OH)H₂O²⁺ cation. The isomerization of this species is accompanied by exchange of two of the four amine protons and it is assumed that this exchange leads to the inversion of the configurations of the nitrogen atoms concerned. The kinetics of the exchange of the amine protons of *trans*-Co(cyclam)(H₂O)₂³⁺ and *trans*-Co(cyclam)(OH)H₂O²⁺ have been examined as a function of pH. It is proposed that the facile hydrogen exchange and isomerization of these hydroxoquo complexes is a consequence of an intramolecular proton transfer from nitrogen to oxygen and that this process allows the otherwise unfavored exchange with inversion of configuration to take place.

Introduction

The substitution reactions of the cobalt(III) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) have been shown to proceed with complete retention of configuration.¹⁻³ In part X¹ we reported that a solution, originally containing *cis*-[Co(cyclam)Cl₂]Cl in 0.01 *M* hydrochloric acid, underwent three spectrophotometrically distinct changes, the first two of which could be identified as successive stereoretentive solvolytic displacements of the coordinated chlorine, *i.e.*

$$\textit{cis}\text{-Co(cyclam)Cl}_2^+ + \text{H}_2\text{O} \longrightarrow \textit{cis}\text{-Co(cyclam)(Cl)H}_2\text{O}^{2+} + \text{Cl}^- \quad (1)$$


The third process, which was very slow under these conditions, was a *cis* to *trans* change since the final spectrum was identical with that of a mixture of *trans*-Co(cyclam)Cl₂⁺ and *trans*-Co(cyclam)(H₂O)Cl₂⁺ at equilibrium under identical conditions.³

It was thought that the main cause of the stereo-

retentive behavior of these complexes was the restriction placed upon the configuration that could be adopted by the secondary nitrogen atoms² and that stereochemical change would require concomitant inversion of the configuration of certain of the nitrogen atoms. Since the most likely path for such an inversion is through the exchange of the amine protons, this paper sets out to examine the isomerization, to identify the reaction path, or paths, and to study the relationship between proton exchange and inversion.

Experimental Section

The preparation, properties, and analyses of the complexes used in this work have been reported elsewhere.¹ All other reagents were of AnalaR grade when available or else of reagent grade. D₂O (99.7%) was obtained from Norsk Hydro, and DCl was obtained as a 20% solution in D₂O (99% D) from E. Merck, A.G., and was diluted as necessary with D₂O. Small quantities of DClO₄ in D₂O were prepared by adding AR perchloric acid (72%) to D₂O and then evaporating this solution to small bulk *in vacuo* over P₂O₅. A fresh sample of D₂O was then added and the process was repeated. Noninterfering buffers have been described elsewhere.³

The isomerization reactions were followed spectrophotometrically by techniques depending upon the rate of the reaction. For the very slow reactions (*t*_{1/2} > 6 hr) the reaction solution was

(1) C. K. Poon and M. L. Tobe, *J. Chem. Soc., A*, 1549 (1968).

(2) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

(3) C. K. Poon and M. L. Tobe, *J. Chem. Soc., A*, 2069 (1967).