

sensitive to nucleophilic attack. The small effect of  $H_2O_2$  appears to indicate that peroxide equilibria are not dominant but does not rule out such reactions completely. Since exclusion of  $O_2$  does not affect the rate, it may be inferred that free radicals are not important in or prior to the rate-determining step.

The structure of  $CrO_5^{3-}$  in the solid states consists of four  $O_2^{2-}$  groups located tetrahedrally about the Cr(V) ion. One oxygen of each peroxide is 1.85 Å. from the Cr(V), the other 1.94 Å. Formation of  $HCrO_5^{2-}$  might be expected to involve a considerable distortion of this structure. For this reason it does not seem possible to rule out a slow protonation step in this reaction. The alternative rapid protonation and rate-determining decomposition is also in accord with the data. The value  $6.9 \times 10^{-9}$  is not unreasonable for the acidity constant of  $HCrO_5^{2-}$ , which would be expected to be more acidic than  $HPO_4^{2-}$  ( $K_a \approx 10^{-12}$ ). However, negative enthalpy is not usual for simple acid dissociation.

Whether or not protonation of  $CrO_5^{3-}$  is rapid, the rate constant  $k_1$  corresponds to decomposition of  $HCrO_5^{2-}$ .

Several studies of the decomposition of peroxides have obtained evidence that decomposition results from the nucleophilic attack of a peroxy anion on a protonated peroxy molecule. Mechanisms of this type have been proposed for the decomposition of Caro's acid ( $H_2SO_5$ )<sup>7,8</sup> and several organic and inorganic peroxy acids.<sup>5,9</sup> In these cases the kinetics are second order. In the case of the peroxychromate(V) ion, first-order kinetics would result if interaction occurs between two peroxide groups on the same ion. The mechanism of decomposition of  $HCrO_5^{2-}$  is likely to involve interaction of adjacent protonated and unprotonated peroxide groups.

*Acknowledgment.* This work was supported by the U. S. Atomic Energy Commission under contract AT-40-1-2842. We are grateful to Professors J. O. Edwards, G. Gordon, and E. Koubek for helpful discussion.

(7) E. Koubek, G. Levey, and J. O. Edwards, *Inorg. Chem.*, **3**, 1331 (1964).

(8) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

(9) J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).

## The Reduction of Various *cis*- and *trans*-Chlorobis-(ethylenediamine)cobalt(III) Complexes by Iron(II)<sup>1</sup>

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*The kinetics of reductions of *cis*- and *trans*-substituted  $Co(en)_2XCl^{+n}$  by  $Fe(II)$  have been studied at 25° and  $\Sigma[ClO_4^-] = 1.0 M$ . For the *trans* complexes, the second-order rate constants corresponding to the rate law  $k[Co(III)][Fe(II)]$  are  $2.4 \pm 0.2 \times 10^{-1}$ ,  $3.6 \pm 0.3 \times 10^{-2}$ ,  $3.2 \pm 0.4 \times 10^{-2}$ ,  $1.3 \times 10^{-4}$ ,  $6.6 \pm 0.3 \times 10^{-5}$ , and  $6.2 \pm 0.4 \times 10^{-2} M^{-1} sec^{-1}$  for  $X = H_2O$ ,  $Br^-$ ,  $Cl^-$ ,  $SCN^-$ ,  $NH_3$ , and  $N_3^-$ , respectively. For the *cis* isomers the second-order rate constants are  $1.6 \pm 0.4 \times 10^{-3}$ ,  $4.6 \pm 0.3 \times 10^{-4}$ ,  $1.7 \times 10^{-4}$ , and  $1.8 \pm 0.1 \times 10^{-5} M^{-1} sec^{-1}$  for  $X = Cl^-$ ,  $H_2O$ ,  $SCN^-$ , and  $NH_3$ , respectively. It is suggested that, except for *trans*- $Co(en)_2N_3Cl^+$ , the reactions proceed by an activated complex that makes use of a  $Cl^-$  bridge, and the observed nonbridging ligand effects are discussed on the basis of a model which involves stretching of the bridge and of the group *trans* to it away from the  $Co(III)$  center and the transfer of an electron from  $Fe^{+2}$  to the  $d_{z^2}$  orbital of cobalt.*

### Introduction

Kinetic and stoichiometric studies of the reduction of cobalt(III) ammine complexes have yielded important information regarding the mechanism of "electron-transfer" reactions.<sup>2</sup> Most of the work in this area

has dealt with complexes of the pentaammine class, the emphasis being placed on the dependence of reaction rates upon the nature of the sixth ligand. Taube<sup>2a,3,4</sup> has called attention repeatedly to the fact that, for inner-sphere mechanisms involving a single bridging ligand, there are ten coordinating positions in addition to the bridge, and that variations in the nature of the groups in these positions give rise to nonbridging ligand effects. With regard to cobalt(III) complexes, such effects have been recently documented. Fraser has studied the effect of chelation by nonbridging ligands on the reductions of aquo-, sulfato-, acetato-, and chlorocobalt(III) complexes by chromium(II) or vanadium(II).<sup>5,6</sup> Kopple and Miller have examined the kinetics of reduction of carboxylatotetraamminecobalt(III) complexes by chromium(II).<sup>7,8</sup> Schendel has examined the effect of successive substitution of ammonia in  $Co(NH_3)_5Cl^{+2}$  by one or two water ligands on the rate of reaction with iron(II).<sup>9</sup> We have demonstrated previously that the rates of

(2) (a) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959); (b) J. Halpern, *Quart. Rev. (London)*, **15**, 207 (1961); (c) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

(3) H. Taube, *Can. J. Chem.*, **37**, 129 (1959).

(4) H. Taube, *Brookhaven Symp. Biol.*, **15**, 1 (1962).

(5) R. T. M. Fraser, *Proc. Chem. Soc.*, 262 (1963).

(6) R. T. M. Fraser, *Inorg. Chem.*, **2**, 954 (1963).

(7) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

(8) K. D. Kopple and R. R. Miller, *Inorg. Chem.*, **2**, 1204 (1963).

(9) D. Schendel, M.S. Thesis, The Pennsylvania State University, Sept. 1964.

(1) This work was supported by Grant GP-2001 from the National Science Foundation.

iron(II) reduction of various azidoamminecobalt(III) complexes are affected profoundly by the nature of the ligands *cis* and *trans* to the azide ion.<sup>10</sup> We wish to report here similar effects encountered in the reduction of various *cis*- and *trans*-substituted chlorobis(ethylenediamine)cobalt(III) complexes by iron(II).

### Experimental

**Preparation of Complexes.** *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl<sup>11</sup> was used as the starting material in the preparation of the other complexes. The crude hydrochloride salt was recrystallized to remove any [Co(en)<sub>3</sub>]Cl<sub>3</sub> impurity. *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>,<sup>12</sup> *cis*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O,<sup>13</sup> *trans*-[Co(en)<sub>2</sub>(NCS)Cl]Br,<sup>14</sup> *cis*-[Co(en)<sub>2</sub>(NCS)Cl]Cl,<sup>15</sup> *trans*-[Co(en)<sub>2</sub>NH<sub>3</sub>Cl]ClO<sub>4</sub>Cl,<sup>16</sup> *cis*-[Co(en)<sub>2</sub>NH<sub>3</sub>Cl]Cl<sub>2</sub>,<sup>17</sup> *trans*-[Co(en)<sub>2</sub>Br<sub>2</sub>]Br,<sup>18</sup> *cis*-[Co(en)<sub>2</sub>OH<sub>2</sub>Cl]Cl·H<sub>2</sub>O,<sup>19</sup> *trans*-[Co(en)<sub>2</sub>BrCl]ClO<sub>4</sub>,<sup>20,21</sup> *trans*-[Co(en)<sub>2</sub>OHCl]Cl·H<sub>2</sub>O,<sup>22,23</sup> and *trans*-[Co(en)<sub>2</sub>N<sub>3</sub>Cl]ClO<sub>4</sub><sup>24</sup> were prepared as described in the references cited. *trans*-[Co(en)<sub>2</sub>Br<sub>2</sub>]ClO<sub>4</sub> was obtained by treating a concentrated solution of the bromide salt with concentrated perchloric acid.

The purity of the complexes was ascertained by comparing the absorption spectra measured in the present work with the spectra reported in the literature. Table I lists the wave lengths of the first absorption maximum and the corresponding molar absorptivities for the complexes investigated.

**Materials.** Solutions of iron(II) perchlorate were prepared by dissolving a known amount of analytical grade iron wire in excess perchloric acid. The iron(II) concentration was determined by titration with standard potassium dichromate solutions using sodium diphenylaminesulfonate as the indicator.<sup>25</sup> The iron(III) concentration was calculated from the difference between the amounts of iron dissolved and iron(II) found. In all cases less than 5% of the total iron was present as iron(III). The perchlorate concentration was determined by passing an aliquot of the iron(II) solution through a Dowex 50W-X8 ion-exchange column in the hydrogen form and titrating the eluent with standard sodium hydroxide using phenolphthalein as the indicator. The determination was also carried out by drawing the eluent into a flask containing a weighed sample of sodium carbonate. The excess carbonate was then titrated to the methyl red end point by delivering standard hydrochloric acid into the boiling solution.<sup>26</sup> The hydrogen ion concentration of the iron(II) solutions was calculated from the perchlorate, iron(II), and iron(III) concentrations.

Table I. Spectral Data for Co(III) Complexes

Complex	$\lambda$ , m $\mu^a$	$A^b$	Ref.
<i>cis</i> -Co(en) <sub>2</sub> NH <sub>3</sub> Cl <sup>2+</sup>	523 (525)	70.5 (72)	<i>c</i>
<i>trans</i> -Co(en) <sub>2</sub> NH <sub>3</sub> Cl <sup>2+</sup>	526 (525)	50.8 (48)	<i>c</i>
<i>cis</i> -Co(en) <sub>2</sub> (NCS)Cl <sup>+</sup>	502 (500)	174 (166)	<i>d</i>
<i>trans</i> -Co(en) <sub>2</sub> (NCS)Cl <sup>+</sup>	557 (560)	132 (146)	<i>d</i>
<i>cis</i> -Co(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	535 (536)	95.5 (89)	<i>e</i>
<i>trans</i> -Co(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	615 (620)	43.2 (41)	<i>e</i>
<i>cis</i> -Co(en) <sub>2</sub> OH <sub>2</sub> Cl <sup>2+</sup>	516 (520)	85.5 (90)	<i>f</i>
<i>trans</i> -Co(en) <sub>2</sub> OH <sub>2</sub> Cl <sup>2+</sup>	587 (590)	29.0 (31)	<i>f</i>
<i>trans</i> -Co(en) <sub>2</sub> BrCl <sup>+</sup>	635 (640)	41.4 (41)	<i>g</i>
<i>trans</i> -Co(en) <sub>2</sub> N <sub>3</sub> Cl <sup>+</sup>	575 (578)	254 (230)	<i>h</i>
<i>trans</i> -Co(en) <sub>2</sub> Br <sub>2</sub> <sup>+</sup>	656 (658)	48.5 (54)	<i>e</i>

<sup>a</sup> Wave length for first absorption maximum. Values in parentheses are from the literature. <sup>b</sup> Molar absorptivity at maximum. Values in parentheses are from the literature. <sup>c</sup> R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956). <sup>d</sup> C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *ibid.*, 1691 (1956). <sup>e</sup> M. Linhard and M. Weigel, *Z. anorg. allgem. chem.*, **271**, 101 (1952). <sup>f</sup> Reference 23. <sup>g</sup> Reference 21. <sup>h</sup> Reference 24.

Iron(III) solutions were prepared by oxidizing iron(II) perchlorate with 30% hydrogen peroxide, the excess peroxide being decomposed by boiling the resulting solution for 30 min.

All other chemicals were reagent grade.

**Kinetic Measurements.** Solutions of the reagents and the volumetric flasks containing weighed amounts of the dry complex salts were kept in a constant temperature bath at 25.0 ± 0.1°. The desired volumes of all reagent solutions except iron(II) were pipetted in the volumetric flask. After complete dissolution of the complex salt had been achieved, the iron(II) solution was added; the resulting solution was made up to volume and then transferred rapidly to a cylindrical spectrophotometric cell of the proper path length (1.0, 2.0, 5.0, or 10.0 cm.). The cell was replaced in the thermostated (25.0 ± 0.1°) cell compartment of a Cary Model 15 recording spectrophotometer, and a recording of optical density vs. time at the desired wave length was obtained. The wave length chosen was usually that corresponding to the first absorption maximum of the cobalt(III) complex under study. For the slower reactions, the optical density corresponding to complete reaction was measured after 10 half-lives.

For some of the more rapid reactions, experiments were also performed by delivering all the reagent solutions except that of iron(II) into the spectrophotometric cell. The cell was placed in the compartment and allowed to equilibrate for a period of 15 min. The iron(II) solution was then pipetted into the cell. At this point, the cell was covered, shaken two to three times, and then replaced rapidly in the cell compartment. In this manner, the first optical density measurement was obtained within 30 sec. The optical density corresponding to complete reaction was measured after 7 half-lives.

In most experiments the iron(II) was in excess with respect to the cobalt(III), and pseudo-first-order rate constants were obtained from the slopes of plots of log ( $D_t - D_\infty$ ) vs. time. The optical densities at time  $t$  and after the reaction is complete are  $D_t$  and  $D_\infty$ , respectively. Since the reaction of *trans*-Co(en)<sub>2</sub>-OH<sub>2</sub>Cl<sup>2+</sup> was rather rapid, some experiments were carried out at low iron(II) concentrations. In these cases, second-order kinetics were obeyed.

- (10) A. Haim, *J. Am. Chem. Soc.*, **85**, 1016 (1963); **86**, 2352 (1964).
- (11) W. C. Fernelius, *Inorg. Syn.*, **2**, 222 (1946).
- (12) M. Linhard and G. Stirn, *Z. anorg. allgem. chem.*, **268**, 118 (1952).
- (13) S. M. Jørgensen, *J. prakt. Chem.*, **41**, 448 (1890).
- (14) A. Werner, *Ann.*, **386**, 133 (1912).
- (15) Reference 14, p. 139.
- (16) Reference 14, p. 171.
- (17) Reference 14, p. 165.
- (18) Reference 14, p. 111.
- (19) Reference 14, p. 123.
- (20) Reference 14, p. 118.
- (21) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).
- (22) J. Meisenheimer, *Ann.*, **438**, 255 (1924).
- (23) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).
- (24) P. J. Staples and M. L. Tobe, *ibid.*, 4812 (1960).
- (25) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," The Macmillan Co., New York, N. Y., 1952, p. 579.
- (26) Reference 25, p. 523.

All reactions were studied at a total perchlorate concentration of 1.0 *M*, maintained by addition of sodium perchlorate. In some cases, the high perchlorate concentration limited the range over which the concentration of the complex could be varied.

## Results

Since many of the reactions investigated in the present study proceed at rather low rates, initially we were concerned about the possibility of aquation or isomerization interfering with the reduction of the cobalt(III) complexes. For the studies with the *trans* complexes, which generally react with iron(II) more rapidly than the corresponding *cis* complexes, it was possible to minimize the complications arising from aquation or isomerization by working at sufficiently high concentrations of iron(II). For the studies with the *cis* complexes it was not practical to increase the iron(II) concentration to the point where aquation or isomerization became negligible compared to reduction. In Table II we present a compilation of the rate constants (25°) for aquation (and isomerization when pertinent) of the complexes studied, together with the maximum contribution of aquation or isomerization under the experimental conditions used for reduction (this maximum contribution corresponds to the lowest [Fe<sup>2+</sup>] reported). An examination of column 5 of Table II shows that for the *cis* complexes the contributions of aquation or isomerization to the disappearance of the reactants were substantial, and the treatment of the data for these cases will be described below. For the *trans* complexes, as shown in column 3 of Table II, the maximum contributions of aquation or isomerization were 8% or less, and for most experiments the contributions were less than 2%. However, it must be noted that the values listed in column 3 of Table II represent the contributions of aquation or isomerization as reduction proceeds. For the reactions of the *trans* complexes (as well as for the *cis* complexes), with the exception of *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>2+</sup>, the times required for the dissolution of the solid complex salts were short compared to the times for the kinetic measurements, and therefore additional aquation prior to addition of iron(II) was unimportant. In these cases it was found that the optical densities did not vary after 7 half-lives had elapsed, and usually the values of *D*<sub>∞</sub> were measured at times corresponding to 10 half-lives. For the reactions of *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>2+</sup> at the higher iron(II) concentrations, however, isomerization during the time required for dissolution of the salt and the additional equilibration in the cell compartment was rather important. In these cases it was found that the optical densities continued to decrease after long times. For example, for the reaction of 2.37 × 10<sup>-3</sup> *M* *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>2+</sup> with 0.064 *M* Fe<sup>2+</sup> the optical densities after 7, 9, 11, 13, 18, and 30 half-lives were 0.142, 0.139, 0.133, 0.130, 0.122, and 0.118, respectively. The slow decrease in optical density after substantially all the *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>2+</sup> had disappeared was caused by the reduction of *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>2+</sup> formed by isomerization of the *trans* complex during dissolution and equilibration.<sup>27</sup> Since the changes in optical densities

(27) The presence of *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>2+</sup> was confirmed directly by scanning the solutions after 7 half-lives had elapsed. The solutions

Table II. Rate Constants<sup>a</sup> for Aquation of *cis*- and *trans*-Co(en)<sub>2</sub>XCl<sup>2+</sup>

X	<i>trans</i>	<i>R</i> <sup>b</sup>	<i>cis</i>	<i>R</i> <sup>b</sup>	Ref.
NH <sub>3</sub>	3.4 × 10 <sup>-7</sup>	0.041	5 × 10 <sup>-7</sup>	0.20	<i>c</i>
NCS	5 × 10 <sup>-8</sup>	0.001	1.1 × 10 <sup>-8</sup>	0.14	<i>d</i>
Cl	3.53 × 10 <sup>-5</sup>	0.02	2.44 × 10 <sup>-4</sup>	0.46	<i>e</i>
Br	4.5 × 10 <sup>-5</sup> <sup>f</sup>	0.08 <sup>g</sup>	...	...	<i>h</i>
Br	1.12 × 10 <sup>-5</sup> <sup>i</sup>	0.08 <sup>g</sup>	...	...	<i>h</i>
H <sub>2</sub> O	2.5 × 10 <sup>-6</sup>	0.0015	1.6 × 10 <sup>-6</sup>	0.017	<i>j</i>
H <sub>2</sub> O	7.0 × 10 <sup>-5</sup> <sup>k</sup>	0.04 <sup>l</sup>	2.6 × 10 <sup>-5</sup> <sup>m</sup>	0.27 <sup>l</sup>	<i>e</i>
N <sub>3</sub>	2.2 × 10 <sup>-4</sup>	0.058	...	...	<i>n</i>
Br <sup>o</sup>	1.39 × 10 <sup>-4</sup>	0.054	...	...	<i>h</i>

<sup>a</sup> At 25°; units are sec.<sup>-1</sup>. <sup>b</sup> Ratio of rate constant for aquation to pseudo-first-order rate constant for reduction at the lowest [Fe<sup>2+</sup>] reported in Tables III and IV. <sup>c</sup> M. L. Tobe, *J. Chem. Soc.*, 3776 (1959). The value for the *cis* complex was calculated from the observed value 4 × 10<sup>-6</sup> sec.<sup>-1</sup> at 62.6° and an assumed *E*<sub>act</sub> = 23 kcal. <sup>d</sup> M. E. Baldwin and M. L. Tobe, *ibid.*, 4275 (1960). <sup>e</sup> Reference 23. <sup>f</sup> Rate constant for loss of Cl<sup>-</sup>. <sup>g</sup> Calculated using rate constant for aquation of both Cl<sup>-</sup> and Br<sup>-</sup>. <sup>h</sup> S. C. Chan and M. L. Tobe, *ibid.*, 5700 (1963). <sup>i</sup> Rate constant for loss of Br<sup>-</sup>. <sup>j</sup> S. C. Chan, *ibid.*, 5137 (1963). <sup>k</sup> Rate constant for *trans* to *cis* isomerization; calculated from data in ref. 23. <sup>l</sup> Calculated using rate constant for isomerization. <sup>m</sup> Rate constant for *cis* to *trans* isomerization; calculated from data in footnote *e*. <sup>n</sup> Reference 24. <sup>o</sup> The complex is Co(en)<sub>2</sub>Br<sub>2</sub><sup>+</sup>.

at long times were found to be very slow, a fairly reliable value for *D*<sub>∞</sub> could be obtained by measuring the optical densities at times corresponding to 7 half-lives.

A summary of the kinetic measurements for the reactions of the *trans*-substituted chlorobis(ethylenediamine)cobalt(III) complexes is presented in Table III. Most of the experiments were performed under pseudo-first-order conditions ([Co(III)]/[Fe<sup>2+</sup>] < 0.05) by following the decrease in light absorption of the cobalt(III) reactant as a function of time. Plots of log (*D*<sub>*t*</sub> - *D*<sub>∞</sub>) vs. time were linear for at least 3 half-lives, and pseudo-first-order rate constants were calculated from the slopes of such plots. In the case of *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup> the reaction was studied in the presence of 0.050 *M* Fe<sup>3+</sup> by following the increase in light absorption of the FeNCS<sup>2+</sup> product as a function of time. By using an excess of iron(III), the ratio [FeNCS<sup>2+</sup>]/[SCN<sup>-</sup>] remained constant as the reaction proceeded, and under these conditions, as shown in Appendix A, the quantity *D*<sub>∞</sub> - *D*<sub>*t*</sub> is proportional to the concentration of *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup>. Therefore, the pseudo-first-order rate constant was obtained from the linear plot (followed for 1 half-life) of log (*D*<sub>∞</sub> - *D*<sub>*t*</sub>) vs. time. A blank experiment under the same conditions as for reduction, except that it was performed in the absence of iron(II), showed undetectable catalysis of thiocyanate aquation by iron(III) during the time of the experiment. From the measured pseudo-first-order rate constants *k*<sub>m</sub> and the known iron(II) concentrations, second-order rate constants *k* were calculated (*k* = *k*<sub>m</sub>/[Fe<sup>2+</sup>]). Five experiments for *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>2+</sup> were performed under comparable concentrations of Co(III) and Fe(II). From the appropriate second-order plots<sup>23</sup> (linear up to 90% reaction), second-order rate constants *k* were obtained. The reductions of the *trans* complexes were found to

were found to exhibit an absorption maximum around 510 mμ with an optical density considerably higher than that corresponding to quantitative reduction to cobalt(II).

(28) The equation is ln {(*D*<sub>0</sub> - *D*<sub>∞</sub>) - (*a/b*)(*D*<sub>0</sub> - *D*<sub>*t*</sub>)/(*D*<sub>*t*</sub> - *D*<sub>∞</sub>)} = (*b* - *a*)*kt*.

**Table III.** The Reactions of *trans*-Co(en)<sub>2</sub>XCl<sup>+n</sup> with Fe<sup>+2</sup> (25°, Σ[ClO<sub>4</sub><sup>-</sup>] = 1.0 M)

X	λ, mμ <sup>a</sup>	[Co(III)] × 10 <sup>3</sup> , M	[Fe <sup>+2</sup> ], M	[H <sup>+</sup> ], M	No. of expt.	k, M <sup>-1</sup> sec. <sup>-1b</sup>
NH <sub>3</sub>	526	3.71–7.00	0.128–0.448	0.10–0.48	5	6.6 ± 0.3 × 10 <sup>-5</sup>
NCS	460	0.105	0.384	0.10	1	1.3 × 10 <sup>-4c</sup>
Cl	615	0.272–1.16	0.064–0.448	0.040–0.748	29	3.2 ± 0.4 × 10 <sup>-2d</sup>
Br	635	0.798–1.68	0.064–0.420	0.038–0.746	7	3.6 ± 0.3 × 10 <sup>-2e</sup>
H <sub>2</sub> O	587	2.29–4.68	0.0064–0.064	0.010–0.865	10	2.4 ± 0.2 × 10 <sup>-1f</sup>
N <sub>3</sub>	575	0.345–1.11	0.064–0.256	0.087–0.730	9	6.2 ± 0.4 × 10 <sup>-2g</sup>
Br <sup>h</sup>	410	0.365–1.28	0.122–0.448	0.064–0.747	23	2.2 ± 0.2 × 10 <sup>-2h,i</sup>

<sup>a</sup> Wave length at which spectrophotometric measurements were performed. <sup>b</sup> Second-order rate constant defined by the rate law  $k[\text{Co(III)}][\text{Fe(II)}]$ ; average values and standard deviations are listed. <sup>c</sup> In the presence of 0.050 M Fe<sup>+3</sup>. <sup>d</sup> One measurement at 325 mμ yielded a value of  $3.07 \times 10^{-2}$ ; measurements in the presence of 0.0148 and 0.059 M Fe<sup>+3</sup> yielded values of  $3.05 \times 10^{-2}$  and  $3.50 \times 10^{-2}$ , respectively. <sup>e</sup> Measurements at 360 mμ gave rate constants approximately 20% lower than the average reported above. Measurements in the presence of 0.0137 and 0.0487 M Fe<sup>+3</sup> yielded values of  $3.43 \times 10^{-2}$  and  $3.74 \times 10^{-2}$ , respectively. <sup>f</sup> The concentration of Fe<sup>+3</sup> varied from  $5.88 \times 10^{-5}$  to  $4.52 \times 10^{-3}$ . There may be a trend toward decreasing rate with increasing [Fe<sup>+3</sup>]. <sup>g</sup> The rate constant  $5.80 \times 10^{-2}$  measured at the highest [H<sup>+</sup>] appears to be somewhat small. <sup>h</sup> The complex is Co(en)<sub>2</sub>Br<sub>2</sub><sup>+</sup>. <sup>i</sup> One measurement at 656 mμ yielded a value of  $2.28 \times 10^{-2}$ .

**Table IV.** The Reactions of *cis*-Co(en)<sub>2</sub>XCl<sup>+n</sup> with Fe<sup>+2</sup> (25°, Σ[ClO<sub>4</sub><sup>-</sup>] = 1.0 M)

X	λ, mμ <sup>a</sup>	[Co(III)] × 10 <sup>3</sup> , M	[Fe <sup>+2</sup> ], M	[H <sup>+</sup> ], M	No. of expts.	k, M <sup>-1</sup> sec. <sup>-1b</sup>
NH <sub>3</sub>	523	2.71–5.12	0.128–0.448	0.100–0.480	5	1.8 ± 0.1 × 10 <sup>-5</sup>
NCS	460	0.091	0.384	0.100	1	1.7 × 10 <sup>-4c</sup>
Cl	505	1.82–1.96	0.128–0.448	0.100–0.164	5	1.6 ± 0.4 × 10 <sup>-3</sup>
H <sub>2</sub> O <sup>d</sup>	505	1.82–1.96	0.064–0.448	0.100–0.164	6	4.6 ± 0.3 × 10 <sup>-4</sup>
H <sub>2</sub> O <sup>e</sup>	516	1.56–3.20	0.256–0.384	0.0448–0.445	6	4.5 ± 0.2 × 10 <sup>-4</sup>
H <sub>2</sub> O <sup>d</sup>	534	1.49–7.10	0.064–0.256	0.0417–0.748	8	4.8 ± 0.3 × 10 <sup>-4</sup>

<sup>a</sup> Wave length at which the spectrophotometric measurements were performed. <sup>b</sup> Second-order rate constant defined by the rate law  $k[\text{Co(III)}][\text{Fe(II)}]$ . Average values and standard deviations are listed. <sup>c</sup> In the presence of 0.050 M Fe<sup>+3</sup>. <sup>d</sup> Extrapolated from measurements with *cis*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>; see text. <sup>e</sup> Starting material is *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+2</sup>

obey the rate law  $k[\text{Co(III)}][\text{Fe}^{+2}]$ . This conclusion was reached by establishing the constancy of  $k$  upon moderate variations in [Co(III)] and rather important variations in [Fe<sup>+2</sup>]. A severe test of the possible dependence of  $k$  upon [H<sup>+</sup>] was carried out, and it was found that  $k$  is independent of [H<sup>+</sup>], a significant result, especially for *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+2</sup> and *trans*-Co(en)<sub>2</sub>N<sub>3</sub>Cl<sup>+</sup>. Average values of  $k$ , together with the corresponding standard deviations, are listed in column 7 of Table III.<sup>29</sup>

A summary of the kinetic measurements for the reactions of the *cis*-substituted chlorobis(ethylenediamine)cobalt(III) complexes is presented in Table IV. All the experiments, except for the run with *cis*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup>, were performed under pseudo-first-order conditions by following the decrease in light absorption of the cobalt(III) reactant as a function of time. In the case of *cis*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup> the formation of FeNCS<sup>+2</sup> in the presence of 0.050 M Fe<sup>+3</sup> was followed as a function of time. A blank experiment showed no appreciable iron(III) catalysis of

(29) The quality of the data leaves something to be desired, as seen from the rather large standard deviations. The extensive studies with *trans*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> (29 runs) and *trans*-Co(en)<sub>2</sub>Br<sub>2</sub><sup>+</sup> (23 runs) reflect our concern about this question. In many instances reproducibility was excellent. For example, three runs with *trans*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> at 0.286, 0.384, and 0.448 M Fe<sup>+2</sup> gave rate constants of  $3.24 \times 10^{-2}$ ,  $3.12 \times 10^{-2}$ , and  $3.16 \times 10^{-2}$  M<sup>-1</sup> sec.<sup>-1</sup>, respectively. In other instances, reproducibility was poor. For example, duplicate experiments for *trans*-Co(en)<sub>2</sub>Br<sub>2</sub><sup>+</sup> at 0.122 M Fe<sup>+2</sup> gave rate constants of  $2.20 \times 10^{-3}$  and  $1.96 \times 10^{-3}$  M<sup>-1</sup> sec.<sup>-1</sup>. In spite of extreme precautions in a number of aspects of the experimental procedure, no clues as to the reasons for the rather large standard deviations have been uncovered. As a consequence, some of the statements in the footnotes of Table III cannot be made more definite.

thiocyanate aquation. However, as shown in Table II, appreciable chloride aquation occurs during reduction. The aquation does not produce free thiocyanate ion and therefore does not contribute to the optical density at 460 mμ. Nevertheless the cobalt(III) available for reduction decreases as aquation proceeds, and it is shown in Appendix A that the plot of  $\log(D_{\infty} - D_t)$  vs. time (which was followed for 1 half-life and conformed to linearity) has a slope equal to  $(k_p + k_a)/2.3$ , where  $k_p$  is the pseudo-first-order rate constant for reduction of *cis*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup> and  $k_a$  the first-order rate constant for aquation (release of chloride ion). The second-order rate constant for reduction ( $k_p/[\text{Fe}^{+2}]$ ) was therefore calculated from the measured slope, the literature value of  $k_a$ ,<sup>30</sup> and the known concentration of iron(II).

Aquation of *cis*-Co(en)<sub>2</sub>NH<sub>3</sub>Cl<sup>+2</sup> is important relative to reduction. The aquation product, *cis*-Co(en)<sub>2</sub>NH<sub>3</sub>OH<sub>2</sub><sup>+3</sup>, is relatively inert with respect to reduction by iron(II) and therefore accumulates in the solution. The kinetic scheme is identical with that for *cis*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup> (see Appendix A), and the slopes of plots of  $\log(D_t - D_{\infty})$  vs. time (linear for 3 half-lives) yielded values for  $k_p + k_a$ , from which the second-order rate constants were calculated.

The reactions of *cis*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> and *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+2</sup> were more complicated than any of the others. As shown in Table II, *cis*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> aquates at a rate comparable to reduction and *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+2</sup> undergoes isomerization in competition with reduction.

(30) Footnote *d* of Table II.

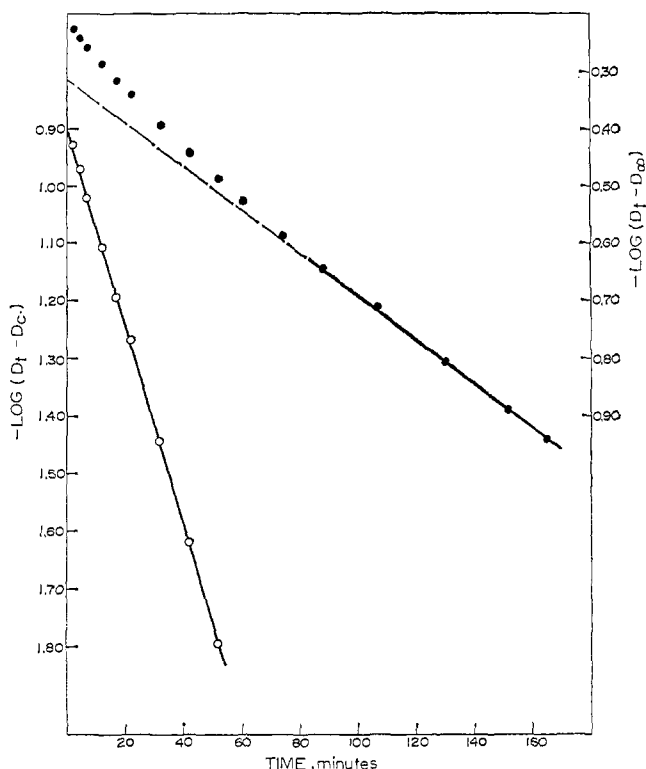
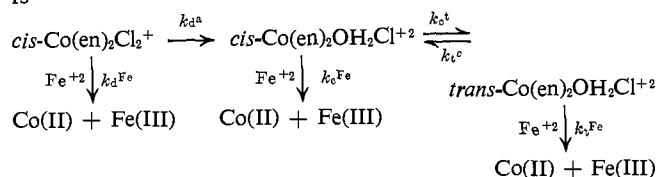


Figure 1. Plots for a typical reaction between  $cis\text{-Co(en)}_2\text{Cl}_2^+$  and  $\text{Fe}^{+2}$  ( $[\text{Co(III)}] = 1.82 \times 10^{-3} M$ ;  $[\text{Fe}^{+2}] = 0.261 M$ ;  $[\text{H}^+] = 0.147 M$ ): ●,  $\log(D_t - D_\infty)$ ; ○,  $\log(D_t - D_c)$ .

For a solution containing initially pure  $cis\text{-Co(en)}_2\text{Cl}_2^+$  in the presence of iron(II), the general kinetic scheme is



Baldwin, Chan, and Tobe<sup>23</sup> have established that aquation of  $cis\text{-Co(en)}_2\text{Cl}_2^+$  yields exclusively the *cis* complex. Under the experimental conditions used the rates of all the reactions, with the exception of the reduction of  $trans\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$ , were of the same order of magnitude. The rate constants for aquation ( $k_d^a$ ) and isomerization ( $k_c^t$  and  $k_c^e$ ) are known (see Table II). The rate constant for reduction of  $trans\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$  ( $k_r^{\text{Fe}}$ ) was measured in the present work (see Table III). The two rate constants to be determined are  $k_d^{\text{Fe}}$  and  $k_t^{\text{Fe}}$ . This determination was accomplished in the following manner. The optical densities of the solutions under study were measured at 505  $m\mu$  (an isosbestic point for  $cis\text{-Co(en)}_2\text{Cl}_2^+$  and  $cis\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$ ) as a function of time. The plots of  $\log(D_t - D_\infty)$  vs. time, where  $D_\infty$  is the optical density after all the Co(III) has been reduced to Co(II), were found to consist of a "fast" rate followed by a "slow" rate. This behavior is illustrated in Figure 1 for one of the experiments listed in Table IV. After a certain period of time (which depended on  $[\text{Fe}^{+2}]$ ), the plots conformed to linearity, and the slopes of the linear portions gave a measure of the pseudo-first-order rate constants for the disappearance of  $cis\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$ . The mathematical derivation is given in Appendix B and, in physical terms,

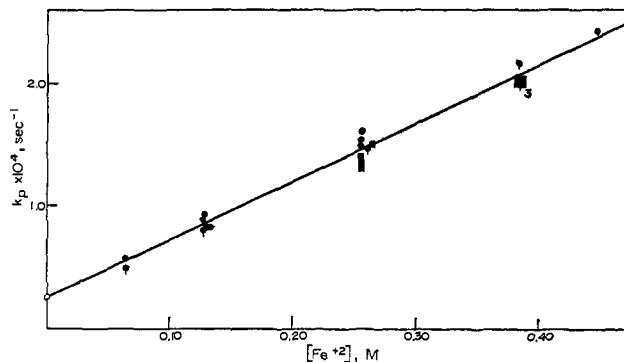


Figure 2. The dependence of the pseudo-first-order rate constant for disappearance of  $cis\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$  upon  $\text{Fe}^{+2}$  concentration: ●, measurements at 505  $m\mu$ ; ○, measurements at 534  $m\mu$ ; ■, measurements at 516  $m\mu$ ; ○, intercept calculated from rate constant for *cis* to *trans* isomerization (the point labeled 3 signifies that two measurements at 516  $m\mu$  and one measurement at 505  $m\mu$  gave identical rate constants).

the linear behavior sets in when the  $cis\text{-Co(en)}_2\text{Cl}_2^+$  reactant has been exhausted (either by reduction or aquation) and the only Co(III) species present in appreciable concentration is  $cis\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$ .<sup>31</sup> The pseudo-first-order rate constants for disappearance of  $cis\text{-Co(en)}_2\text{Cl}_2^+$  were obtained from the slopes of plots of  $\log(D_t - D_c)$  vs. time, where  $D_c$  is the optical density at time  $t$  obtained by extrapolating the linear portion of the  $\log(D_t - D_\infty)$  vs. time plots to time zero. The behavior encountered is illustrated in Figure 1. As shown in Appendix B, the slopes of the  $\log(D_t - D_c)$  plots are equal to  $(k_d^a + k_d^{\text{Fe}}[\text{Fe}^{+2}])/2.3$ . Values of  $k_d^{\text{Fe}}$  were calculated from the known values of  $k_d^a$  and  $[\text{Fe}^{+2}]$ .

The validity of the treatment outlined above was checked by measuring independently the rate constant for the disappearance of pure  $cis\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$ . The optical density measurements were performed at 516  $m\mu$ , and the pseudo-first-order rate constants were obtained from the slopes of plots of  $\log(D_t - D_\infty)$  vs. time (linear for 3 half-lives). The pseudo-first-order rate constants for disappearance of  $cis\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$  measured at 516 and 505  $m\mu$  are plotted vs.  $[\text{Fe}^{+2}]$  in Figure 2. Also included in Figure 2 are measurements at 534  $m\mu$ . These measurements were carried out using  $cis\text{-Co(en)}_2\text{Cl}_2^+$  as the starting material. Since 534 is not an isosbestic point, the measurements are useless in determining the rate of disappearance of  $cis\text{-Co(en)}_2\text{Cl}_2^+$ . However, after the  $cis\text{-Co(en)}_2\text{Cl}_2^+$  is consumed, the measurements are useful in determining the rate of disappearance of  $cis\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$ . The agreement between the three sets of data is good, and this lends strong support for the interpretation of the measurements in the  $cis\text{-Co(en)}_2\text{Cl}_2^+ - \text{Fe}^{+2}$  system. Figure 2 illustrates another important feature of the system: the disappearance of  $cis\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$  proceeds by two parallel paths, one first order in  $[\text{Fe}^{+2}]$  and one independent of  $[\text{Fe}^{+2}]$ . The path independent of  $[\text{Fe}^{+2}]$  corresponds to the isomerization  $cis \rightarrow trans$  followed by the rapid reaction of  $trans\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$  with  $\text{Fe}^{+2}$ , a reaction which is 3600 times faster than that of the *cis* complex. The mathematical treatment in Appendix B shows that the pseudo-

(31) It will be shown that  $trans\text{-Co(en)}_2\text{OH}_2\text{Cl}^{+2}$  disappears as rapidly as it is formed.

first-order rate constant for the disappearance of *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup> is given by  $k_c^t + k_c^{\text{Fe}}[\text{Fe}^{+2}]$ . Therefore, the intercept in Figure 2 is identified as  $k_c^t$  and the slope as  $k_c^{\text{Fe}}$ . Actually, the intercept in Figure 2 was taken as  $2.6 \times 10^{-5} \text{ sec.}^{-1}$ , the literature value<sup>23</sup> for  $k_c^t$ , and it is noteworthy that the present measurements are in excellent agreement with the literature value. Values of  $k_c^{\text{Fe}}$  for the individual runs were obtained from the measured pseudo-first-order rate constants and the known values of  $k_c^t$  and  $[\text{Fe}^{+2}]$ .

The reductions of the *cis* complexes were found to obey the rate law  $k[\text{Co(III)}][\text{Fe(II)}]$ . This conclusion was reached by establishing the constancy of  $k$  upon moderate variations in Co(III) and rather important variations in  $[\text{Fe}^{+2}]$  and  $[\text{H}^+]$ . The  $[\text{H}^+]$  independence for *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup> is of special significance. Average values of  $k$ , together with the corresponding standard deviations, are listed in column 7 of Table IV. In spite of the fact that the *cis* systems are more complicated than the corresponding *trans* systems, the kinetic data for the *cis* compounds appear to be of reasonable quality. An exception occurs for *cis*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>; the rate constant is of poor quality since it is obtained from measurements of the small differences  $D_i - D_\infty$ .

Studies with *cis*-Co(en)<sub>2</sub>Br<sub>2</sub><sup>+</sup> and *cis*-Co(en)<sub>2</sub>N<sub>3</sub>Cl<sup>+</sup> were not carried out because of our inability to prepare pure samples of these compounds, although it must be admitted that a great effort was not spent in purifying the samples obtained. Some attempts were made to study the reduction of *cis*-Co(en)<sub>2</sub>BrCl<sup>+</sup>. Unfortunately, aquation is very important as compared to reduction and yields both *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup> and *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Br<sup>+</sup>.<sup>32</sup> Preliminary experiments seemed to indicate that the log ( $D_i - D_\infty$ ) vs. time plot consisted of three exponentials, and therefore studies were not carried out any further.

## Discussion

The nonbridging ligand effects observed in the reductions of *cis*- and *trans*-substituted chlorobis(ethylenediamine)cobalt(III) complexes by iron(II) can be classified in the following three categories: (a) effects of geometry—relative rates of reduction of various pairs of *cis* and *trans* isomers; (b) effects of changing the nature of one nonbridging ligand—variation in rates along a series of constant geometry (*cis* or *trans*); (c) effects of chelation—change in rates upon substitution of ammonia by ethylenediamine. The present investigation represents a fairly systematic study of effects a and b, and a few incidental observations on effect c.

The observed effects have an intrinsic interest in that they may provide a better understanding of electron-transfer reactions. In addition, these effects might be used to adduce evidence for the mechanism of reduction of cobalt(III) complexes by iron(II). It must be stated at the outset that even for the most reactive of the complexes studied (*trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup>), the rate of disappearance of FeCl<sup>+</sup> (if formed as the primary product of the reaction) is significantly larger

than the rate of reduction of Co(III), and therefore a direct test of mechanism (inner- or outer-sphere) does not seem feasible.<sup>35</sup> In the past, attempts have been made to develop indirect criteria to establish mechanism, and some correlations between the sensitivity of the rates of reduction of Co(NH<sub>3</sub>)<sub>5</sub>X<sup>+n</sup> complexes to the nature of X and mechanism have been made.<sup>36,37</sup> Perhaps comparisons of the effects outlined above in the reduction of Co(III) complexes for reducing agents which are known to proceed by an inner-sphere mechanism (Cr<sup>+2</sup>) or an outer-sphere mechanism (Ru(NH<sub>3</sub>)<sub>6</sub><sup>+2</sup>) might be useful in determining the mechanism for reducing agents such as Eu<sup>+2</sup>, V<sup>+2</sup>, Fe<sup>+2</sup>, where the direct test fails. Too few data have been recorded to allow us to judge the utility of rate comparisons for nonbridging ligand effects. However, since CoCl<sup>+</sup> has been shown to react with Fe<sup>+2</sup> via a bridged activated complex,<sup>38</sup> it is reasonable to assume a similar mechanism for our reductions.

Once a bridging mechanism is assumed, it is necessary to inquire about the nature of the bridging ligand for complexes of the type Co(en)<sub>2</sub>XCl<sup>+n</sup>.<sup>39</sup> For X = NH<sub>3</sub>, there is no doubt that Cl<sup>-</sup> will be the bridging ligand. For X = SCN<sup>-</sup>, since Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>+</sup> reacts at least 100 times faster than Co(NH<sub>3</sub>)<sub>5</sub>NCS<sup>+2</sup>,<sup>9,37</sup> there is little doubt that Cl<sup>-</sup> will be preferred over SCN<sup>-</sup>. For X = H<sub>2</sub>O, the lack of a path inversely proportional to  $[\text{H}^+]$  and the fact that Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>+</sup> reacts at least 10<sup>3</sup> times faster than Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> make it unlikely that H<sub>2</sub>O is acting as the bridge, and again it is safe to assume Cl<sup>-</sup> bridging. For X = N<sub>3</sub><sup>-</sup>, we are inclined to believe that N<sub>3</sub><sup>-</sup> is the bridging ligand. First, Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub><sup>+2</sup> reacts approximately six times faster than Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>+2</sup>,<sup>9,10,37</sup> showing that when NH<sub>3</sub> is *trans* to the bridging group, N<sub>3</sub><sup>-</sup> is a more efficient bridge than Cl<sup>-</sup>. Second, substitution of NH<sub>3</sub> by N<sub>3</sub><sup>-</sup> in the *trans* position of Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub><sup>+2</sup> produces a modest increase (a factor of 4.2) in the rate of reduction, whereas substitution of NH<sub>3</sub> by Cl<sup>-</sup> in the *trans* position of Co(en)<sub>2</sub>NH<sub>3</sub>Cl<sup>+2</sup> produces a large increase (a factor of 245) in the rate of reduction; if similar effects of Cl<sup>-</sup> and N<sub>3</sub><sup>-</sup> as *trans* ligands are operative in *trans*-Co(en)<sub>2</sub>N<sub>3</sub>Cl<sup>+</sup>, then it is reasonable to suggest that Cl<sup>-</sup> would greatly facilitate attack at N<sub>3</sub><sup>-</sup>. Third, there is no H<sup>+</sup>-dependent path (up to 0.730 M H<sup>+</sup>) for the reduction of *trans*-Co(en)<sub>2</sub>N<sub>3</sub>Cl<sup>+</sup>; since appreciable acid catalysis was observed in the reduction of *trans*-Co(NH<sub>3</sub>)<sub>4</sub>(N<sub>3</sub>)<sub>2</sub><sup>+</sup>,<sup>10</sup> reduction of *trans*-Co(en)<sub>2</sub>N<sub>3</sub>Cl<sup>+</sup> via a Cl<sup>-</sup> bridge would be expected to exhibit acid catalysis; no such catalysis was observed, however, and attack at N<sub>3</sub><sup>-</sup> is indicated. For X = Br<sup>-</sup>, there is great uncertainty as to the preferred bridging ligand. Probably both Cl<sup>-</sup> and Br<sup>-</sup> serve as bridges. Nevertheless, it might be argued

(35) Calculations indicate that at 1 M Fe<sup>+2</sup> and 1 M H<sup>+</sup>, the concentration of FeCl<sup>+</sup> would reach a maximum after 0.26 sec. At this time, only approximately 6% of the *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup> would have reacted, and approximately 1.3% of the original *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup> would have been transformed into FeCl<sup>+</sup> by reaction with Fe<sup>+2</sup>. It is doubtful whether such a small amount of FeCl<sup>+</sup> could be detected in the presence of large amounts of Co(III) and Fe(II).

(36) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

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

(38) T. J. Conocchioli, G. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 1453 (1964).

(39) The present discussion is patterned after the one given previously for complexes of the class Co(NH<sub>3</sub>)<sub>4</sub>XN<sub>3</sub><sup>+n</sup>.<sup>10</sup>

(32) Footnote h of Table II.

(33) R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

(34) R. J. Campion, T. J. Conocchioli, and N. Sutin, *ibid.*, **86**, 4591 (1964).

Table V. Effects of Geometry, Substitution of One NH<sub>3</sub>, and Chelation on the Rates of Reduction of Cobalt(III) Ammine Complexes (25 °)

Complex	Reductant	R <sub>1</sub> <sup>a</sup>	R <sub>2</sub> <sup>b</sup>	R <sub>3</sub> <sup>c</sup>	R <sub>4</sub> <sup>d</sup>	R <sub>5</sub> <sup>e</sup>	Mechanism	Ref.
Co(en) <sub>2</sub> NH <sub>3</sub> Cl <sup>2+</sup>	Fe <sup>2+</sup>	3.7	1	1	0.012	0.045	Unknown	This work
Co(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	Fe <sup>2+</sup>	20	44 <sup>f</sup>	245 <sup>f</sup>	...	...	Unknown	This work
Co(en) <sub>2</sub> (NCS)Cl <sup>+</sup>	Fe <sup>2+</sup>	0.8	10	2	...	...	Unknown	This work
Co(en) <sub>2</sub> OH <sub>2</sub> Cl <sup>2+</sup>	Fe <sup>2+</sup>	520	26	3600	...	...	Unknown	This work
Co(en) <sub>2</sub> BrCl <sup>+</sup>	Fe <sup>2+</sup>	...	...	≤ 530 <sup>g</sup>	...	...	Unknown	This work
Co(NH <sub>3</sub> ) <sub>4</sub> (N <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Fe <sup>2+</sup>	0.2 <sup>f</sup>	21	4.2 <sup>f</sup>	...	...	Unknown	h
Co(NH <sub>3</sub> ) <sub>4</sub> OH <sub>2</sub> N <sub>3</sub> <sup>2+</sup>	Fe <sup>2+</sup>	68	41	2800	...	...	Unknown	h
Co(NH <sub>3</sub> ) <sub>4</sub> (N <sub>3</sub> H)N <sub>3</sub> <sup>2+</sup>	Fe <sup>2+</sup>	...	...	>158	...	...	Unknown	h
Co(en) <sub>2</sub> NH <sub>3</sub> Cl <sup>2+</sup>	V <sup>2+</sup>	11	...	...	0.16	1.8	Unknown	i
Co(en) <sub>2</sub> NH <sub>3</sub> SO <sub>4</sub> <sup>+</sup>	V <sup>2+</sup>	? <sup>i</sup>	...	...	0.80 (?) <sup>j</sup>	0.80 (?) <sup>j</sup>	Unknown	k
Co(NH <sub>3</sub> ) <sub>4</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	0.2	...	...	...	...	Outer sphere	l
Co(en) <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	10	...	...	...	...	Outer sphere	l
Co(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> <sup>3+</sup>	Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup>	...	80	...	...	...	Outer sphere	l
Co(en) <sub>2</sub> NH <sub>3</sub> SO <sub>4</sub> <sup>2+</sup>	Cr <sup>2+</sup>	? <sup>i</sup>	...	...	0.15 (?) <sup>j</sup>	0.15 (?) <sup>j</sup>	Bridged	k
Co(en) <sub>2</sub> NH <sub>3</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Cr <sup>2+</sup>	? <sup>i</sup>	...	...	1 (?) <sup>j</sup>	1 (?) <sup>j</sup>	Bridged	k
Co(NH <sub>3</sub> ) <sub>4</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Cr <sup>2+</sup>	1 (?) <sup>m</sup>	...	42 <sup>f</sup>	...	...	Bridged	n, o
Co(en) <sub>2</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Cr <sup>2+</sup>	>40 (?), <sup>p</sup>	<0.25 (?), <sup>p</sup>	10 (?), <sup>q</sup>	<0.007 (?), <sup>p</sup>	0.27 (?), <sup>q</sup>	Bridged	k
Co(NH <sub>3</sub> ) <sub>4</sub> OH <sub>2</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Cr <sup>2+</sup>	...	260 <sup>r</sup>	...	...	...	Double bridged	o
Co(NH <sub>3</sub> ) <sub>4</sub> OH <sub>2</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Cr <sup>2+</sup>	...	<20 <sup>s</sup>	...	...	...	Double bridged	o
Co(NH <sub>3</sub> ) <sub>4</sub> (OH <sub>2</sub> ) <sub>2</sub> <sup>3+</sup>	Cr <sup>2+</sup>	...	7 <sup>f</sup>	...	...	...	Bridged	o

<sup>a</sup> Ratio of rate constant for *trans* complex to rate constant for *cis* complex. <sup>b</sup> Ratio of rate constant for *cis* complex to rate constant for corresponding complex where the *cis* ligand has been replaced by NH<sub>3</sub>. <sup>c</sup> Ratio of rate constant for *trans* complex to rate constant for corresponding complex where the *trans* ligand has been replaced by NH<sub>3</sub>. <sup>d</sup> Ratio of rate constant for *cis* complex to rate constant for corresponding complex where all ethylenediamine groups have been replaced by NH<sub>3</sub>. <sup>e</sup> Ratio of rate constant for *trans* complex to rate constant for corresponding complex where all ethylenediamine groups have been replaced by NH<sub>3</sub>. <sup>f</sup> Corrected for statistical factor. <sup>g</sup> Higher limit obtained by assuming Cl<sup>-</sup> bridging only. <sup>h</sup> Reference 10. <sup>i</sup> Reference 5. <sup>j</sup> The geometry of the reactant was not specified. <sup>k</sup> Reference 6. <sup>l</sup> J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964). <sup>m</sup> A numerical value has not been reported for the rate constant of the *cis* isomer. Fraser, ref. n, states that *cis*- and *trans*-Co(NH<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub><sup>+</sup> react at similar rates. <sup>n</sup> R. T. M. Fraser, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p. 32K. <sup>o</sup> Reference 7. <sup>p</sup> Fraser<sup>6</sup> reports that *cis*-Co(en)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub><sup>+</sup> reacts only by an acid-dependent path. Assuming that a 10% contribution of the acid-independent path at 0.2 M H<sup>+</sup> could have been detected, we estimate the higher limit of 0.1 M<sup>-1</sup> sec.<sup>-1</sup>. <sup>q</sup> Since the geometry of the Co(en)<sub>2</sub>NH<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sup>+</sup> was not specified,<sup>6</sup> these values must be considered with caution. <sup>r</sup> The *cis* ligand replaced is H<sub>2</sub>O. <sup>s</sup> Since more than 80% of the Cr(III) product at 1.0 M H<sup>+</sup> is Cr(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub><sup>+</sup>, the value of 5 M<sup>-1</sup> sec.<sup>-1</sup> is an upper limit for the rate constant *via* a H<sub>2</sub>O bridge.

that since Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>, *trans*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, and *trans*-Co(en)<sub>2</sub>BrCl<sup>+</sup> react faster than their respective bromine analogs,<sup>9,37</sup> then attack of Fe<sup>2+</sup> at Cl<sup>-</sup> will be somewhat more favorable than attack at Br<sup>-</sup>. In this context it is pertinent to indicate that, in principle, the bridging group may change in going from a *cis* isomer to the corresponding *trans* isomer, especially if the bridging abilities of X and Cl<sup>-</sup> are not very different.<sup>40</sup> However, for X = H<sub>2</sub>O, NH<sub>3</sub>, and SCN<sup>-</sup>, the relative bridging abilities are such that attack at Cl<sup>-</sup> is more favorable than at X, for *cis* and *trans* isomers.

The nonbridging ligand effects observed in the present work cover a range of reactivities of 1.3 × 10<sup>4</sup>. This range is not as wide as that observed for the reduction of complexes of the pentaammine class by Cr<sup>2+</sup> (a range of ca. 10<sup>7</sup>), but still represents a remarkable effect. The data obtained in the present investigation, as well as literature data for the reduction of *cis*- and *trans*-cobalt(III) complexes, are summarized in Table V. The values listed in column 3 give a measure of the reactivities of *trans* complexes as compared to the corresponding *cis* isomers; the values listed in columns 4 and 5 give a measure of the change in rate brought about by substitution of one NH<sub>3</sub> by another ligand in the *cis* or *trans* positions, respectively; the values listed in columns 6 and 7 represent the magnitude of chelate effects in the *cis* and *trans* positions, respectively. The following generalizations can be made: (1) *trans*

complexes react faster than the corresponding *cis* isomers; (2) rates of reaction of a series of *trans* isomers cover a wider range than the rates of the corresponding *cis* isomers; (3) chelation of nonbridging ligands (substitution of ammonia by ethylenediamine) results in a decrease in reactivity. Admittedly these generalizations are based on a rather limited amount of experimental information, and exceptions are not infrequent. Nevertheless, it seems useful to discuss these generalizations on the basis of the model used previously to rationalize observations on the rates of reduction of azidoamminecobalt(III) complexes by iron(II).<sup>10</sup>

Most pertinent discussions of relative reactivities of *cis* and *trans* isomers are based on Orgel's treatment.<sup>42</sup> Orgel argues that in the reduction of cobalt(III) complexes by a bridging mechanism, the bridging ligand moves from oxidant to reductant and the electron is transferred from the reductant to the unoccupied d<sub>z<sup>2</sup></sub> orbital of cobalt(III). For a pair of *cis* and *trans* isomers of the type CoA<sub>4</sub>XY<sup>n+</sup>, where Y is the bridging ligand, the relative stabilization of the d<sub>z<sup>2</sup></sub> orbital will depend on the ligand field strengths of X and A. If X has a smaller ligand field than A, the *trans* isomer should react more rapidly than the *cis* isomer, whereas the opposite situation will obtain if X has a stronger ligand field than A. Taube<sup>2a,3</sup> has extended Orgel's ideas and made the interesting suggestion that in the reduction of cobalt(III) complexes both the bridging ligand and the group *trans* to it move away from the cobalt(III) center to make the d<sub>z<sup>2</sup></sub> orbital avail-

(40) Keller and Moore<sup>41</sup> report that the relative rates for Cl to Br attack in the reactions of *cis*- and *trans*-Co(en)<sub>2</sub>BrCl<sup>+</sup> with Cr<sup>2+</sup> are 1:1.5 and 1:1.1, respectively.

(41) R. N. Keller and M. C. Moore, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich, April 1965, p. 9M.

(42) L. Orgel, Report of the Tenth Solvay Conference, Brussels, 1956, p. 289.

able to the incoming electron; stretching of the two ligands along the *Z* axis lowers the energy of the  $d_{z^2}$  orbital. From this it follows that for a series of complexes with a common bridge but different ligands in the *trans* position, the stronger the field of the *trans* ligand the farther away it must be moved to lower the energy of the  $d_{z^2}$  orbital to the necessary extent.<sup>43</sup> This suggestion receives some support from measurements of oxygen and nitrogen isotope fractionation effects in the reaction of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ <sup>44,45</sup> and also from the importance of the  $\text{H}^+$ -catalyzed path in the reaction of *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$  with  $\text{Fe}^{+2}$ . It is noteworthy that since  $e_g$  electrons affect bond lengths to a larger extent than  $t_{2g}$  electrons, the strong tetragonal distortion indicated in the model outlined above is consistent with Franck-Condon restrictions as related to the increased radius of  $\text{Co}(\text{II})$  as compared to  $\text{Co}(\text{III})$ , and also with a  $\text{Co}(\text{II})$  product formed in the electronic configuration  $t_{2g}^6 e_g^1 (d_{z^2})$ . On the basis of this model, it is expected that for a series of related complexes that make use of the same bridge, two important factors in determining relative rates of reduction will be the ligand field strength of the group *trans* to the bridge and the energy required to stretch the metal-ligand bonds along the *Z* axis. The ligand field strengths of the various groups of interest in the present study are well documented, but very limited information is available for force constants of metal-ligand vibrations. Therefore, we will make use of the known rates of aquation as a rough indication of the ease of removal of the ligands in the activated complex. Admittedly, this is a poor approximation, and the only justifications in using it are the lack of information about force constants and the fact that aquation involves stretching of the ligand-metal bond.

The generalizations presented above are consistent with the model under discussion. Thus, in going from a *cis* to a *trans* isomer in compounds of the class  $\text{Co}(\text{en})_2\text{XCl}^{+n}$ , ethylenediamine is replaced by the ligand X which in all cases has a weaker ligand field strength and is easier to remove than ethylenediamine, and an increase in rate is observed. The effect is rather modest for  $\text{NH}_3$  (factor of 3.7), but becomes sizable for  $\text{Cl}^-$  (factor of 20) and very important for  $\text{H}_2\text{O}$  (factor of 520). The general trend observed is not unexpected: since the ligand field strength of  $\text{NH}_3$  is only slightly smaller than that of ethylenediamine, whereas  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  have considerably smaller ligand fields, a larger difference in rates between *cis* and *trans* isomers is predicted for  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  than for  $\text{NH}_3$ . However, since the order of decreasing ligand field strength is  $\text{en} > \text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^-$ , the much higher effect for  $\text{H}_2\text{O}$  as compared to  $\text{Cl}^-$  could not have been predicted on the basis of ligand field strength considerations alone. The ease of removal of the bridging ligand and of the group *trans* must be considered also. For *cis*- and *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^{+2}$  the rates of aquation differ by a factor of 7 (*cis* faster than *trans*), and therefore in going from the *cis* to the *trans* isomer we would anticipate a decrease in rate on the basis of the ease of removal of the bridging ligand. Opposing this effect,

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

(44) R. K. Murmann, H. Taube, and F. A. Posey, *ibid.*, 79, 262 (1957).

(45) However, it must be noted that there is no significant nitrogen (of  $\text{NH}_3$ ) isotope fractionation when *cis*- and *trans*- $\text{Co}(\text{en})_2\text{NH}_3\text{X}^{+n}$  ( $\text{X} = \text{Cl}^-, \text{H}_2\text{O}, \text{OH}^-$ ) react with  $\text{Cr}^{+2}$ : H. Taube, private communication.

we would anticipate an increase in rate on the basis of the ease of removal and ligand field strength of the *trans* ligand. Therefore, it would appear that the relative rates of reduction of *cis*- and *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^{+2}$  reflect the interplay of counteracting effects. On the other hand, for *cis*- and *trans*- $\text{Co}(\text{en})_2\text{OH}_2\text{Cl}^{+2}$  (as well as for *cis*- and *trans*- $\text{Co}(\text{en})_2\text{NH}_3\text{Cl}^{+2}$ ) the rates of aquation differ by less than a factor of two, and therefore the ease of removal of the bridging ligand would not be expected to play an important role in determining the relative reactivities of the *cis* and *trans* isomers. The difference in rates, in this case, can be ascribed solely to differences in ease of removal and ligand field strength between ethylenediamine and water. In spite of these considerations, it would appear that there is still a high reactivity associated with  $\text{H}_2\text{O}$  in the *trans* position, and this question will be discussed below. However, it is appropriate at this point to note that although thermodynamic considerations may be important in determining reactivity,<sup>29</sup> for the case of *cis*- and *trans*- $\text{Co}(\text{en})_2\text{OH}_2\text{Cl}^{+2}$  reacting with  $\text{Fe}^{+2}$  these considerations are not relevant since the equilibrium constant for *cis* to *trans* isomerization is 0.37.<sup>23</sup>

Of the reductions by  $\text{Fe}^{+2}$ , exceptions to the generalization under consideration are observed for  $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$  and  $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$ . The increased reactivity of *cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$  as compared to the *trans* isomer was ascribed to a double-bridged activated complex. A similar explanation might be advanced for the  $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$  system if  $\text{Fe}^{+2}$  could bond to both  $\text{Cl}^-$  and  $\text{SCN}^-$  in the activated complex, an unlikely situation in view of the slow rate of reduction of  $\text{Co}(\text{NH}_3)_5\text{NCS}^{+2}$ . Another explanation might be provided by a comparison of the rates of aquation ( $\text{Cl}^-$  loss) of *cis*- and *trans*- $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^{+2}$ . As shown in Table II, the *cis* complex aquates approximately 200 times faster than the *trans* complex. Therefore, in going from the *cis* to the *trans* isomer, an increase in rate of reduction would be expected on the basis that  $\text{SCN}^-$  has a weaker ligand field and is easier to remove than ethylenediamine, but a decrease in rate would be expected on the basis that the  $\text{Cl}^-$  bridge is more difficult to remove in the *trans* than in the *cis* complex. Apparently the latter effect is predominant, and *cis*- $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$  is reduced more rapidly than *trans*- $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$  as the result of a *decreased* reactivity for the *trans* isomer rather than an *increased* reactivity for the *cis* isomer. This interpretation receives some support when the effect of substituting  $\text{NH}_3$  by  $\text{SCN}^-$  in the *cis* or *trans* positions of  $\text{Co}(\text{en})_2\text{NH}_3\text{Cl}^{+2}$  is considered. Substitution in the *cis* position increases the rate of reduction by a factor of ten, whereas a factor of only two is observed for the *trans* position. This is the opposite of what is observed in most other systems, where substitution of  $\text{NH}_3$  by X in the *trans* position produces a higher increase in rate than in the *cis* position. These considerations again point out to a decreased reactivity of *trans*- $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$ .

Turning to reactions with  $\text{Cr}^{+2}$ , the rate laws for the reductions of *cis*- and *trans*- $\text{Co}(\text{en})_2(\text{O}_2\text{CCH}_3)_2^+$  are  $k_1[\text{Co}(\text{III})][\text{Cr}(\text{II})][\text{H}^+]$  and  $(k_1 + k_2[\text{H}^+])[\text{Co}(\text{III})][\text{Cr}(\text{II})]$ , respectively.<sup>6</sup> Therefore, considering only the  $\text{H}^+$ -independent paths, the *trans* isomer reacts faster than the *cis*, in agreement with our model. However, it is noteworthy that Fraser<sup>6</sup> attributes the lack of a



H<sup>+</sup>-independent path for the *cis* isomer to crowding of the acetate groups, although it is not clear how addition of a proton would relieve this situation. Only the qualitative statement that rates are approximately the same for *cis*- and *trans*-Co(NH<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub><sup>+</sup> has been made,<sup>46</sup> and the H<sup>+</sup> dependence and the values of the rate constants for the *cis* isomer are lacking.

In the reactions of Co(NH<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub><sup>+</sup> and Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> with Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, the *cis* isomer is more reactive than the *trans* isomer for the acetate system, whereas the opposite result is observed for the chloride system,<sup>47</sup> and it is interesting to note that all of these reactions proceed by an outer-sphere mechanism.

The relative rates of reduction of the series *cis*- and *trans*-Co(en)<sub>2</sub>XCl<sup>+</sup> are also consistent with the proposed model. For the *trans* series the order of decreasing rate of reduction is H<sub>2</sub>O > Br<sup>-</sup> > Cl<sup>-</sup> > SCN<sup>-</sup> > NH<sub>3</sub>, the over-all change in reactivity being 3600. Except for H<sub>2</sub>O, this is the order expected on the basis of both the ligand field strengths (NH<sub>3</sub> > SCN<sup>-</sup> > Cl<sup>-</sup> > Br<sup>-</sup>) and the ease of removal (the order is probably Br<sup>-</sup> > Cl<sup>-</sup> > SCN<sup>-</sup> > NH<sub>3</sub>) of the *trans* groups under consideration. From the rate constants for Cl<sup>-</sup> aquation, however, the following order of decreasing ease of removal (and therefore of decreasing rate) of the bridge would be expected: Br<sup>-</sup> > Cl<sup>-</sup> > H<sub>2</sub>O > NH<sub>3</sub> > SCN<sup>-</sup>. The abnormally low rate of aquation of *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup> was used above to account for the relative rates of reduction of *cis*- and *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup> and also for the mild increase in rate (only a factor of two) in going from *trans*-Co(en)<sub>2</sub>NH<sub>3</sub>Cl<sup>+</sup> to *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup>. The large rate of reduction of *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup> cannot be accounted for on the basis of either the ligand field of H<sub>2</sub>O or the ease of removal of Cl<sup>-</sup>, and on the basis of the proposed model it is not unreasonable to ascribe this large rate to the ease of removal of H<sub>2</sub>O. In this context, it is noteworthy that the remarkable reactivity of H<sub>2</sub>O in the *trans* position was also observed in the reductions of azidoamminecobalt(III) complexes by iron(II).<sup>48</sup> Another point to be emphasized is the large range of reactivities observed for the *trans* complexes. The observation is consistent with the proposed model; the nature of the *trans* group is of utmost importance in determining reactivity.

For the *cis* complexes the order of decreasing rates is Cl<sup>-</sup> > H<sub>2</sub>O > SCN<sup>-</sup> > NH<sub>3</sub>, the over-all change in reactivity being 44. Again these results provide support for the proposed model. In the case of the *cis* complexes, the group *trans* to the bridging ligand is always ethylenediamine, and relatively minor changes in rate are brought about by changing the nature of the *cis* ligand. No simple explanation can be given for the observed order in the *cis* complexes; for a fairly narrow range of reactivities, the relative contributions of various factors (such as differences in charges and oxidation potentials, ease of removal of the bridging ligand) will be important in determining the over-all rate order.

(46) Reference *n* of Table V.

(47) Reference *l* of Table V.

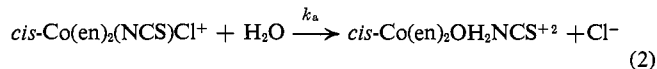
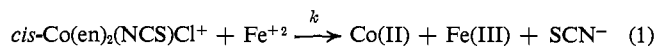
(48) An alternate interpretation of the high reactivities of *trans*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup> and *trans*-Co(NH<sub>3</sub>)<sub>4</sub>OH<sub>2</sub>N<sub>3</sub><sup>2+</sup> is that for these complexes the bridging ligand is H<sub>2</sub>O rather than Cl<sup>-</sup> or N<sub>3</sub><sup>-</sup>. However, the lack of a 1/[H<sup>+</sup>] path in the reductions of these complexes makes this alternative unlikely. Moreover, N<sub>3</sub><sup>-</sup> in the *trans* position only causes a mild increase in reactivity (Table V).

The observations on the effect of chelation are incidental to the main theme of the present paper. However, it is noteworthy that the results for *cis*- and *trans*-Co(en)<sub>2</sub>NH<sub>3</sub>Cl<sup>+</sup> reacting with Fe<sup>2+</sup> do not conform to the solvation treatment of chelation effects.<sup>6</sup> Perhaps part of the decrease in rate of reduction when ammonia is substituted by ethylenediamine either in the *cis* or *trans* positions is to be ascribed to a decrease in the ease of removal of the bridge. In addition, the decrease in rate for the *cis* complex is consistent with substitution of ammonia by ethylenediamine in the *trans* position.

The most important feature of the present investigation has been the demonstration that dramatic changes in the rates of reduction of cobalt(III) complexes can be brought about by relatively small changes in the nature and/or geometrical position of one non-bridging ligand. In view of the magnitude of the observed effects, it is tempting to suggest that a bridged mechanism is operative in these reductions. In making this suggestion, it is implied that bridged mechanisms will exhibit a substantial discrimination to changes in the nature and/or geometrical position of one non-bridging ligand, whereas outer-sphere mechanisms will exhibit a modest discrimination. Additional experiments to prove or disprove the adequacy of this hypothesis are planned.

## Appendix A

*Treatment of the Data for cis- and trans-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup>.* The kinetic scheme for the reaction of *cis*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup> with Fe<sup>2+</sup> is



The following definitions are made: *cis*-Co(en)<sub>2</sub> = R; *k<sub>p</sub>* = *k*[Fe<sup>2+</sup>]; extinction coefficients are denoted by *E* with a subscript corresponding to the formula of the compound; *l* is the path length of the cell; concentrations are denoted by brackets with a subscript indicating time (0, *t*, or ∞); Fe<sup>3+</sup> is in excess and the concentration at all times is [Fe<sup>3+</sup>]<sub>0</sub>; *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>NCS<sup>2+</sup> is inert with respect to reaction with Fe<sup>2+</sup> and accumulates in the solution; the formation constant of FeNCS<sup>2+</sup> is *K*.

The integrated rate equations for reactions 1 and 2 are

$$[\text{R(NCS)Cl}^+]_t = [\text{R(NCS)Cl}^+]_0 e^{-(k_p+k_a)t} \quad (3)$$

$$[\text{ROH}_2\text{NCS}^{2+}]_t - [\text{ROH}_2\text{NCS}^{2+}]_\infty = -\frac{k_a[\text{R(NCS)Cl}^+]_0}{k_p + k_a} e^{-(k_p+k_a)t} \quad (4)$$

Equation 5 is derived from the contributions of all species to absorption of light.

$$D_\infty - D_t = E_{\text{FeNCS}}l\{[\text{FeNCS}^{2+}]_\infty - [\text{FeNCS}^{2+}]_t\} + E_{\text{Co}}l\{[\text{Co}^{2+}]_\infty - [\text{Co}^{2+}]_t\} + E_{\text{ROH}_2\text{NCS}}l\{[\text{ROH}_2\text{NCS}^{2+}]_\infty - [\text{ROH}_2\text{NCS}^{2+}]_t\} - E_{\text{R(NCS)Cl}}l[\text{R(NCS)Cl}^+]_t \quad (5)$$

By making use of stoichiometric considerations and of the formation constant for FeNCS<sup>2+</sup>, expressions for [Co<sup>2+</sup>]<sub>*t*</sub>, [Co<sup>2+</sup>]<sub>∞</sub>, [ROH<sub>2</sub>NCS<sup>2+</sup>]<sub>*t*</sub>, [ROH<sub>2</sub>NCS<sup>2+</sup>]<sub>∞</sub>, [FeNCS<sup>2+</sup>]<sub>*t*</sub>, and [FeNCS<sup>2+</sup>]<sub>∞</sub> are obtained and intro-

duced in eq. 5 to yield

$$D_{\infty} - D_t = M \{ [\text{ROH}_2\text{NCS}^{+2}]_t - [\text{ROH}_2\text{NCS}^{+2}]_{\infty} \} + \frac{N[\text{R}(\text{NCS})\text{Cl}^{+2}]_t}{(6)}$$

where  $M$  and  $N$  are defined as

$$M = l \left( \frac{E_{\text{FeNCS}} K [\text{Fe}^{+3}]_0}{1 + K [\text{Fe}^{+3}]_0} + E_{\text{CO}} - E_{\text{ROH}_2\text{NCS}} \right)$$

$$N = l \left( \frac{E_{\text{FeNCS}} K [\text{Fe}^{+3}]_0}{1 + K [\text{Fe}^{+3}]_0} + E_{\text{CO}} - E_{\text{RNCSCl}} \right)$$

Introducing eq. 3 and 4 in eq. 6 and simplifying

$$D_{\infty} - D_t = [\text{R}(\text{NCS})\text{Cl}^{+2}]_0 \left( N - \frac{Mk_a}{k_p + k_a} \right) e^{-(k_p + k_a)t}$$

Therefore a plot of  $\log(D_{\infty} - D_t)$  vs.  $t$  will have a slope equal to  $-(k_p + k_a)/2.3$ . For the case of *trans*-Co(en)<sub>2</sub>(NCS)Cl<sup>+</sup>,  $k_a$  is negligible compared to  $k_p$ , and the slope is  $-k_p/2.3$ .

## Appendix B

*Treatment of the Data for cis-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>.* The definitions used in Appendix A are followed. In addition, ROH<sub>2</sub>Cl<sup>+</sup> is used to denote the *cis* isomer, and  $E$  is the extinction coefficient of both *cis*-Co(en)<sub>2</sub>Cl<sup>+</sup> and *cis*-Co(en)<sub>2</sub>OH<sub>2</sub>Cl<sup>+</sup> at the isosbestic point (505 mμ).

The differential equations for the kinetic scheme are integrated by standard methods, and the solutions are added to give

$$[\text{RCl}_2^+]_t + [\text{ROH}_2\text{Cl}^{+2}]_t = Q e^{-(k_d^a + k_d^{\text{Fe}} [\text{Fe}^{+2}])t} - S e^{-(k_o^t + k_o^{\text{Fe}} [\text{Fe}^{+2}])t} \quad (7)$$

where  $Q$  and  $S$  are defined as

$$Q = \frac{[\text{RCl}_2^+]_0 \{ k_c^t + (k_c^{\text{Fe}} - k_d^{\text{Fe}}) [\text{Fe}^{+2}] \}}{k_c^t - (k_c^{\text{Fe}} - k_d^{\text{Fe}}) [\text{Fe}^{+2}] - k_d^a}$$

$$S = \frac{[\text{RCl}_2^+]_0 k_d^a}{k_c^t - (k_c^{\text{Fe}} - k_d^{\text{Fe}}) [\text{Fe}^{+2}] - k_d^a}$$

Equation 8 is derived from the contributions of all species to light absorption and from stoichiometric considerations.

$$D_t - D_{\infty} = l(E - E_{\text{CO}})([\text{RCl}_2^+]_t + [\text{RClOH}_2^{+2}]_t) \quad (8)$$

Substitution of eq. 7 in eq. 8 yields

$$D_t - D_{\infty} = U e^{-(k_d^a + k_d^{\text{Fe}} [\text{Fe}^{+2}])t} - V e^{-(k_o^t + k_o^{\text{Fe}} [\text{Fe}^{+2}])t} \quad (9)$$

where  $U = l(E - E_{\text{CO}})Q$  and  $V = l(E - E_{\text{CO}})S$ .

At relatively long times the first exponential in eq. 9 becomes negligible and eq. 10 is obtained. From eq. 10, the linear portion of the  $\log(D_t - D_{\infty})$  vs.

$$[D_t - D_{\infty}] \text{ (for } t \text{ large)} = -V e^{-(k_o^t + k_o^{\text{Fe}} [\text{Fe}^{+2}])t} \quad (10)$$

$t$  plot gives a slope equal to  $-(k_o^t + k_o^{\text{Fe}} [\text{Fe}^{+2}])/2.3$ .

$D_c$  is defined as the value of  $D$  obtained by extrapolating the linear portion of the  $\log(D_t - D_{\infty})$  vs.  $t$  plot to zero time. Therefore

$$[D_c - D_{\infty}] \text{ (for } t \text{ small)} = V e^{-(k_o^t + k_o^{\text{Fe}} [\text{Fe}^{+2}])t} \quad (11)$$

Subtracting eq. 11 from eq. 9, we obtain

$$D_t - D_c = U e^{-(k_d^a + k_d^{\text{Fe}} [\text{Fe}^{+2}])t} \quad (12)$$

From eq. 12, a plot of  $\log(D_t - D_c)$  vs.  $t$  gives a slope equal to  $-(k_d^a + k_d^{\text{Fe}} [\text{Fe}^{+2}])/2.3$ .

## The Mechanism of the Oxidation of Sulfur(IV) by Chromium(VI) in Acid Solution<sup>1</sup>

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The reactions between chromium(VI) and sulfur(IV) have been studied in aqueous acid solution. The stoichiometry varies from a Cr(VI)/S(IV) mole ratio of 1:2 to 2:3 as the starting concentrations are changed in the range  $0.12 \leq [\text{Cr(VI)}]/[\text{S(IV)}] \leq 1.4$ . The kinetics of the reaction path which gives 1:2 stoichiometry in 0.5 M sodium acetate buffer in the range  $4.18 \leq \text{pH} \leq 5.05$  follow the rate law

$$-d[\text{Cr(VI)}]/dt = k_{\text{obsd}} [\text{Cr(VI)}] [\text{S(IV)}]^2 [\text{H}^+] / \{ 1 + K_1 [\text{S(IV)}] \}$$

$K_1$  is interpreted to be the equilibrium constant for the formation of CrSO<sub>6</sub><sup>2-</sup> from HSO<sub>3</sub><sup>-</sup> and HCrO<sub>4</sub><sup>-</sup> and has a value of 36 M<sup>-1</sup>. The rate constant  $k_{\text{obsd}}$  is  $1.37 \times 10^8 \text{ M}^{-3} \text{ sec}^{-1}$  at 25.0°. The activation energy is 4.5 kcal./mole and the activation entropy is -13 e.u. A mechanism is proposed and compared with the Westheimer mechanisms for organic oxidations with Cr(VI)

(1) Presented in part before the Inorganic Chemistry Division, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

and with Mason's mechanism for the Cr(VI)-As(III) reaction.

## Introduction

It has been known for a long time that the oxidation of sulfur(IV) by oxidizing agents such as chromium(VI) and manganese(VII) yielded dithionate as well as sulfate as the reaction products.<sup>2,3</sup> It appeared as though this were a reaction in which several different techniques could be used to obtain information with respect to chromium(VI) oxidation-reduction reaction mechanisms. These techniques included rapid mixing and standard kinetics by means of spectrophotometry, oxygen-18 tracer analysis, and careful analysis of the stoichiometry of the reaction. All three of these measurements could be useful individually in ascertain-

(2) J. Kleinberg, W. Argersinger, and E. Griswold, "Inorganic Chemistry," D. C. Heath and Co., Boston, Mass., 1960, p. 448.

(3) H. Basset, *J. Chem. Soc.*, 83, 692 (1903).