possible that the distribution between inner-sphere and outer-sphere forms of the activated complexes differs for the different systems. Only after a resolution into the different components has been made can one hope to discuss the ligand effects with any degree of success.

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Configuration Changes in the Reactions of Diazidobis(ethylenediamine)cobalt(III) Complexes with Nitrous Acid

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The reaction of nitrous acid with *cis*- or *trans*-$[Co(en)_2(N_3)_2]^+$ takes place so that in each of the cases resolution into two stages can be done with little difficulty, and the steric course in each stage can be described. *cis*-$[Co(en)_2(N_3)_2]^+$ reacts to form 77 ± 3% *cis*-$[Co(en)_2N_3H_2O]^{+2}$ and 23 ± 3% *trans*-$[Co(en)_2N_3H_2O]^{+2}$. *cis*-$[Co(en)_2N_3H_2O]^{+2}$ reacts further without change in configuration. *trans*-$[Co(en)_2(N_3)_2]^+$ reacts in the first stage with retention of configuration but *trans*-$[Co(en)_2N_3H_2O]^{+2}$ reacts to form 40 ± 5% of the *cis* diaquo product and 60 ± 5% of the *trans*. In the reaction of D-*cis*-$[Co(en)_2(N_3)_2]^+$ with excess nitrous acid there is no racemization of the product, which retains *cis* configuration.

Introduction

Considerable interest has been shown in determining the factors governing the mechanism and steric course of replacement reactions on cobalt(III) complexes.[1-3] Many of the reactions studied have involved complexes of the general type $[Co(en)_2XY]^{+n}$, where X, usually Cl, is the ligand replaced while Y is retained, the influence of Y on the rate, mechanism, and steric course being under investigation. Observations on the replacement of chloride and bromide ion during acid hydrolysis (aquation) and Ag^+ assisted aquation have led to the formulation of rules predicting the molecularity and possible steric course of replacement reactions.[3]

In this paper we propose to describe the configuration changes which accompany the aquation of a very labile species produced by the reaction of nitrous acid with coordinated azide ion. There is ample evidence[4,5] that free azide ion reacts with nitrous acid to form the nitrosyl azide intermediate which decomposes rapidly to yield N_2 and N_2O. If coordinated azide reacts similarly the resulting complex would be expected to be quite labile and readily aquated. Other work[6] dealing with the extent of formation of products of the type $Co^{III}(NH_3)_5L$, where the reaction of nitrous acid with the azido complex takes place in the presence of L, indicates that an intermediate species is produced initially and that water and L then compete for occupation of the sixth coordination position. We find the reaction of excess nitrous acid with either *cis*- or *trans*-$[Co(en)_2(N_3)_2]ClO_4$ in perchlorate media leads to the formation of *cis*- and *trans*-$[Co(en)_2(H_2O)_2]^{+3}$ as the only cobalt-containing products.

Experimental

Materials. *cis*-$[Co(en)_2(N_3)_2]ClO_4$.—The nitrate salt was prepared from cobalt(II) according to the procedure of Staples and Tobe[7] and was twice recrystallized to remove any *trans* isomer which may have been present. The perchlorate salt was obtained by adding excess sodium perchlorate to a warm solution of the nitrate salt and cooling in ice. To ensure complete conversion to the perchlorate, the above procedure was repeated twice. The salt was washed with ethanol and ether and stored in a desiccator.

Anal. Calcd. for *cis*-$[Co(en)_2(N_3)_2]ClO_4$: C, 13.25; H, 4.68; N, 38.63; Co, 16.25. Found: C, 13.52; H, 4.68; N, 38.44; Co, 16.22.

D-*cis*-$[Co(en)_2(N_3)_2]ClO_4$ was prepared according to the procedure of Staples and Tobe[7] and was repeatedly recrystallized to remove the *cis* isomer until a constant absorption spectrum was obtained.

Anal. Found: C, 13.51; H, 4.66; N, 38.33; Co, 16.31.

cis- and *trans*-$[Co(en)_2N_3H_2O]^{+2}$ were not isolated in solids but studied in solutions as described later.

cis-$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$ and *trans*-$[Co(en)_2(H_2O)_2]Br_3$ were prepared by Werner's methods,[8,9] and the spectra were found to agree with those reported.[10]

All other chemicals were reagent grade and used without further purification. Sodium nitrite solutions were standardized against ceric ion.[11]

Kinetic and Isomerization Studies.—Kinetic and isomerizations studies were carried out spectrophotometrically using a two-armed mixing chamber that fitted directly into the ground joints of a 10-cm. spectrophotometer cell. The reagents were thermostated at 25.0 ± 0.1° and pipetted into the mixing chamber.

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(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1960.

(2) R. G. Wilkins, *Quart. Rev.* (London), **16**, 316 (1962).

(3) C. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

(4) K. Clusius and E. Effenberger, *Helv. Chim. Acta*, **38**, 1843 (1955).

(5) G. Stedman, *J. Chem. Soc.*, 1702 (1960), and preceding papers.

(6) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

(7) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

(8) A. Werner, *Ber.*, **40**, 282 (1907).

(9) A. Werner, *ibid.*, **40**, 269 (1907).

(10) J. Bjerrum and S. E. Rasmussen, *Acta Chim. Scand.*, **6**, 1265 (1952).

(11) A. H. Bennett and H. F. Harwood, *Analyst*, **60**, 677 (1935).

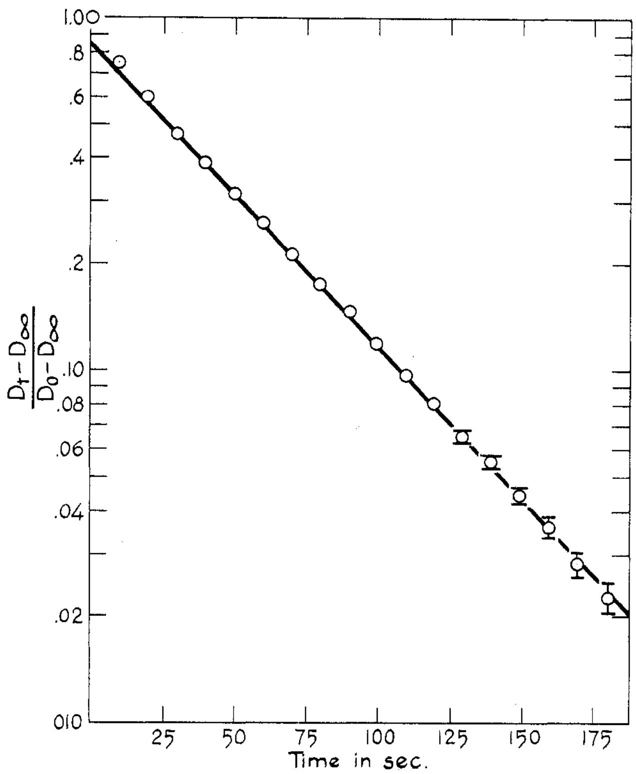

Figure 1.—Experiment 4-2 showing initial curvature for the first phase of the reaction followed by the linear portion for *trans*-$[Co(en)_2N_3H_2O]^{+2}$–HONO–H^+.

Inverting the mixing chamber initiated the reaction. The reaction mixture was thereupon immediately placed in the thermostated cell compartment of a Cary Model 14 recording spectrophotometer. This procedure gave a recording of optical density *vs.* time with an initial point within 10 sec. after mixing. Measurements, except as noted below, were made at 537 mμ,[12] the isosbestic point we observe for the isomerization of *cis*- and *trans*-$[Co(en)_2N_3H_2O]^{+2}$. In most reactions the concentration of complex was small compared to those of the other reagents and pseudo-first-order rate constants were evaluated from plots of log $(D_t - D_\infty)/(D_0 - D_\infty)$ *vs.* time where D_0, D_t, and D_∞ are the optical densities at time zero, time t, and after complete reaction. Some of the reactions of *cis*-$[Co(en)_2(N_3)_2]^+$ were carried out with a large excess of hydrogen ion but with the concentrations of complex and nitrous acid nearly equal. In these cases second-order plots were made using a calculated value of D_∞. No deviation from linearity was observed until approximately 70% reaction, whereupon the second step of the reaction began to compete with the first.

The isomeric compositions of the products were obtained by spectrophotometric analysis after complete reaction and by analyzing the kinetic behavior of the second step of the reaction.

In order to facilitate the discussion of the rates the complexes will be numbered as follows: **1**, *cis*-$[Co(en)_2(N_3)_2]^+$; **2**, *trans*-$[Co(en)_2(N_3)_2]^+$; **3**, *cis*-$[Co(en)_2N_3H_2O]^{+2}$; **4**, *trans*-$[Co(en)_2N_3H_2O]^{+2}$; **5**, *cis*-$[Co(en)_2(H_2O)_2]^{+3}$; **6**, *trans*-$[Co(en)_2(H_2O)_2]^{+3}$. Rate constants will be written as follows: k_{ab} to indicate conversion of complex a to complex b and k_{cd+ce} to indicate conversion of c into a mixture of d and e.

Reactions such as the spontaneous aquation of an azide ligand or *cis–trans* isomerizations, which might be expected to occur concurrently with nitrous acid oxidation, all are slow under our conditions compared to the oxidation reaction and were disregarded.[10,12] The spontaneous decomposition[13] of nitrous acid seldom amounted to as much as 3% and was disregarded.

Results

***trans*-$[Co(en)_2(N_3)_2]^+$ and *trans*-$[Co(en)_2N_3H_2O]^{+2}$.**—A solution of *trans*-$[Co(en)_2(N_3)_2]ClO_4$ was mixed with a large excess of nitrous acid and hydrogen ion. A first-order plot of the data for the entire reaction was linear to >95% completion except for curvature at the beginning of the reaction (see Figure 1). The initial curvature was attributed to the conversion of *trans*-diazido to aquoazido and the linear portion to the slower conversion of the aquoazido to diaquo. The linearity of the plots of log $(D_t - D_\infty)/(D_0 - D_\infty)$ *vs.* time during the second phase of the reaction was taken as an indication that only one aquoazido species, presumably the *trans*, was reacting. By varying the initial concentration of hydrogen ion and nitrous acid the rate law for the loss of *trans*-aquoazido was established as $-d(\mathbf{4})/dt = k_{45+46}(\mathbf{4})(HONO)(H^+)$ with $k_{4+546} = 110 \pm 5\ M^{-2}$ sec.$^{-1}$ (see Table I.)

TABLE I

KINETICS OF THE REACTION *trans*-$[Co(en)_2N_3OH_2]^{+2}$–HONO–H^+ AT 25° AND $\mu = 0.05$

Expt.	(complex), 10^4M	$\Sigma(NO_2^-)$, 10^4M^a	$\Sigma(H^+)$, 10^4M^b	(H^+), 10^4M^c	k_{45+46}, M^{-2} sec.$^{-1}$
4-1	2.94	83.3	203	123	112
4-2	2.94	83.3	304	222	115
4-3	2.94	117	287	172	120
4-4	2.83	50	220	171	109
4-5	2.83	200	300	110	114
4-6	3.02	33.3	127	95	111[d]
4-7	3.02	33.3	127	95	108[e]
4-8	1.00	25	380	355	108

[a] Concentration of added $NaNO_2$; $\Sigma(NO_2^-) = (NO_2^-) + (HONO)$. [b] Concentration of added $HClO_4$; $\Sigma(H^+) = (H^+) + (HONO)$. [c] Calculated from $\Sigma(NO_2^-)$, (ΣH^+), and the dissociation constant of HONO, 5×10^{-4}. [d] Measured at 560 mμ. [e] Measured at 520 mμ.

Further indication that the *trans*-diazido complex reacted stereospecifically to give only *trans*-aquoazido was obtained by repeating the reaction and making measurements of optical density at 500 mμ where ε for *trans*-diazido is 87 M^{-1} cm.$^{-1}$, ε for *trans*-aquoazido is 131 M^{-1} cm.$^{-1}$,[12] and ε for *cis*-aquoazido is 241 M^{-1} cm.$^{-1}$.[12] Under these conditions only a slight initial rise in optical density was observed followed by a slower first-order decay. Using the rate constant obtained later for k_{24}, the actual rise was calculated to correspond to $\epsilon = 110 \pm 10\ M^{-1}$ cm.$^{-1}$ for *trans*-aquoazido. This value is lower than that reported by Staples and Tobe. Since the formation of the *cis*-aquoazido isomer would result in an increase of ε, our results indicate that the separation of the two isomers by Staples and Tobe may have been incomplete.

Since within experimental error *trans*-diazido reacts cleanly to give *trans*-aquoazido, the rate of loss of diazido was calculated by assuming a simple series reaction: *trans*-diazido $\xrightarrow{k_{24}}$ *trans*-aquoazido $\xrightarrow{k_{45+46}}$ products. For such a reaction series the concentrations and

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[12] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4803 (1960), report the isobestic point at 533 mμ.

[13] E. Abel, H. Schmidt, and E. Romer, *Z. physik. Chem.*, **148**, 337 (1930), and preceding papers.

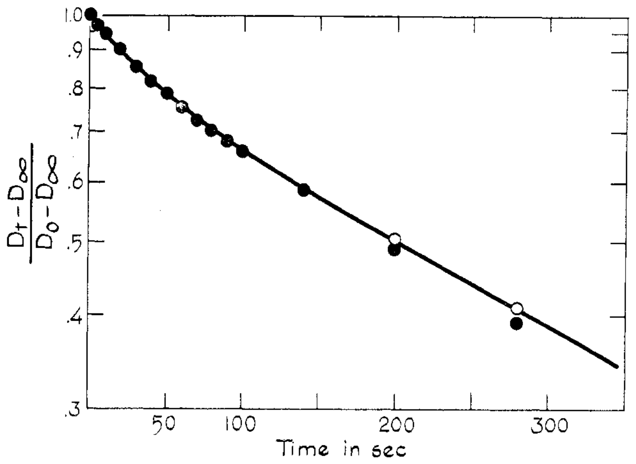

Figure 2.—Details of expt. 2-4. Solid line observed; solid points calculated for k_{24} = 850 M^{-2} sec.$^{-1}$, k_{45+46} = 110 M^{-2} sec.$^{-1}$; open points k_{24} = 850 M^{-2} sec.$^{-1}$, k_{45+46} = 115 M^{-2} sec.$^{-1}$.

hence optical densities can be calculated as a function of initial concentration, time, and rate constants. The rate constant k_{24} was obtained by using it as a variable to fit a calculated optical density to the observed value at several times during the initial stage of the reaction (see Figure 2). By varying initial hydrogen ion and nitrous acid concentrations the following rate law was derived: $-d(\mathbf{2})/dt = k_{24}(\mathbf{2})(\text{HONO})(\text{H}^+)$ with k_{24} = 850 ± 50 M^{-2} sec.$^{-1}$.

Table II

Kinetics of the Reaction *trans*-$[\text{Co(en)}_2(\text{N}_3)_2]^+$–HONO–$\text{H}^+$ at 25° and μ = 0.05

Expt.	(complex), 10^4M	$\Sigma(\text{NO}_2^-)$, 10^4M	$\Sigma(\text{H}^+)$ 10^4M	(H^+), 10^4M	k_{24}, M^{-2} sec.$^{-1}$
2-1	2.94	83.3	203	123	930
2-2	3.00	33.4	127	95	870[a]
2-3	3.02	33.3	127	95	840[a]
2-4	3.02	33.3	127	95	850
2-5	3.03	60.6	135	78	750
2-6	3.03	45.5	106	63	830

[a] Measured at 560 mμ.

Since *trans*-aquoazido was produced without isomerization from *trans*-diazido, any isomerization in the final diaquo product must arise during the conversion of *trans*-aquoazido to diaquo. After ten to twelve half-lives for the aquoazido–diaquo reaction a full spectral scan of the product was made from 600 to 450 mμ. Throughout this range the spectra could be accounted for by a mixture of *cis*- and *trans*-diaquo in a ratio of 0.40 ± 0.05 to 0.60 ± 0.05, respectively. These ratios were independent of initial hydrogen ion concentration over the range 0.9–0.02 M H^+.

***cis*-$[\text{Co(en)}_2(\text{N}_3)_2]^+$ and *cis*-$[\text{Co(en)}_2\text{N}_3\text{H}_2\text{O}]^{+2}$.**—A solution of *cis*-$[\text{Co(en)}_2(\text{N}_3)_2]^+$ was mixed with excess hydrogen ion and nitrous acid to provide pseudo-first-order conditions of concentration. After allowing sufficient time for the first step of the reaction to go to >99.5% completion an arbitrary time zero and D_0' were observed for the second stage of the reaction.

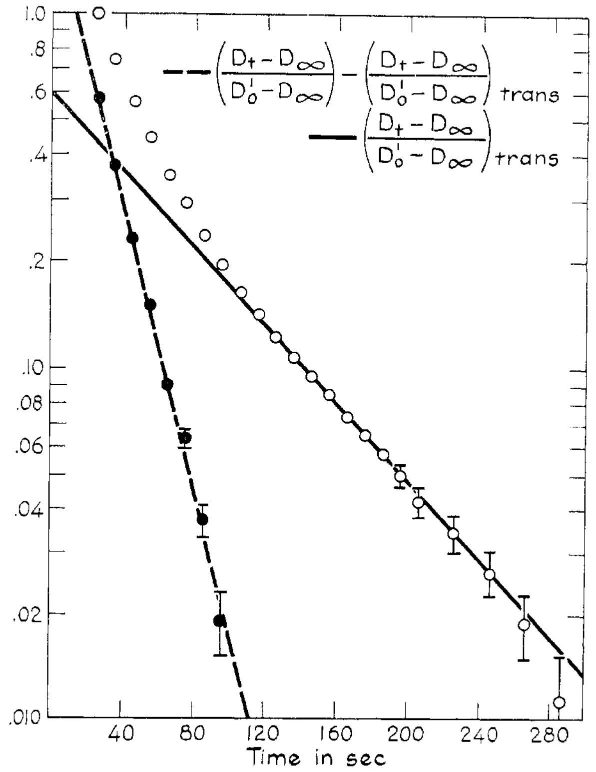

Figure 3.—Experiment **3**-7. Open points observed, solid line fit using k_{45+46} = 110 M^{-2} sec.$^{-1}$. The difference between the solid line and open points gives the solid points used to calculate k_{35}.

A first-order plot was made of the spectrophotometric data for the reaction, but linearity was not observed (for the second stage of the reaction) even after the arbitrary time zero. Since no diazido remained at this point, the curvature was attributed to the reaction of a mixture of *cis*- and *trans*-aquoazido and the kinetics handled as two independent parallel first-order reactions. The slower rate for the reaction of *trans*-aquoazido is known from the experiments with the *trans*-diazido complex, so the reaction was followed as long as possible (>95%) until the *cis* isomer was consumed and only *trans* remained. The data for the last few per cent of reaction in the plot of log $(D_t - D_\infty)/(D_0' - D_\infty)$ were then fitted with a straight line with a slope calculated from the known value of k_{45+46}, and the line was extrapolated through the chosen time zero ordinate. With this line a value of $[(D_t - D_\infty)/(D_0' - D_\infty)]_{trans}$ was read from the graph. This value, corresponding to change in optical density due to the *trans* isomer, was subtracted from the observed $(D_t - D_\infty)/(D_0' - D_\infty)$. A plot of the log of this difference *vs.* time gave a straight line, the slope of which was used to calculate pseudo-first-order rate constants for the loss of *cis*-aquoazido (see Figure 3). Varying initial concentrations gave a rate law of the form $-d(\mathbf{3})/dt = k_{35}(\mathbf{3})(\text{HONO})(\text{H}^+)$ with k_{35} = 440 ± 25 M^{-2} sec.$^{-1}$ (see Table III). Discussion of the steric course below will show that k_{35} and not k_{35+36} is the correct notation for the rate constant.

Since the reaction of the first azido group on *cis*-$[\text{Co(en)}_2(\text{N}_3)_2]^+$ leads to the formation of both *cis*-

TABLE III

KINETICS OF THE REACTION *cis*-$[Co(en)_2N_3OH_2]^{+2}$ AT 25° AND $\mu = 0.05$

Expt.	(complex), 10^4M	$\Sigma(NO_2^-)$, 10^4M	$\Sigma(H^+)$, 10^4M	(H^+), 10^4M	k_{24}, M^{-2} sec.$^{-1}$
3-1	2.96	83.3	233	203	405
3-2	2.96	83.3	186	107	450
3-3	2.96	83.3	186	107	495[a]
3-4	3.17	62.5	253	192	425
3-5	3.17	75	201	129	425
3-6	3.17	66.7	190	126	490
3-7	1.00	25	190	166	425

[a] Measured at 500 mμ.

and *trans*-aquoazido isomers, the method used to evaluate k_{24} cannot be applied easily to the evaluation of k_{13+14}. Instead either pseudo-second-order reactions were observed with the *cis*-diazido complex and nitrous acid in approximately equal concentrations and hydrogen ion in large excess, or pseudo-first-order conditions were provided with a large excess of nitrous acid buffer. Standard rate plots were made with a calculated value for D_∞. The slopes of the initial linear portion of the plots were used to calculate the rate. The rate law obtained by varying initial conditions was $-d(\mathbf{1})/dt = k_{13+14}(\mathbf{1})(HONO)(H^+)$ with $k_{13+14} = 2860 \pm 160\ M^{-2}$ sec.$^{-1}$ (see Table IV).

TABLE IV

KINETICS OF THE REACTION *cis*-$[Co(en)_2(N_3)_2]^+$–HONO–H^+ AT 25° AND $\mu = 0.05$

Expt.	(complex), 10^4M	$\Sigma(NO_2^-)$, 10^4M	$\Sigma(H^+)$, 10^4M	(H^+), 10^4M	k_{13+14}, M^{-2} sec.$^{-1}$
1-1	0.525	14.2	30.0	18.8	2810
1-2	0.525	14.2	60.0	47.2	3060
1-3	6.00	4.00	105	101.2	2900
1-4	6.00	5.00	117	112.2	2780
1-5	3.00	6.67	187	180.5	2600
1-6	6.00	4.00	105	101.2	2110[a]
1-7	6.00	4.00	305	301.1	2470[b]
1-8	6.00	4.00	104	101.2	5360[c]

[a] Ionic strength 0.011. [b] Ionic strength 0.031. [c] Ionic strength 0.50.

The amount of *cis*- and *trans*-aquoazido formed from the reaction of *cis*-$[Co(en)_2(N_3)_2]^+$ was determined from the optical density data for the second stage of the reaction. $(D_t - D_\infty)_{trans}$ was converted to concentration of *trans*-aquoazido using the equation $(D_t - D_\infty)_{trans} = \epsilon' bc$ where ϵ' is the change in extinction coefficient for the reaction of *trans*-aquoazido to products. Similarly $(D_t - D_\infty) - (D_t - D_\infty)_{trans}$ and ϵ'' were used to calculate the concentration of *cis*-aquoazido at time t with ϵ'' the change in extinction coefficient for the reaction of *cis*-aquoazido to *cis*-diaquo.

Treating the reactions *cis*-diazido → *cis*-aquoazido → *cis*-diaquo as a simple series in which only the fraction k_{13}/k_{13+14} of the *cis*-diazido was converted to *cis*-aquoazido gave the concentration of *cis*-aquoazido as

$$(\mathbf{3}) = \frac{k'_{13}(\mathbf{1})_0}{k'_{35} - k'_{13+14}} \left(e^{-(k'_{13+14})t} - e^{-(k'_{35})t}\right)$$

where $(\mathbf{1})_0$ is the initial concentration of *cis*-diazido and primed rate constants are pseudo-first-order constants obtained by multiplying the unprimed constants by the concentrations of hydrogen ion and nitrous acid.

For the reaction *cis*-diazido → *trans*-aquoazido → products, the expression is

$$(\mathbf{4}) = \frac{k'_{14}(\mathbf{1})_0}{k'_{45+46} - k'_{13+14}} \left(e^{-(k'_{13+14})t} - e^{-(k'_{35})t}\right)$$

Since t was chosen so large that all of the *cis*-diazido was essentially consumed, $e^{-(k'_{13+14})t}$ becomes nearly zero and the expressions rearrange to

$$k'_{13} = \frac{(\mathbf{3})}{(\mathbf{1})_0} \frac{k'_{13+14} - k'_{35}}{e^{-(k'_{35})t}}$$

$$k'_{14} = \frac{(\mathbf{4})}{(\mathbf{1})_0} \frac{k'_{13+14} - k'_{45+46}}{e^{-(k'_{45+46})t}}$$

Using these equations k'_{13} and k'_{14} were calculated for various times during each run. The sum k'_{13+14} was found to be within the expected range of 2860 ± 160 M^{-2} sec.$^{-1}$ for k_{13+14}. The per cent of *cis*-aquoazido initially formed, *i.e.*, the ratio k'_{13}/k'_{13+14}, was found to be 77 ± 3% for various times during a number of runs.

cis-Diazido was converted to diaquo with excess nitrous acid and hydrogen ion, and the spectra were recorded between 600 and 450 mμ. Throughout this range the product spectra could be accounted for as a mixture of 86 ± 2% *cis*- and 14 ± 2% *trans*-diaquo. These percentages were independent of initial hydrogen ion concentration over the range 0.9–0.008 M H^+. Since 23% of the aquoazido formed in the first step was *trans* and since 60% of this reacts to form *trans*-diaquo, all of the observed *trans*-diaquo can be accounted for without invoking its formation from *cis*-aquoazido. Thus the reaction of *cis*-aquoazido must go with 100 ± 4% retention of *cis* configuration.

To determine whether or not racemization took place in the reactions of the *cis* isomers a solution of D-*cis*-$[Co(en)_2(N_3)_2]^+$ was mixed with excess nitrous acid and perchloric acid to produce a mixture of *cis*- and *trans*-diaquo. The solution was nearly saturated with sodium bicarbonate to produce chelated $[Co(en)_2CO_3]^+$ and $[\alpha]$D measured. Dwyer, Sargeson, and Reid[14] have shown that D-*cis*-diaquo reacts with retention of configuration to give D-$[Co(en)_2CO_3]^+$ with $[\alpha]$D 1250 for the iodide salt. Using this value for $[\alpha]$D the diaquo produced from D-*cis*-diazido was

TABLE V

SUMMARY OF RESULTS AT 25.0°, $\mu = 0.05$
rate = k[complex][HONO][H^+]

Species	Rate constant, M^{-2} sec.$^{-1}$	% *cis* product
cis-$[Co(en)_2(N_3)_2]^+$	2860 ± 160	77 ± 3
cis-$[Co(en)_2N_3OH_2]^{+2}$	440 ± 25	100 ± 5
trans-$[Co(en)_2(N_3)_2]^+$	850 ± 50	0 ± 5
trans-$[Co(en)_2N_3OH_2]^{+2}$	110 ± 5	40 ± 5

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[14] F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Am. Chem. Soc.*, **85**, 1215 (1963).

calculated to be 79 ± 3% active. Comparison of this value with the 77 ± 3% obtained for the amount of *cis*-aquoazido obtained form *cis*-diazido leads to the conclusion the D-*cis*-diazido reacts to form only D-*cis*-aquoazido and *trans*-aquoazido. The D-*cis*-aquoazido then further reacts to form only D-*cis*-diaquo and the *trans*-aquoazido reacts to form both *trans*-diaquo and racemic *cis*-diaquo.

Discussion

There is good evidence[4,5] that the reaction of N_3^- with HONO to form N_2 and N_2O proceeds *via* a nitrosyl azide intermediate, and this formulation will be adopted. The form of the rate law for the various complexes and the variation of rate with ionic strength for the *cis*-diazido complex are consistent with nitrosyl transfer either as NO^+ or from the hydrated species $H_2NO_2^+$. The data presented here provide no basis for distinguishing between the two paths.

Once coordinated nitrosyl azide has been formed electronic rearrangement within this ligand leads to the formation of N_2 $(+N_2O)$[15] as a good leaving group. In general the Co–N_2 $(+N_2O)$ bond would be expected to be easily broken, requiring little rearrangement of the remaining ligands to reach the transition state, and thus might lead to the formation of a pentacoordinated square-pyramidal intermediate.[6]

The study of Pearson and Moore of the spontaneous aquation of $[Co(NH_3)_5NO_3]^{+2}$ in SCN^- and Br^- media[16] does not prove that an intermediate of reduced coordination number is not formed in the induced aquation of $[Co(NH_3)_5N_3]^{+2}$. However, it does prove that the conclusion reached in ref. 6 on the mechanism of the spontaneous aquation is not valid. The contention that different reaction paths are followed for the spontaneous aquation of anionic ligands and the induced aquations is further supported by the stereochemistry observed for the spontaneous aquation of *cis*- and *trans*-$[Co(en)_2N_3Cl]^+$ to give the aquoazido ion. These spontaneous aquations yield 100 and 20% *cis*-aquoazido, respectively.[12] A similar difference between spontaneous and induced aquations is observed for the spontaneous and Hg^{+2} induced aquations of D-*cis*-$[Co(en)_2Cl_2]^+$ which yield 100% D-*cis*-[17] and 70%-D-*cis*-chloroaquo,[18] respectively.

The difference in stereochemistry between the spontaneous and induced loss of ligands may lie in the amount of reorganization of the remaining ligands leading to the intermediate. This has been suggested in one of Wilmarth's alternative explanations for the mechanisms of the nitrous acid and the proton induced aquations of $[Co(CN)_5N_3]^{-3}$.[19] If this is the case the spontaneous or induced nature of the aquation would not be a critical factor, but the nature and position of the remaining ligands and the amount of reorganization required or permitted by the exact nature of the leaving group would be critical factors.

An ion of reduced coordination number can resume an octahedral configuration in a number of different ways. The actual path followed would be expected to depend on the geometry of the intermediate and the nature of the remaining ligands and their positions on the complex. In this connection it is pertinent to note that water tends to add *trans* to coordinated azide but *cis* to coordinated water.

The retention of configuration for the reaction of *trans*-diazido to form *trans*-aquoazido can be interpreted in terms of an ion of reduced coordination number that is stable with respect to rearrangement. Back bonding from the cobalt to empty orbitals on the azide ligand could stabilize a tetragonal pyramid intermediate. Since edge displacement reactions of *trans* ions require formation of *cis* product, edge displacement is limited to less than experimental error or about 5%.

Knowledge of the product distribution for the reaction of D-*cis*-$[Co(en)_2(N_3)_2]^+$ does not necessarily lead to an unequivocal assignment of mechanism. However, assuming an SN1 loss of N_2 $(+N_2O)$, a trigonal bipyramid intermediate with the remaining azide located on the trigonal plane explains the observations. This species retains the optical activity of the starting material. Addition of water at any edge of the trigonal plane leads to the product, addition adjacent to the azide leads to D-*cis*-aquoazido, and addition remote to the azide leads to *trans*-aquoazido. Statistically this would lead to $^2/_3$ D-*cis* and $^1/_3$ *trans*, but deviation from these values is not unexpected as the two sites are not identical and may exhibit different susceptibility to attack by water. (Since the azide ligand *cis* to the departing group is in a position to donate π-bonding electrons into the $d_{x^2-y^2}$ orbital made available by the loss of the sixth ligand, the driving force for the collapse to a trigonal bipyramid may be to increase overlap between the π-bonding orbitals.)

A pentacoordinated transition state or intermediate formed by the loss of N_2 $(+N_2O)$ from *trans*-aquoazido can have little stabilization *via* π-bonding between the ligands and the cobalt center. Lacking stabilization the ion would be more susceptible to isomerization before or during the addition of water. The product may then reflect a competition between direct addition and a rearrangement process, or competition between direct addition of water and a concerted attack by water hydrogen-bonded to the coordinated water.

The reaction of D-*cis*-$[Co(en)_2N_3H_2O]^{+2}$ to form D-*cis*-$[Co(en)_2(H_2O)_2]^{+3}$ by way of a species of reduced coordination number requires that no significant changes of geometry occur while the complex has coordination number five. This implies the formation of a square pyramid that is maintained without isomerization or racemization until and during the coordination of water at the vacant site. Hydrogen bonding between water molecules in the first and second coordination spheres cannot be disregarded as hydrogen-

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[15] It is assumed that N_2 rather than N_2O is left in the coordination sphere of Co(III), but there is no proof that this is in fact the case.

[16] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

[17] J. P. Mathieu, *Bull. soc. chim., France*, [5] **4**, 687 (1937).

[18] A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).

[19] A. Haim, R. J. Grassi, and W. K. Wilmarth, Symposium on Mechanisms of Inorganic Reaction, University of Kansas, 1964, p. 33.

bonded water in the second coordination sphere would be in a prime position to occupy the vacant site.

The loss of a proton to produce a hydroxo ligand on the pentacoordinated species made by the reaction of *cis-* or *trans*-aquoazido would facilitate π-bonding between cobalt and oxygen and possibly lead to a trigonal bipyramid intermediate and different product distribution than for the corresponding aquo pentacoordinated ions. However, for neither isomer does varying the hydrogen ion over the range 0.90–0.03 M significantly alter the over-all product distribution. In light of this behavior either the hydroxo path does not make a significant contribution or the hydroxo path leads to a product distribution similar to that for the aquo ligand path.

The present results are consistent with but do not prove formation of a five-coordinated intermediate. Further work is in progress attempting to produce, by other methods, the intermediate species postulated here.

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Acyclic Imides as Ligands. I. Diacetamide Complexes of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Perchlorates

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Diacetamide is shown to form a series of new complexes having the general formula $[M(C_4H_7O_2N)_3](ClO_4)_2$, where M = Mn(II), Fe(II), Co(II), Ni(II), or Zn(II). The compound $[Cu(C_4H_7O_2N)_2](ClO_4)_2$ is also reported. Infrared studies demonstrate that diacetamide assumes the *trans-trans* configuration upon complexation to the metal ions with coordination occurring through oxygen. Magnetic and visible–near-infrared spectral data are as expected for octahedral complexes with weak field ligands. Conductivity data indicate that each of the complexes is a 1:2 electrolyte in dilute acetone solution.

Introduction

Considerable study has been made of the complexing ability of the amide linkage over the past few years. Recent publications by Bull,[1] Drago,[2] and Rollinson[3] and their various co-workers have illustrated the great range of amide-to-metal ion complexes which may be prepared. Lindquist[4] has included a list of amide-containing complexes in his recent summary of compounds involving oxygen-donating ligands. A perusal of these references reveals that nearly all of the amide complexes which have been reported are complexes of simple organic amides, whereas very few references are made to the complexing abilities of acyclic imides. Of outstanding interest in this regard have been the recent crystallographic examinations of some biuret ($NH_2CONHCONH_2$) complexes of cadmium(II), mercury(II), copper(II), and zinc(II). Whereas bis(biuret)cadmium chloride and bis(biuret)mercury(II) chloride have been shown to exist as infinite chains in the crystalline state[5] with the biuret molecules serving as monodentate ligands, the corresponding zinc(II) and copper(II) compounds are true molecular adducts with the biuret molecules serving as neutral chelating ligands with bond formation occurring exclusively through oxygen.[6] To our knowledge, the only reported complexes derived from acyclic imides are a 1:1 adduct between tin(II) chloride and N-phenyldiacetamide (N,N-diacetylaniline)[7] and bis(dibenzamido)copper(II).[8] We wish to report here some of our investigations on the complexing capability of diacetamide ($CH_3CONHCOCH_3$) with a series of dipositive transition metal ions.

Experimental

Reagents.—Diacetamide was prepared and purified according to the method of Polya and Tardrew.[9] Hydrated metal perchlorates were used as obtained from the G. Frederick Smith Co. Ethyl acetate (Baker Analyzed reagent), nitromethane (Matheson Coleman and Bell, Spectrograde), and absolute ethanol were used as received. Acetone (Baker Analyzed) was stored over Drierite and distilled as needed.

Preparation of Complexes.—The following general procedure was used for the preparation of the diacetamide complexes. Separate solutions of 0.010 mole of the metal perchlorate hydrate in 25 ml. of ethyl acetate and 4.04 g. (0.040 mole) of diacetamide in 25 ml. of ethyl acetate were filtered into a common receiver. Precipitation of the solid complexes usually began immediately.

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