Reduction by Iron(II), Equilibrium, and Rate of Isomerization in the cis–$trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ System

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The rate of Fe^{+2} reduction of an equilibrium mixture of cis- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ has been measured at 25° and Σ[ClO$_4$$^-$] = 0.50 M. Above 1.5×10^{-3} M [Fe^{+2}], a "fast" and a "slow" rate are observed with rate coefficients (seconds) 24[Fe^{+2}] and 1.42×10^{-3} + 0.355[Fe^{+2}], respectively. At very low [Fe^{+2}], $<1 \times 10^{-4}$ M, a single rate is observed with rate coefficient 4.33[Fe^{+2}]. From these measurements the following quantities have been derived: k_t^{Fe} and k_c^{Fe}, the rate constants for the reductions of the $trans$ and cis isomers by Fe^{+2}, are 24 and 0.355 M^{-1} sec.$^{-1}$, respectively; k_{isom} and K, the rate constant and equilibrium constant for cis to $trans$ isomerization, are 1.42×10^{-3} sec.$^{-1}$ and 0.22, respectively. The Fe^{+2} reductions of the isomers are assumed to proceed via a bridged activated complex that makes use of N$_3$$^-$ in the bridge. The reactivities of various azidoamminecobalt(III) complexes are discussed on the basis of the ligand field strength of the group $trans$ to the bridging ligand and of a model which requires the bridging ligand and the group $trans$ to it to move away from the cobalt center for electron transfer to occur.

In connection with studies on the formation of cis- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ by reaction of cis- or $trans$-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ with Ce(IV), Hg^{+2}, and H$^+$,[1] it became necessary to measure the rate of cis–$trans$ isomerization in the Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ system. Various attempts to achieve fractional crystallization of an equilibrium mixture of cis- and $trans$-Co(NH$_3$)$_4$-(OH$_2$)N$_3$$^{+2}$ or to prepare one of the two isomers were unsuccessful.[1] Therefore, it was decided to obtain the rate of isomerization by an indirect method based on the difference in reactivities of the isomers toward a common reagent. Iron(II) was chosen as the reagent because previous experience with the analogous diazido system[2] indicated that some difference in the reactivities of the geometric isomers could be expected and because of our interest in the reduction of Co(III) complexes by Fe^{+2}.

Experimental

Materials.—Iron(II) perchlorate solutions were prepared by dissolving analytical grade iron wire in excess perchloric acid. The Fe^{+2} concentration was determined with Ce(IV) using Fe(o-phen)$_3$$^{+2}$ as an indicator, and the H$^+$ concentration by passing the solution through a Dowex 50 ion-exchange column in the H$^+$ form and titrating the [H$^+$] in the eluent with standard NaOH. All other chemicals were reagent grade.

Preparation of Complexes.—cis- and $trans$-[Co(NH$_3$)$_4$(N$_3$)$_2$]-(ClO$_4$) were prepared as described by Linhard.[3] Equilibrium mixtures of cis- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ were prepared by the acid-catalyzed (HClO$_4$) aquation of cis- or $trans$-Co(NH$_3$)$_4$-(N$_3$)$_2$$^+$.[1]

Procedure.—Solutions of cis- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ and all other reagents except the Fe^{+2} solution were pipetted in a volumetric flask which was placed in a constant temperature bath at $25 \pm 0.1°$. After temperature equilibration had been reached, the Fe^{+2} solution was added, and the solution was made up to volume and rapidly transferred to a spectrophotometric cell of the desired path length (1, 2, 5, or 10 cm.). The cell was placed in the thermostated ($25 \pm 0.1°$) cell holder of a Cary Model 14 recording spectrophotometer, and a recording of optical density $vs.$ time at the desired wave length was obtained. The rapid initial decrease in optical density (see below) was measured in some experiments by pipetting the solutions directly into the spectrophotometric cell, a procedure which permits one to obtain the first optical density measurement within 0.5 min. of mixing. In all the experiments the Fe^{+2} was in excess with respect to the Co-(III), and therefore pseudo-first-order rate constants k were obtained from the slopes of plots of log ($D_i - D_\infty$) $vs.$ time. The

optical densities of the solution at time t and after reaction is complete are D_i and D_∞, respectively.

Results

As shown in Table I the acid-catalyzed aquations of cis- and $trans$-Co(NH$_3$)$_4$(N$_3$)$_2$$^+$ yielded solutions which displayed identical absorption spectra. Even at 1.18

TABLE I

ABSORPTION SPECTRUM OF AN EQUILIBRIUM MIXTURE OF cis- AND $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$

Wave length, mμ	Extinction coefficient^a	Wave length, mμ	Extinction coefficient^a
600	92 (0)	420	203 (0)
580	140 (1)	400	360 (0)
560	188 (1)	380	662 (7)
550	209 (1)	350	2320 (30)
540	222 (1)	330	5540 (30)
532^b	225 (1)	320	7260 (10)
520	218 (2)	308^b	8200 (0)
510	200 (2)	300	7550 (50)
490	142 (3)	290	5760 (20)
470	93 (2)	280	3460 (50)
457^c	83 (1)	270	1770 (0)
440	109 (1)		

^{a} Average value and deviation from the average for the two sources of Co(NH$_3$)$_4$(OH)$_2$N$_3$$^{+2}$. ^{b} Absorption maximum. ^{c} Absorption minimum.

M H$^+$ concentration and 25°, conditions under which the half-lives for the aquations of the cis and $trans$ isomers are 3 and 4 min., respectively,[1] identical spectra were obtained. Furthermore, isosbestic points were observed at 508 and 478 mμ for the reaction of the cis isomer, and at 534, 463, 313, and 267 mμ for that of the $trans$ isomer, indicating that in both reactions cis- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ were formed in the same proportions, and/or that the rate of cis–$trans$ isomerization for Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ was rapid compared to the rate of production of the isomers.[4] Since the spectra of solutions of Co(NH$_3$)$_4$(OH$_2$)N$_3$$^{+2}$ prepared in this manner did not change for several days at 25°, it was concluded that such solutions contained an equilibrium mixture of the cis and $trans$ isomers.[5]

(1) A. Haim, to be published.

(2) A. Haim, $J. Am. Chem. Soc.$, **85**, 1016 (1963).

(3) M. Linhard, M. Weigel, and H. Flygare, $Z. anorg. allgem. Chem.$, **263**, 233 (1950).

(4) The mechanistic significance of these observations will be discussed elsewhere.[1]

A summary of the rate measurements for the Fe^{+2} reduction of an equilibrium mixture of cis- and trans-$Co(NH_3)_4(OH_2)N_3^{+2}$ is presented in Table II. For

TABLE II

KINETICS[a] OF THE REDUCTION OF AN EQUILIBRIUM MIXTURE OF cis- AND trans-$Co(NH_3)_4(OH_2)N_3^{+2}$ BY Fe^{+2}

Expt.	$[Co(NH_3)_4-$ $(OH_2)N_3^{+2}]$, $M \times 10^6$	$[Fe^{+2}]$, $M \times 10^4$	$[H^+]$, M	$10^4 k$, sec.$^{-1}$	k', sec.$^{-1}$
1	129	210	0.46	8.88	
2	129	106	0.46	5.25	
3	129	106	0.23	4.97	
4	129	106	0.114	5.17	
5	129	52.8	0.46	3.35	
6	260	52.8	0.46	3.23[b]	
7	260	52.8	0.46	3.18[c]	
8	260	52.8	0.46	3.20[d]	
9	138	50.3	0.46	3.17	
10	129	21.0	0.46	2.27	
11[e]	138	16.6	0.46	1.90	0.043
12	129	10.6	0.46	1.68	
13[e]	16.8	8.4	0.121	1.58	0.017
14[e]	16.8	4.2	0.121	1.08	0.0098
15	4.5	2.1	0.118	0.777	
16	4.5	1.06	0.118	0.433	
17	4.5	0.53	0.118	0.207	
18[f]	180	191	1.27	13.3	
19[f]	180	76.5	1.20	5.97	
20[f]	180	45.9	1.21	4.38	
21[f]	180	15.3	1.22	2.43	

[a] At 25°, $\Sigma[ClO_4^-]$ = 0.50 M, λ = 308 mμ. [b] Measured at 532 mμ. [c] Measured at 400 mμ. [d] Measured at 340 mμ. [e] Rapid mixing, see Experimental. [f] $\Sigma[ClO_4^-]$ = 1.30 M.

most experiments extrapolation of the plot of log $(D_t - D_\infty)$ vs. time to time 0 yielded a value of D_0, the optical density at the time 0, smaller than that calculated from the known Co(III) concentration in solution. Experiments 11, 13, and 14, where rapid mixing in the spectrophotometric cell permitted making optical density measurements soon after mixing, serve to demonstrate that the lack of agreement between the calculated and extrapolated values of D_0 is caused by a rapid reaction. After the initial rapid decrease in optical density, plots of log $(D_t - D_\infty)$ vs. time were linear, and the rate coefficients k listed in column 5 of Table II are obtained from the slopes of the linear plots. The rate coefficients k' corresponding to the rapid initial decrease in optical density were obtained for experiments 11, 13, and 14 from the slopes of log $(D_t - D_c)$ vs. time. The optical density D_c at time t is obtained by extrapolating the linear portion of the log $(D_t - D_\infty)$ plots to time 0. The values of k', listed in column 6 of Table II, are not very accurate because the quantities $D_t - D_c$ are small differences between two large quantities. As an illustration of the behavior observed and the treatment of the data, the plots corresponding to experiment 14 of Table II are given in Fig. 1.

The values listed in column 5 of Table II show that k is independent of $[H^+]$ from 0.114 to 0.46 M (expt. 2–4) and of the wave length at which the measurements were

(5) At higher temperatures and longer times, a further decrease in optical density is observed, corresponding to the formation of $Co(NH_3)_4(OH_2)_2^{+3}$. Since only freshly prepared solutions were used in the present investigation, the concentrations of the diaquo species are negligible in all the experiments.
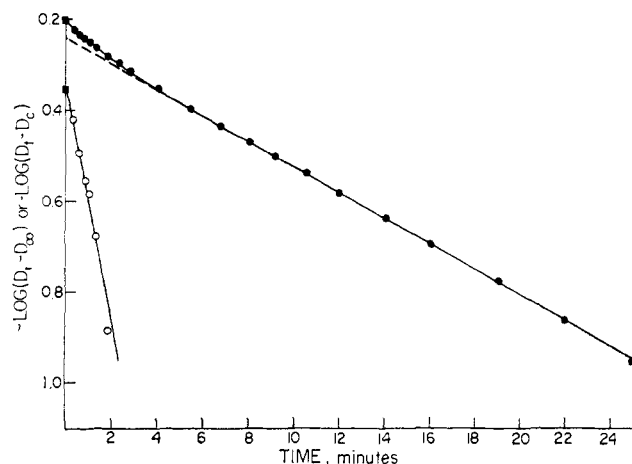

Fig. 1.—Plots for experiment 14 of Table II: ●, log $(D_t - D_\infty)$; ○, log $(D_t - D_c)$; ■, calculated values at time 0.

made (expt. 5–8). A remarkable feature of the results is that, for $[Fe^{+2}] > 1.5 \times 10^{-3}$ M, the functional dependence of k upon $[Fe^{+2}]$ is described by a straight line which has a positive intercept. This is illustrated in Fig. 2 where the values of k at $\Sigma[ClO_4^-]$ = 1.30 and 0.50
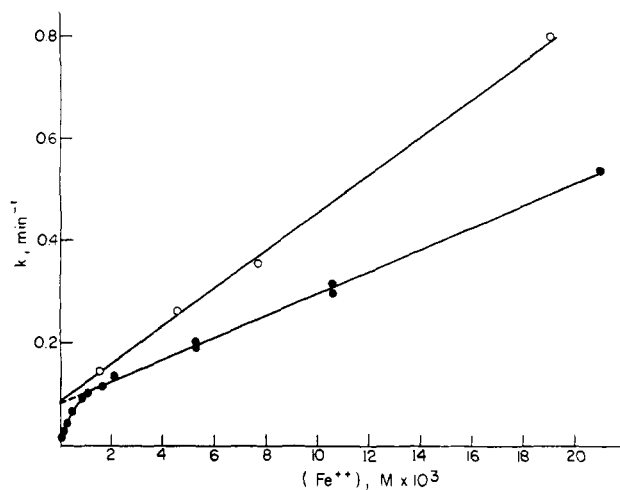

Fig. 2.—The dependence of the pseudo-first-order rate coefficient upon Fe^{+2} concentration: ●, $\Sigma[ClO_4^-]$ = 0.50 M; ○, $\Sigma[ClO_4^-]$ = 1.30 M.
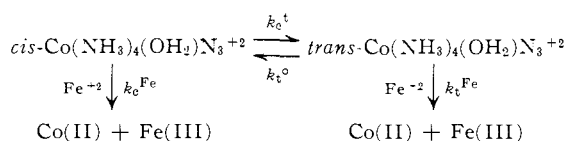
M are plotted against $[Fe^{+2}]$. Although the slopes of the linear portions of the plots increase with increasing ionic strength, the intercepts are apparently independent of the ionic strength: at $\Sigma[ClO_4^-]$ = 1.30 M, k = 1.47 $\times$ 10^{-3} + 0.613$[Fe^{+2}]$, and at $\Sigma[ClO_4^-]$ = 0.50 M, k = 1.42 $\times$ 10^{-3} + 0.355$[Fe^{+2}]$ (time in seconds). Below $[Fe^{+2}]$ = 1.5 $\times$ 10^{-3} M, the k vs. $[Fe^{+2}]$ plot displays downward curvature, and k eventually approaches 0. The rate coefficient k' is approximately linear in $[Fe^{+2}]$, as indicated by the equation k' = 24$[Fe^{+2}]$, and independent of $[H^+]$ (expt. 11, 13).

Anticipating the discussion presented below, the two observed rates correspond to the different reactivities of cis- and trans-$Co(NH_3)_4(OH_2)N_3^{+2}$ toward Fe^{+2}. In order to correlate the reactivity and geometry of the isomers, the following experiment was performed. A solution 4.21 $\times$ 10^{-3} M in Fe^{+2}, 4.0 $\times$ 10^{-3} M in Co-(III), 0.14 M in H^+, and 0.20 M in ClO_4^- was made up

and the absorption was measured between 600 and 500 mμ at approximately 1-min. intervals. It was observed that the position of the maximum shifts from 532 mμ for the equilibrium mixture of the isomers to 513 mμ after 7 min. when the more reactive isomer has presumably been consumed.

Discussion

The results obtained in the present investigation are consistent with the following kinetic scheme

$$cis\text{-Co(NH}_3)_4(\text{OH}_2)\text{N}_3{}^{+2} \xrightleftharpoons[k_t{}^o]{k_c{}^t} trans\text{-Co(NH}_3)_4(\text{OH}_2)\text{N}_3{}^{+2}$$

$$\text{Fe}^{+2} \downarrow k_c{}^{\text{Fe}} \qquad\qquad\qquad \text{Fe}^{-2} \downarrow k_t{}^{\text{Fe}}$$

$$\text{Co(II)} + \text{Fe(III)} \qquad\qquad \text{Co(II)} + \text{Fe(III)}$$

Two limiting cases, relevant to the conditions used in this study, will be considered.

A. "High" Fe^{+2} Concentration.—Under these conditions, equilibrium between the *cis* and *trans* isomers is not rapidly established as compared to reaction with Fe^{+2}, and two rates are observed: a "fast" rate governed by the rate coefficient k and a "slow" rate governed by the rate coefficient k'. As will be shown below, $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$ is the more reactive of the two isomers, and, therefore, the rate coefficient k' is identified as $k_t{}^{\text{Fe}}$ (Fe^{+2}) with $k_t{}^{\text{Fe}} = 24$ sec.$^{-1}$.[6] After the more reactive *trans* isomer is consumed, a "slow" rate (k) is observed, and this rate corresponds to the disappearance of the *cis* isomer. As shown in Fig. 2 such disappearance proceeds by two parallel paths: one first order in $[\text{Fe}^{+2}]$ with rate constant 0.355 M^{-1} sec.$^{-1}$, and one independent of $[\text{Fe}^{+2}]$ with rate constant 1.42×10^{-3} sec.$^{-1}$. In terms of the proposed kinetic scheme, these rate constants are identified as $k_c{}^{\text{Fe}}$ and $k_c{}^t$, respectively. The path independent of $[\text{Fe}^{+2}]$ arises because once the *cis* isomer reacts by the $k_c{}^t$ path, the *trans* product disappears rapidly by reaction with Fe^{+2}. The observed effect of ionic strength on $k_c{}^{\text{Fe}}$ and $k_c{}^t$ is consistent with the interpretation adopted: $k_c{}^{\text{Fe}}$ increases with increasing ionic strength as expected for a reaction between two positively charged ions, whereas $k_c{}^t$ is ionic strength independent as expected for an isomerization reaction.

B. "Low" Fe^{+2} Concentration.—Under these conditions, equilibrium between *cis*- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$ is maintained and the rate coefficient k is given by $Kk_t{}^{\text{Fe}}[\text{Fe}^{+2}]/(1+K)$, where $K = k_c{}^t/k_t{}^c$. The value of $Kk_t{}^{\text{Fe}}/(1+K)$ is obtained from the limiting slope of the k vs. $[\text{Fe}^{+2}]$ plot as $[\text{Fe}^{+2}]$ tends to 0, and has the value 4.33 M^{-1} sec.$^{-1}$. Combining this value with those of $k_t{}^{\text{Fe}}$ and $k_c{}^t$ obtained above, it is concluded that $K = 0.22$ and $k_t{}^c = 6.33 \times 10^{-3}$ sec.$^{-1}$. Therefore, the rate constant for approach to equilibrium is $k_c{}^t + k_t{}^c = 7.75 \times 10^{-3}$ sec.$^{-1}$.

Independent support for the proposed scheme is obtained from the studies of the reactions of *cis*- and $trans$-Co(NH$_3$)$_4$(N$_3$)$_2{}^+$ with Ce(IV) to form *cis*- and

$trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{-2}$. For this system, unlike the H$^+$-catalyzed system, isosbestic points are not observed[1] showing that *cis*- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$ are not formed in equilibrium proportions. At sufficiently high Ce(IV) and H$^+$ concentrations the disappearance of Co(NH$_3$)$_4$(N$_3$)$_2{}^-$ is fast compared to the rate of *cis–trans* isomerization of Co(NH$_3$)$_4$N$_3{}^{+2}$, and therefore, it is possible to observe the nonequilibrium mixture approach equilibrium. Two such experiments were performed: at [Ce(IV)] $= 0.05$ M and [H$^+$] $= 0.23$ M, the rate constant for isomerization (measured from changes in optical density at 500 mμ) is 0.8×10^{-3} sec.$^{-1}$; at [Ce(IV)] $= 0.07$ M and [H$^+$] $= 0.31$ M, the value is 6.0×10^{-3} sec.$^{-1}$. The results are not of very high accuracy because the isomerization is very fast and small changes in optical density were measured. Therefore, the agreement with the value 7.75×10^{-3} sec.$^{-1}$ obtained from the Fe^{+2} experiments can be considered satisfactory.

The identification of $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$ as the more reactive (toward Fe^{-2}) of the two isomers was achieved by observing the shift in the position of the first absorption maximum of the equilibrium mixture of *cis*- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$ upon treatment with Fe^{+2}. The maximum shifts from 532 mμ for the equilibrium mixture to 513 mμ for the less reactive isomer. Comparing these results with the known absorption spectra[7] of *cis*- and $trans$-Co(en)$_2$(OH$_2$)N$_3{}^{-2}$, it is apparent that $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$ is the "fast" isomer and *cis*-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$ is the "slow" one.

The results obtained in the present investigation do not permit distinction between a bridged and outersphere mechanism for the reduction of *cis*- and $trans$-Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$ by Fe^{+2}. However, as indicated before,[2] it is profitable to discuss the present results *assuming* that a bridge mechanism obtains.

For complexes of the type A$_4$MXY, such as Co(NH$_3$)$_4$(OH$_2$)N$_3{}^{+2}$, where X and Y are potential bridging ligands, it is first necessary to inquire whether X or Y (or both in the case of the *cis* isomer) will provide the most efficient bridge. Few data of this type are available in the literature. Ball and King[8] have demonstrated that the exchange of Cr between Cr^{+2} and CrX^{+2} (X $=$ F$^-$, Cl$^-$, Br$^-$, NCS$^-$, N$_3{}^-$) makes use of X$^-$ rather than H$_2$O in the bridged activated complex. Kopple and Miller[9] have suggested that the reaction of *cis*-Co(NH$_3$)$_4$(OH$_2$)(OAc)$^{+2}$ with Cr^{+2} proceeds *via* a double-bridged activated complex. The usual comparison in establishing the relative efficiency of ligands as bridging groups involves measuring relative rates of reaction of complexes of the type A$_5$MX with a common reducing agent. For the case of present interest, the relative efficiency of N$_3{}^-$ and H$_2$O as bridging ligands, Candlin, Halpern, and Trimm[10] have shown that Co(NH$_3$)$_5$N$_3{}^{+2}$ is *ca.* 10^6 times more reactive than Co(NH$_3$)$_5$OH$_2{}^{+3}$ toward Cr^{+2}. The two comparisons indicated above show that N$_3{}^-$ is a much better bridging ligand than H$_2$O in the reductions of Cr(III) or Co(III) by Cr^{+2}. Since the Fe^{+2} reduction of Co(NH$_3$)$_5$N$_3{}^{+2}$ is much faster than that[11] of Co(NH$_3$)$_5$-

(6) It must be noted that, because of the very rapid rate of the reaction governed by the coefficient k', low Fe^{+2} concentrations had to be used. These concentrations were in fact so low that some of the assumptions used in the discussion are not completely appropriate. However, since this rate coefficient corresponds essentially to initial rate studies, and since the measurement of k' is not very accurate, the approximations used appear to be justified.

(7) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960), report maxima at 515 and 550 mμ for the *cis* and *trans* isomers, respectively.
(8) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).
(9) K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).
(10) J. P. Candlin, J. Halpern, and D. L. Trimm, to be published.

OH_2^{-3}, it appears reasonable to conclude that, if a bridged mechanism is operative, N_3^- is the preferred bridging ligand.

Some support for this conclusion is obtained from the observed $[H^+]$ independence of the rates of Fe^{+2} reduction of cis- and trans-$Co(NH_3)_4(OH_2)N_3^{+2}$. For the reactions of $CrCl^{+2}$ and CrF^{+2} with Cr^{+2}, which involve Cl^- and F^- as bridging ligands, no $[H^+]$ dependence is observed.[8] On the other hand, for the reaction of $Co(NH_3)_5OH_2^{+3}$ there is an important contribution of the $[H^+]^{-1}$ dependent path,[12] even at 1 M $[H^+]$. Apparently, unless OH^- can act as a bridge, there is not much to be gained when H_2O loses a proton.[13]

In Table III we summarize the rate constants for the reduction of various azidoamminecobalt(III) complexes by Fe^{+2}. Some features of interest emerge

TABLE III

RATE CONSTANTS FOR THE REDUCTION OF Co(III) AZIDE
COMPLEXES BY Fe^{+2} (25°)

Complex	k, M^{-1} sec.$^{-1}$
$Co(NH_3)_5N_3^{+2}$	0.0087
trans-$Co(NH_3)_4(N_3)_2^+$	0.0733
cis-$Co(NH_3)_4(N_3)_2^-$	0.185
cis-$Co(NH_3)_4(OH_2)N_3^{-2}$	0.355
trans-$Co(NH_3)_4(N_3H)N_3^{-2}$	>1.37[a]
trans-$Co(NH_3)_4(OH_2)N_3^{+2}$	24

[a] Assuming that the acid-catalyzed path corresponds to the rapid formation of $Co(NH_3)_4(N_3H)N_3^{+2}$ with equilibrium constant smaller than 1.

from an examination of these rates constants. First, the reactivities of the various complexes relative to $Co(NH_3)_5N_3^{+2}$ cover a range of ca. 3×10^3, indicating that the effect of substituting a single nonbridging ligand in the coordination sphere of Co(III) is not a minor, second-order effect. Second, any influence of the charge of the Co(III) complex is overshadowed by other effects in determining the over-all reactivity patterns. In trying to understand such patterns, it is noteworthy that substitution of the trans NH_3 in $Co(NH_3)_5N_3^{+2}$ by H_2O, N_3^-, or HN_3 results in a considerable increase in rate. Orgel[14] has suggested that in the reduction of Co(III) and Cr(III) complexes the electron gained by the oxidant is accepted in the d_{z^2} orbital, and that decreasing the ligand field of the group trans to the bridging ligand stabilizes the d_{z^2} orbital and thus increases the reaction rate. The relative rates of reaction of Cr^{-2} with trans-$CrCl_2^{+1}$ [5] and $CrCl^{+2}$,[16] $Cr(NH_3)_5Cl^{+2}$ [17] and $CrCl^{-2}$, and $Co(NH_3)_5OAc^{+2}$ [18] and trans-$Co(NH_3)_4(OAc)_2^-$ [9] are consistent with this proposal. However, the reactivity order $Co(NH_3)_5N_3^{+2} <$ trans-$Co(NH_3)_4(N_3)_2^+ <$ trans-$Co(NH_3)_4(OH_2)N_3^{+2}$ is not in agreement with Orgel's proposal since the order of increasing ligand field strength is $N_3^- < H_2O < NH_3$.[7] Taube[19] has suggested

(11) Unpublished experiments by D. Schendel and A. Haim.
(12) A. Zwickel and H. Taube, J. Am. Chem. Soc., **81**, 1288 (1959).
(13) A. Zwickel and H. Taube, Discussions Faraday Soc., **29**, 73 (1960).
(14) L. Orgel, Report of the Tenth Solvay Conference, Brussels, 1956, p. 289.
(15) H. Taube and H. Myers, J. Am. Chem. Soc., **76**, 2103 (1954).
(16) H. Taube and E. L. King, ibid., **76**, 4053 (1954).
(17) A. E. Ogard and H. Taube, ibid., **80**, 1084 (1958).
(18) D. K. Sebera and H. Taube, ibid., **83**, 1785 (1961).

that the d_{z^2} orbital that accepts the electron is made available by removing the bridging ligand and the group trans to it. On this interpretation it would be expected that not only the ligand field strength would be of immediate interest, but also the tendency of the trans ligand to move away from the cobalt center. On this basis it is possible to rationalize the reactivity order for the trans-substituted complexes. Thus, although H_2O has a larger ligand field strength than N_3^-, trans-$Co(NH_3)_4(OH_2)N_3^{+2}$ reacts faster than trans-$Co(NH_3)_4(N_3)_2^+$ because H_2O can leave the coordination sphere of Co more readily than N_3^-. These considerations have already been used to explain the acid catalysis of the trans-$Co(NH_3)_4(N_3)_2^+$-Fe^{-2} reaction.[2]

Turning to the cis-substituted complexes, it is noteworthy that substitution of the cis NH_3 in $Co(NH_3)_5$-N_3^{-2} by H_2O or N_3^- results in a considerable increase in rate, and that cis-$Co(NH_3)_4(OH_2)N_3^{+2}$ reacts slower than trans-$Co(NH_3)_4(OH_2)N_3^{-2}$, whereas the opposite order prevails for the diazido isomers. The results for the aquo isomers are consistent with Orgel's discussion of the relative reactivities of cis and trans isomers.[14] In order to account for the increased reactivity of cis-$Co(NH_3)_4(N_3)_2^-$, it was suggested previously[2] that a double-bridged activated complex is operative. This hypothesis is still attractive, specially in view of the results for the aquo isomers and of the recent finding that cis-$Co(en)_2(OAc)_2^+$ reacts with Cr^{+2} via an acid-dependent path.[20] On the basis of the limited data available, it is perhaps surprising that cis-$Co(NH_3)_4(OH_2)N_3^{+2}$ is considerably more reactive than $Co(NH_3)_5N_3^{+2}$. For example, cis-$Co(NH_3)_4(OH_2)_2^{-3}$ [9] reacts with Cr^{-2} only seven times faster (after correcting for the statistical factor) than $Co(NH_3)_5OH_2^{+3}$, and tracer studies show that both the mono and diaquo complexes react via a single-bridged activated complex.[21] For the reaction of cis-$Co(NH_3)_4(OH_2)OAc^{-2}$ with Cr^{+2}, which proceeds 260 times faster than that of $Co(NH_3)_5OAc^{+2}$, Kopple and Miller[9] have suggested a double-bridged activated complex. The lack of a $[H^+]^{-1}$ path for the reduction of cis-$Co(NH_3)_4(OH_2)$-N_3^{+2} makes it unlikely that a double-bridged mechanism is operative in this system and we refer to the recent discussion of Kopple and Miller[22] regarding the increased reactivity of cis-substituted tetraamminecobalt(III) complexes.

The picture implied in the description given above is that the bridging ligand and the group trans to it move away from the cobalt center for electron transfer to occur. This is what would be expected if the Co(II) formed is in the $t_{2g}^6 e_g^1$ (d_{z^2}) configuration[14] for which an elongation of the octahedron along the z-axis would be predicted on the basis of the Jahn–Teller effect. At present we are searching for such a Co(II) intermediate in the $Co(NH_3)_5N_3^{+2}$-Fe^{+2} system.

No conclusions about the mechanism of cis–trans isomerization for the $Co(NH_3)_4(OH_2)N_3^{+2}$ system can be drawn from the present study. Some comparisons with related systems are, however, in order. The value $K = [trans]/[cis] = 0.22$ compares favorably with the value 0.37 reported for the corresponding ethylenediamine system.[7] The rate constant for isom-

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erization is, however, much larger: $k_{\text{isom}}^{\text{NH}_3} = 7.75 \times 10^{-3}$ sec.$^{-1}$ for the ammine system as compared to $k_{\text{isom}}^{\text{en}} = 9.8 \times 10^{-5}$ sec.$^{-1}$ for the ethylenediamine system,[7] giving a ratio of $k_{\text{isom}}^{\text{NH}_3}/k_{\text{isom}}^{\text{en}} = 80$. This value appears reasonable when compared with the value of 50 for the ratio of the rate constants for isomerization of $Co(NH_3)_4(OH_2)_2^{+3}$ and $Co(en)_2(OH_2)_2^{+3}$.[23,24]

A comparison of the rate constant for the Fe^{+2} reduction of $trans$-$Co(NH_3)_4(OH_2)N_3^{+2}$ with the rate constants for the formation[25] of FeN_3^{+2} suggests that a direct test of mechanism (bridged or outer sphere) could, in principle, be achieved in this system: at sufficiently high $[Fe^{+2}]$ the rate of Fe^{+2} oxidation becomes comparable to the rate of equilibration between Fe^{+3}, N_3^{-}, and FeN_3^{+2}, and therefore the identification of the immediate Fe(III) product is apparently possible. This test will be carried out as soon as the rapid mixing and flow apparatus of the type described by Dulz and Sutin[26] becomes available.[27]

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(27) Such apparatus is under construction in the laboratories of Prof. R. W. Taft, Jr., of this department.