935. *Mechanism and Steric Course of Octahedral Aquation. Part III.* Aquation and Basic Hydrolysis of Some Azidobis(ethylenediamine)-cobalt*(III) *Salts.*

By P. J. STAPLES and M. L. TOBE.

The kinetics of the aquation of the *cis*- and *trans*-chloroazidobis(ethylenediamine)cobalt(III) cations have been studied, and the Arrhenius parameters determined. Aquation of the *cis*-isomer proceeds with complete retention of configuration but the *trans*-isomer yields 20% of the *cis*-product at 25°. The chlorine is replaced far more easily than the azide group. The aquoazidobis(ethylenediamine)cobalt(III) cations isomerise to an equilibrium composition of 73% *cis*- and 27% *trans*-isomer. The kinetics of the rearrangement have been studied. The rates of the reaction between *cis*- and *trans*-$[\mathrm{Co\,en_2N_3Cl}]^+$ and hydroxide ions have been measured, and the steric courses of the reactions determined. The *trans*-isomer yields 13% of *cis*- and the *cis*-isomer yields 49% of *trans*-hydroxoazido-product. The rates of reaction of the *cis*- and *trans*-$[\mathrm{Co\,en_2(N_3)_2}]^+$ and the *cis*- and *trans*-$[\mathrm{Co\,en_2N_3(OH)}]^+$ cations with hydroxide ions are also reported. In the reactions of the complexes with hydroxide ions, the azide group seems to behave as an electron-withdrawing group, in the same way as, but to a smaller extent than, the nitro-group. A second mode of action appears in the reaction with water, in which an electron-releasing effect, similar to that of chlorine, becomes important.

ALTHOUGH the thermal decomposition of azido-complexes has been investigated [1] and the rôle of the azide ion as a substituting reagent [2] has been examined, no work has yet been published on the influence of the co-ordinated azide group on the lability of other ligands in the complex. This paper deals mainly with the labilising and directing effects of the azide group in some bis(ethylenediamine)cobalt(III) ions.

(1) *Isomerisation of the* cis- *and* trans-*Aquoazidobis(ethylenediamine)cobalt*(III) *Cations in Aqueous Solution.*—An aqueous solution of *trans*-aquoazidobis(ethylenediamine)-cobalt(III) perchlorate slowly changes colour from violet to purplish-red at room temperature. No co-ordinated azide ions are released during this process, which must therefore be an isomerisation. The kinetics were followed spectrophotometrically at 25°. The spectrum of the solution when equilibrium was attained was different from that of the pure *cis*-aquoazido-isomer, and the same spectrum was obtained irrespective of whether *cis*- or *trans*-$[\mathrm{Co\,en_2N_3H_2O}](\mathrm{ClO_4})_2$ was used. These final spectra, shown in Fig. 1, correspond exactly with that expected for a mixture of the *cis*- and *trans*-aquoazidoperchlorates having a composition of 73% *cis*- and 27% *trans*-isomer.

The kinetic form of the reaction was that of two opposing reactions of first order:

$$cis\text{-}[\mathrm{Co\,en_2N_3H_2O}]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[\mathrm{Co\,en_2N_3H_2O}]^{2+}$$

The specific rate of approach to equilibrium from either isomer was calculated directly from the optical densities by means of the equation

$$k_1 + k_{-1} = (2{\cdot}303/t)\log_{10}(D_0 - D_\infty)/(D_t - D_\infty)$$

to give the values in Table 1. There is no significant dependence of the rate of isomerisation upon the pH of the solution over the range pH 2—6.

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* Part II, *J.*, 1960, 4275.

[1] Linhard, Weigel, and Flygare, *Z. anorg. Chem.*, 1950, **263**, 233.

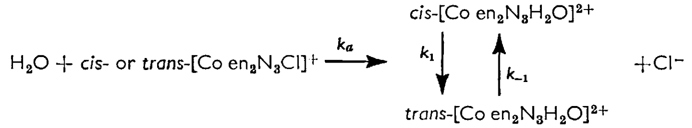
[2] Brown and Ingold, *J.*, 1953, 2674; Basolo, Bergmann, Stone, and Pearson, *J. Amer. Chem. Soc.*, 1954, **76**, 3079; Pearson, Henry, and Basolo, *ibid.*, 1957, **79**, 5379, 5382.

TABLE 1. *First-order rate constants* ($k_1 + k_{-1}$ *in* sec.$^{-1}$) *of approach to equilibrium, in the reverse interconversion of* cis- *and* trans-*aquoazidobis(ethylenediamine)cobalt*(III) *perchlorate in dilute aqueous perchloric acid* (10^{-2}N) *at* 25°.

Initial confign.	Initial [Co salt] (mmole/l.)	$10^5(k_1 + k_{-1})$	*cis* (%) at equilibrium
trans	1·05	9·8	73
,, ...	0·94	9·8	
cis	0·70	10·0	

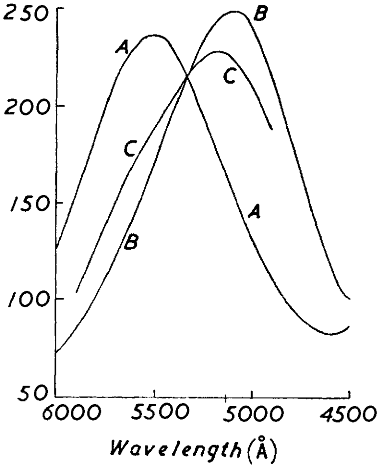
This is the fastest isomerisation of aquo-complexes of the type [Co $en_2A(H_2O)]^{n+}$ that has so far been reported,[3] but recent work [4] has indicated that the isomerisation of the *cis*- and *trans*-[Co $en_2ClH_2O]^{2+}$ cations proceeds at a similar rate ($k_1 + k_{-1} = 9{\cdot}3 \times 10^{-5}$ sec.$^{-1}$ at 25°).

(2) *Aquation of* cis- *and* trans-*Chloroazidobis(ethylenediamine)cobalt*(III) *Salts.*—(a) *Basic chemistry.* The *cis*- and *trans*-chloro-salts have been well characterised,[5] and their configurations proved by optical resolution of the *cis*-isomer.



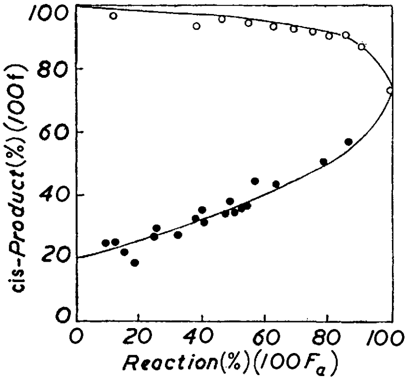
A dilute acid aqueous solution of a salt of either series slowly produces free chloride ions at room temperature. A study of the changing absorption spectrum indicates successive processes having comparable rates. The first is the aquation of the chloro-complex, and the second the isomerisation described in Section (1). At very much longer reaction times a second aquation step can be observed in which the azide group is displaced.

FIG. 1. *"Infinity" absorption spectra for the isomerisation of cis- or trans-*[Co $en_2N_3H_2O]^{2+}$.



A = *trans*-[Co $en_2N_3H_2O]^{2+}$. *B* = *cis*-[Co $en_2N_3H_2O]^{2+}$. *C* = *Equilibrium spectrum* = 73% *cis*-isomer.

FIG. 2. *Product analyses during the aquation of* ○, *cis*-[Co $en_2N_3Cl]^+$ *and* ●, *trans*-[Co $en_2N_3Cl]^+$.



(b) *Kinetics.* The aquation was followed by estimating the concentration of chloride

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[3] (*a*) Ingold, Nyholm, and Tobe, *J.*, 1956, 1691; Part I, Tobe, *J.*, 1959, 3776; (*b*) Ašperger and Ingold, *J.*, 1956, 2862.

[4] Tobe, unpublished results.

[5] Staples and Tobe, following paper.

ions in the reaction solution with silver nitrate. There was no evidence for the formation of addition compounds between the complex cations and silver ions, nor was the aquation accelerated in the presence of an excess of silver ions. The application of a spectrophotometric method to the determination of the rate constants was hindered by the subsequent rearrangement of the aquoazido-products. The absorption spectra of the chloroazido- and aquoazido-bis(ethylenediamine)cobalt(III) cations have already been reported[5] and it will be seen that at 5330 Å the aquoazido-isomers have identical molar extinction coefficients which differ from those of the chloroazido-isomers. The rate of change of optical density at 5330 Å has been used to determine spectrophotometric rate constants but the method does not give reliable values for the *cis*-isomer because of the small percentage change of absorption. Table 2 contains the first-order rate constants determined by the two methods outlined above.

TABLE 2. *Titrimetric and spectrophotometric rate constants for the aquation of* cis- *and* trans-*chloroazidobis(ethylenediamine)cobalt*(III) *cation in aqueous perchloric acid* (pH 2).

[Titrimetric rate constants were derived graphically by plotting $\log_{10}(V_\infty - V_t)$ against time, V_∞ and V_t being the titres of silver nitrate after ten half-lives and at time t respectively ($k_1 = 2{\cdot}303 \times$ slope). Spectrophotometric rate constants were determined graphically from the plot of $\log_{10}(\varepsilon_\infty - \varepsilon_t)$ against time, where ε_∞ and ε_t are the apparent molar extinction coefficients of the solution at 5330 Å after ten half-lives and at time t respectively ($\varepsilon_\infty = 214$).]

		trans-[Co en_2N_3Cl](ClO_4)			*cis*-[Co en_2N_3Cl]$_2$(S_2O_6)	
Temp.	Method	Initial [Complex] (mmole/l.)	10^4k_1 (sec.$^{-1}$)		Initial [Complex] (mmole/l.)	10^4k_1 (sec.$^{-1}$)
10·1°	Titrn.	1·98	0·32	Titrn.	0·40	0·35
,,	,,	6·00	0·32	,,	1·00	0·34
,,	,,	9·65	0·33	,,	2·02	0·35
24·65	Spec.	1·00	2·0			
,,	,,	2·48	2·1			
,,	,,	4·82	2·0			
,,	,,	10·1	2·0			
25·00	Titrn.	1·62	2·2	Titrn.	0·51	2·4
,,	,,	2·71	2·2	,,	2·00	2·4
,,	,,	2·98	2·3	Spec.	1·34	2·3
35·0	,,	1·00	8·7	Titrn.	1·00	8·0
,,	,,	2·98	8·7	,,	2·32	7·9

(c) *Steric course.* It has already been shown that the *cis*- and *trans*-aquoazidobis-(ethylenediamine)cobalt(III) cations, formed as a result of the aquation reaction, readily isomerise at 25° to give an equilibrium mixture containing 73% of the *cis*- and 27% of the *trans*-isomer. The rate constant for the approach to equilibrium ($k_1 + k_{-1}$) is smaller than the rate constants for the aquation, k_a, but of the same order of magnitude. Consequently, it is not possible to determine the steric course of the reaction by measuring the isomeric composition of the product when all the chloro-complex has reacted. The problem was solved by making full spectrophotometric analyses of the mixture while the reaction was in progress and then, by plotting the composition of the product against the fraction of the reaction completed, the composition of the product of aquation was determined by extrapolation to zero reaction. The extrapolation was guided by fitting a theoretical curve of the correct functional form to the data. The function used was

$$\frac{f - f_\infty}{f_0 - f_\infty} = \frac{k_a}{(k_1 + k_{-1}) - k_a}\left\{\frac{(1 - F_a) - (1 - F_a)^{(k_1+k_{-1})/k_a}}{F_a}\right\}$$

where F_a is the fraction of the chloro-complex that has reacted, f is the fraction of the aquo-product having the *cis*-configuration, and f_∞ is the value of f at equilibrium; f_0 is the fraction of *cis*-isomer produced by the actual act of aquation and is used as a variable in order to obtain the best fit of the curve to the experimental data. The derivation of this function has already been given.[3] A full spectrophotometric analysis was possible in the study of the aquation of the *trans*-cation but, owing to the similarity of the absorption spectra of *cis*-$[Co\ en_2N_3Cl]^+$ and *cis*-$[Co\ en_2N_3H_2O]^{2+}$, spectrophotometric measurements could only be used to determine the concentration of the *trans*-aquo-product. The analysis was completed by introducing titrimetric data to distinguish between the *cis*-chloro- and the *cis*-aquo-complex.

The data for both the *cis*- and the *trans*-chloroazido-isomer are plotted in Fig. 2, where it will be seen that the reaction between *trans*-$[Co\ en_2N_3Cl]^+$ and water at 25° yields 20% of *cis*- and 80% of *trans*-$[Co\ en_2N_3H_2O]^{2+}$, whereas the *cis*-chloro-isomer yields 100% of *cis*-product under the same conditions.

(3) *Kinetics and Products of the Reaction of Hydroxide Ions with the* cis- *and* trans-*Chloroazidobis(ethylenediamine)cobalt*(III) *Cations in Water.*—(a) *Kinetics.* The rate of release of chloride from the isomeric chloroazidobis(ethylenediamine)cobalt(III) cations

$$OH^- + \textit{cis- or trans-}[Co\ en_2N_3Cl]^+ \longrightarrow \textit{cis- and trans-}[Co\ en_2N_3(OH)]^+ + Cl^-$$

is considerably increased in the presence of hydroxide ions. The reaction proceeds to completion and produces a mixture of *cis*- and *trans*-$[Co\ en_2N_3(OH)]^+$ cations and is followed by a very much slower reaction whereby the azide is displaced. The kinetics of this step have been studied separately and are reported in Section 4. The second step is too slow to interfere with the first reaction and can be ignored. The rate of the reaction at 0° was measured titrimetrically by estimating the amount of chloride liberated. A sampling method was used, the reaction being stopped by pouring the solution into a small excess of ice-cold dilute nitric acid. The kinetics follow a second-order rate law, $d[Cl^-]/dt = k_2[complex][OH^-]$, and the second-order rate constants are collected in Table 3.

TABLE 3. *Second-order titrimetric rate constants for the replacement of chloride by hydroxide in* cis- *and* trans-*chloroazidobis(ethylenediamine)cobalt*(III) *salts in aqueous solution at* 0°.

[The rate constants were calculated by using the integrated formula, $k_2 = [2{\cdot}303/t(b - a)]\{\log_{10}[a(b - x)/b(a - x)]\}$ l. sec.$^{-1}$ mole^{-1}, where *a* and *b* are the concentrations of complex and hydroxide respectively at time $t = 0$, and *x* is the concentration of chloride ions at time *t* (sec.). Hydroxide ions were introduced as carbonate-free sodium hydroxide solution.]

Initial [Co salt] (mmole/l.)	Initial $[OH^-]$ (mmole/l.)	k_2 (l. sec.$^{-1}$ mole^{-1})	Initial [Co salt] (mmole/l.)	Initial $[OH^-]$ (mmole/l.)	k_2 (l. sec.$^{-1}$ mole^{-1})
	trans-$[Co\ en_2N_3Cl](ClO_4)$			*cis*-$[Co\ en_2N_3Cl]_2(S_2O_6)$	
1·16	5·00	0·41	1·24	2·92	0·18
1·37	5·00	0·41	1·12	3·52	0·17
1·90	5·00	0·40	1·16	4·70	0·17
1·52	8·00	0·44			

TABLE 4. *Proportions in which* cis- *and* trans-*hydroxoazidobis(ethylenediamine)cobalt*(III) *cations are formed in the reaction of hydroxide ions with* cis- *and* trans-*chloroazidobis-(ethylenediamine)cobalt*(III) *salts in water at* 0°.

	ε_{5000}
cis-$[Co\ en_2N_3H_2O]^{2+}$	241
trans-$[Co\ en_2N_3H_2O]^{2+}$	131
Aquo-cation mixture from *cis*-$[Co\ en_2N_3Cl]^+$	187
Aquo-cation mixture from *trans*-$[Co\ en_2N_3Cl]^+$	146

cis-$[Co\ en_2N_3Cl]^+$ gives 51% *cis*- and 49% *trans*-product
trans-$[Co\ en_2N_3Cl]^+$ gives 13% *cis*- and 87% *trans*-product

(b) *Steric course.* The steric course of the reaction between *cis*- or *trans*-$[Co\ en_2N_3Cl]^+$ and hydroxide ions was determined by allowing the complex to react with excess of sodium hydroxide for ten half-lives at 0°. The solution was then acidified and made up to a known volume, and the spectrum measured. There was no indication that any co-ordinated azide had been replaced by hydroxide in this time nor was there any evidence for any rearrangement of the hydroxoazido-isomers. Separate experiments showed that protonation and deprotonation were instantaneous and caused no steric change. The isomeric distribution of the *cis*- and *trans*-aquoazidobis(ethylenediamine)cobalt(III) cations in the acidified reaction product was calculated from the spectrophotometric data and the results are collected in Table 4.

(4) *Kinetics of the Reaction of Hydroxide Ions with the* cis- *and* trans-*Hydroxoazidobis-(ethylenediamine)cobalt*(III) *Cations in Water.*—In the presence of hydroxide ions, the *cis*- or *trans*-$[Co\,en_2N_3(OH)]^+$ cations slowly lose co-ordinated azide and form a mixture of *cis*- and *trans*-$[Co\,en_2(OH)_2]^+$. The progress of the reaction was followed at 25° by estimating the concentration of azide ions in solution. The complex cations were removed from the solution by a cation-exchange resin and the concentration of the azide in the effluent was measured colorimetrically. This method could be applied to solutions far too dilute for the argentometric method to be of use.

$$OH^- + \textit{cis- or trans-}[Co\,en_2N_3(OH)]^+ \longrightarrow \textit{cis- and trans-}[Co\,en_2(OH)_2]^+ + N_3^-$$

The reaction was studied in the presence of sufficient excess of sodium hydroxide for the kinetic form to be of first order. Pseudo-first-order rate constants were obtained graphically from the slope of the semilogarithmic plot of $\log_{10}([N_3^-]_\infty - [N_3^-]_t)$ against time. The pseudo-first-order rate constants were divided by the concentration of the hydroxide ions to give the second-order rate constants, and both are given in Table 5.

The complex ion was provided as a solution of its hydroxide and was obtained by the following method. It has been shown [5] that *cis*- and *trans*-$[Co\,en_2N_3Cl]^+$ salts react very rapidly with an excess of mercuric perchlorate in 0·1M-perchloric acid to give the *cis*- and *trans*-$[Co\,en_2N_3H_2O]^{2+}$ cations with complete retention of configuration. The appropriate amount of chloroazido-salt was weighed out and dissolved in water. An excess of mercuric perchlorate solution acidified with a little perchloric acid was added, and the solution shaken and passed down a column of Amberlite IRA-400 anion-exchange resin in the hydroxide form. All anions were replaced by hydroxide ions and the mercuric species were retained on the column as insoluble mercuric hydroxide. The effluent, therefore, contained only hydroxoazidobis(ethylenediamine)cobalt(III) hydroxide. It was shown that there was no noticeable loss of co-ordinated azide from the complex as a result of this treatment. The effluent was brought to the temperature of the reaction, a known amount of sodium hydroxide was added, and the solution adjusted to a known volume with water.

TABLE 5. *Rate constants for the replacement of azide by hydroxide in* cis- *and* trans-*hydroxoazidobis(ethylenediamine)cobalt*(III) *salts in aqueous solution at* 25·1°.

[The pseudo-first-order rate constants k_1' were determined graphically from the slope of the semilogarithmic plot of $\log_{10}([N_3^-]_\infty - [N_3^-]_t)$ against time. The "infinity" azide concentration was determined experimentally. Second-order rate constants, $k_2 = k_1'/[OH^-]$, are also reported.]

Confign.	[Complex] (mmole/l.)	[Hydroxide] (N)	$10^4k'$ (sec.$^{-1}$)	10^3k_2 (l. sec.$^{-1}$ mole^{-1})
cis	1·20	0·0500	1·40	2·80
,,	1·20	0·0500	1·40	2·80
,, *	1·25	0·0500	1·42	2·84
trans	0·80	0·0500	0·59	1·18
,,	0·80	0·0500	0·64	1·28
,, *	1·23	0·0500	0·59	1·18

* Spectrophotometric rate constants.

The steric course of this reaction has not been determined. Difficulties may arise because of the rearrangement of the product.

(5) *Kinetics and Products of the Reaction of Hydroxide Ions with the* cis- *and* trans-*Diazidobis(ethylenediamine)cobalt*(III) *Cations in Water.*—(a) *Kinetics.* The kinetics of the reaction were studied by measuring the rate at which the co-ordinated azide ions were

displaced in the presence of a large excess of sodium hydroxide. The kinetic form of the

$$\mathrm{OH^-} + cis\text{- or } trans\text{-}[\mathrm{Co\,en_2(N_3)_2}]^+ \longrightarrow cis\text{- and } trans\text{-}[\mathrm{Co\,en_2N_3(OH)}]^+ + \mathrm{N_3^-}$$

reaction was complicated because the hydroxoazido-products can undergo further reaction with hydroxide ions (Section 4) at a rate that is less than, but of the same order of magnitude as, that of the diazido-complexes.

Since the concentration of the hydroxide was much greater than that of the complex, it was possible to treat the reaction as a sequence of first-order processes. The pseudo-first-order rate constants of the first step were sufficiently large compared to those of the succeeding steps for them to be determined by measuring the initial slope of the semi-logarithmic plot of $\log_{10}([\mathrm{N_3^-}]_\infty - [\mathrm{N_3^-}]_t)$ against time, where $[\mathrm{N_3^-}]_t$ was the concentration of free azide ions in the solution at time *t*, and $[\mathrm{N_3^-}]_\infty$ was the calculated concentration of azide ions that would be present in solution if only one of the two azido-groups in the complex was replaced by hydroxide. At later reaction times the semilogarithmic plot became steeper as the second stage of the reaction gained importance. The *trans*-diazido-isomer gave a linear plot for the first half-life, and the initial slope could be measured easily. The semilogarithmic plot for the *cis*-isomer curved away at earlier reaction times but it was still possible to guide the slope by the point representing $[\mathrm{N_3^-}]_0 = 0$.

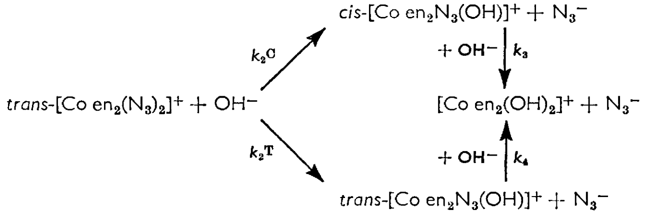
The pseudo-first-order rate constants were determined for two concentrations of hydroxide and are reported in Table 6, together with the derived second-order rate constants, k_2.

TABLE 6. *Colorimetric rate constants for the replacement of the first azide group in* cis- *and* trans-*diazidobis(ethylenediamine)cobalt*(III) *perchlorate by hydroxide ions in aqueous solution at* 25·1°.

Confign.	Initial [complex] (mmole/l.)	$[\mathrm{OH^-}]$ (N)	10^4k_1 (sec.$^{-1}$)	10^3k_2 (l. sec.$^{-1}$ mole^{-1})
trans	1·02	0·0200	2·27	11·4
,, ...	0·52	0·0250	2·77	11·1
,, ...	1·02	0·0250	2·86	11·5
,, ...	1·01	0·0333	3·84	11·5
,, ...	1·34	0·0333	3·65	11·0
cis	0·64	0·0500	3·33	6·66
,, ...	0·80	0·0500	3·32	6·64
,, ...	1·53	0·0500	3·37	6·74
,, ...	0·64	0·1000	6·66	6·66
,, ...	1·53	0·1000	6·44	6·44
,, ...	2·51	0·1000	6·46	6·46

(b) *Steric course.* Owing to the relative ease with which the hydroxoazido-products undergo further reaction with hydroxide ions, it was not possible to determine the steric course of the reaction by a spectrophotometric technique. During the reaction, the solution contains five light-absorbing species and the accuracy of the measurements does not permit the analysis of a five-component mixture.

Use has been made of the difference in the reactivity of the *cis*- and *trans*-hydroxoazido-bis(ethylenediamine)cobalt(III) isomers in determining the steric course of the first step of the reaction. The ratio in which these products were formed could be deduced by studying the amount of azide released at the later stages of the reaction as a function of time. The system was treated as two simultaneous consecutive reactions, *e.g.*, in the case of the *trans*-isomer:



Since the reaction was carried out in the presence of a large excess of hydroxide ions, the individual steps could be treated as first-order processes. For a given hydroxide concentration, k_1^C, k_1^T, k_3', and k_4' were the pseudo-first-order rate constants, such that $k_2^C = k_1^C[OH^-]$, etc. Values for $(k_1^C + k_1^T)$, k_3', and k_4' were calculated from the appropriate rate constants from Tables 5 and 6. The fraction of the hydroxoazido-complexes having the *cis*-configuration when produced as a result of the replacement of the first azide group by hydroxide, $f_{cis} = k_1^C/(k_1^C + k_1^T)$, was used as a variable in the plotting of a family of curves for $[N_3]^-/A_0$ against time, where A_0 is the initial concentration of the diazido-complex. These curves are compared with the experimental data in Figs. 3 and 4, which show that the experimental data are best satisfied when $f_{cis} = 0{\cdot}30 \pm 0{\cdot}05$ for the *trans*-diazido-complex and $f_{cis} = 0{\cdot}55 \pm 0{\cdot}05$ for the *cis*-diazido-complex.

FIG. 3. *Experimentally determined values of* $[N_3^-]/A_0$, ●, *plotted against time for the displacement of the azide in cis-*$[Co\,en_2(N_3)_2]^+$ *by hydroxide ions. The full lines are calculated for the values of %* cis-*product* ($100 f_{cis}$) *stated.*

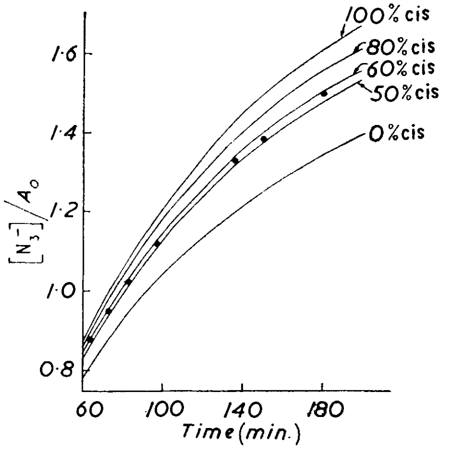
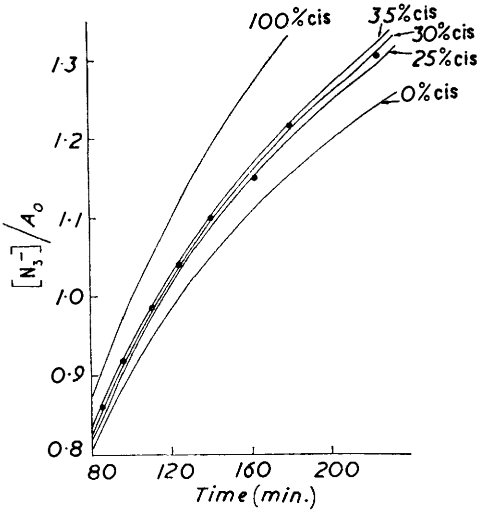


FIG. 4. *Experimentally determined values of* $[N_3^-]/A_0$, ●, *plotted against time for the displacement of the azide in trans-*$[Co\,en_2(N_3)_2]^+$ *by hydroxide ions. The full lines are calculated for the values of %* cis-*product* ($100 f_{cis}$) *stated.*



The expression used to calculate $[N_3^-]/A_0$ was:

$$[N_3^-]/A_0 = 2 - 2\exp(-k_1t) - \frac{k_1^C}{k_3' - k_1}\left\{\exp(-k_1t) - \exp(-k_3'/t)\right\} - \frac{k_1^T}{k_4' - k_1}\left\{\exp(-k_1t) - \exp(-k_4'/t)\right\}$$

where $k_1 = (k_1^C + k_1^T)$. The values of the rate constants substituted in this expression are given in Table 7.

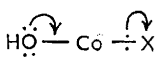
TABLE 7. *Pseudo-first-order rate constants used in the determination of the steric course of hydroxide substitution.*

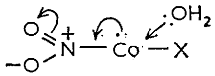
trans-$[Co\,en_2(N_3)_2](ClO_4)$	*cis*-$[Co\,en_2(N_3)_2](ClO_4)$
Temperature = 25·1°	Temperature = 25·1°
[Hydroxide] = 0·025N	[Hydroxide] = 0·0500N
k_1 = 2·82 × 10^{-4} sec.$^{-1}$	k_1 = 3·30 × 10^{-4} sec.$^{-1}$
k_3' = 0·70 × 10^{-4} sec.$^{-1}$	k_3' = 1·40 × 10^{-4} sec.$^{-1}$
k_4' = 0·308 × 10^{-4} sec.$^{-1}$	k_4' = 0·616 × 10^{-4} sec.$^{-1}$

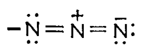
SUMMARY AND DISCUSSION

The results reported in the foregoing sections are collected in Table 8.

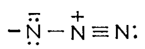
The rates of the aquation of complex ions of the type [Co $en_2AX]^{n+}$, where X is the group that is replaced by water, have been shown to be very dependent upon the nature, and to a less extent, on the position of the non-participating group A and the mechanisms deduced from this have been discussed elsewhere.[3b,6-8] It has been postulated that a group that provides a conjugative electron displacement towards the cobalt atom (+*T*), *e.g.*, (I), can facilitate an S_N1 dissociative mechanism, whereas a group that can provide such a displacement away from the cobalt atom (—*T*), *e.g.*, (II), can facilitate an associative S_N2 mechanism. It is of interest to see where the co-ordinated azide group fits into this scheme as a labilising and orienting group. The normal state of the azide in the complex is expected to be a hybrid of the two canonical forms, (III) and (IV), so that, at first sight, a (+*T*) interaction would be expected, similar to that of co-ordinated chlorine. The possibility of a (—*T*) effect, similar to that of the nitro-group, cannot be overlooked: *i.e.*, (V).


(I)

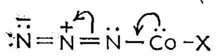

(II)


$-\ddot{\mathrm{N}}=\overset{+}{\mathrm{N}}=\overset{-}{\ddot{\mathrm{N}}}:$

(III)


$-\overset{=}{\ddot{\mathrm{N}}}-\overset{+}{\mathrm{N}}\equiv\mathrm{N}:$

(IV)


(V)

The azide group can therefore act in either direction, depending upon the requirements of the reaction, and can, in this respect, be likened to a phenyl group attached to a carbon

TABLE 8. *Rates, products, and Arrhenius parameters of reactions of azidobis(ethylenediamine)cobalt*(III) *salts in aqueous solution.*

$k = B \exp(-E/\mathbf{R}T)$

Displaced group	Temp.	Rate constant	*cis*-Product (%)	*E* (kcal. mole⁻¹)	$\log_{10} B$
(A) *cis*- or *trans*-[Co $en_2N_3Cl]^+ + H_2O \longrightarrow$ *cis*- & *trans*-[Co $en_2N_3H_2O]^{2+} + N_3^-$					
		10^4k_1 (sec.$^{-1}$)			
cis-Cl	10·1°	0·34			
,, ...	25·0	2·0	100	21·7	12·3
,, ...	35·0	8·0			
trans-Cl	10·1	0·33			
,, ...	24·65	2·0			
,, ...	25·0	2·2	20	23·1	13·3
,, ...	35·0	8·7			
(B) *cis*- or *trans*-[Co $en_2N_3X]^+ + OH^- \longrightarrow$ *cis*- & *trans*-[Co $en_2N_3(OH)]^+ + N_3^-$					
		k_2 (l. sec.$^{-1}$ mole^{-1})			
cis-Cl	0·0	0·17	51		
trans-Cl	0·0	0·41	13		
cis-N_3	25·1	0·0066	55		
trans-N_3	25·1	0·011	30		
(C) *cis*- or *trans*-[Co $en_2(OH)N_3]^+ + OH^- \longrightarrow$ *cis* & *trans*-[Co $en_2(OH)_2]^+ + N_3^-$					
		k_2 (l. sec.$^{-1}$ mole^{-1})			
cis-N_3	25·1	0·0028			
trans-N_2	25·1	0·0012			
(D) *cis*-[Co $en_2N_3H_2O]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ *trans*-[Co $en_2N_3H_2O]^{2+}$					
		$10^4(k_1 + k_{-1})$ sec.$^{-1}$)			
cis- or *trans*-H_2O	25·0	0·98	73		

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[6] Basolo, *Record Chem. Prog.*, 1957, **18**, 1.

[7] Ingold, " Theoretical Organic Chemistry," Butterworths Scientific Publications, London, 1959, p. 98.

[8] Baldwin and Tobe, *J.*, 1960, 4275.

reaction centre. The data in Table 8 indicate that, whatever the mechanism, the co-ordinated azide group provides a strong labilising effect on the chlorine. Rate data alone cannot indicate whether the azide group behaves like the nitro-group or like the chloro-group, but the steric course of the reaction can contribute to this problem. It has been shown that bimolecular aquation proceeds with full retention of configuration.[5,6] *trans*-Complexes that undergo unimolecular aquation, on the other hand, react with about 50% stereo-change.[3a,7,8] The aquation of *trans*-$[Co\,en_2N_3Cl]^+$ proceeds with 20% stereo-change, which indicates that the reaction is not exclusively bimolecular in character and might even indicate that the reaction is wholly unimolecular provided a reasonable explanation can be given for the relatively small amount of steric change. A tentative suggestion is that both mechanisms are operating, the complex being presented with two alternative modes of reaction. There will be an inherent tendency to undergo an S_N1 dissociation due to the $(+T)$ effect of the azide group, but some cations may be presented with a water molecule suitably placed for bimolecular reaction. The azide electrons would then be polarised so that the $(-T)$ effect would facilitate the bimolecular reaction. Little can be said about the mechanism of the aquation of the *cis*-$[Co\,en_2N_3Cl]^+$ cation because a *cis*-complex of this type always seems to retain its configuration on aquation whatever the mechanism. It has been reasoned, however, that the $(+T)$ effect is more effective from a ligand when it is *cis* to the outgoing group, whereas the $(-T)$ effect is transmitted more readily to the *trans*-position.[9] These factors would combine to make the S_N1 process most probable.

The reactions between the chloroazido-complexes and hydroxide ions are mechanistically unambiguous. Bimolecular attack by the hydroxide ion would completely overshadow the unimolecular dissociation and cause the azide group to utilise its $(-T)$ effect. The steric course of hydroxide substitution in the chloroazido-complexes is very similar to that in the corresponding nitrochloro-isomers[3b] and the reactions are comparatively slow. On the other hand, there is a considerable difference between the behaviour of these complexes and that of the chlorohydroxo- and chloroisothiocyanato-complexes.

The rate constants for the displacement of the azide group from these complexes by hydroxide are very much smaller than those for the removal of chlorine under similar conditions. Equilibrium studies on the $[Co\,en_2(N_3)_2]^+$, azide, and water system indicate that the stability constant of the azido-complex is considerably greater than that of the corresponding chloro-complex. This is not surprising in view of the difference in the basicity of these two ligands.

Experimental.—*Preparations.* The methods used for the preparation of the complexes have already been described.[5] The criteria used to determine purity were analyses and full agreement of the visible absorption spectrum with that of a specimen of known purity.

Methods of measurement. Spectrophotometric measurements were made by using silica cells and a Unicam S.P. 500 Quartz spectrophotometer.

Ionic chloride was determined titrimetrically with standard silver nitrate solution, the end-point being determined potentiometrically. A silver-wire electrode was used and this half-cell was connected to a calomel standard electrode by an agar–potassium nitrate salt bridge. The titrations were carried out in beakers immersed in an ice–salt bath.

The concentration of ionic azide was determined by the method of Staples.[10] An aliquot portion of the reaction mixture was passed through a column of Amberlite IR-120 cation-exchange resin in the sodium form. (If the resin is in the H^+ form all the co-ordinated azide is replaced by water and appears in the effluent.) The effluent and the washings were passed into a solution containing a known excess of sodium nitrite and 2·0 ml. of 0·1N-perchloric acid. The reaction, $HN_3 + HNO_2 \longrightarrow H_2O + N_2 + N_2O$, was shown to be stoicheiometric and complete within 2 min. at room temperature. The concentration of the unchanged nitrite

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[9] Ingold, Nyholm, and Tobe, *Nature*, 1960, **187**, 477.

[10] Staples, *Chem. and Ind.*, in the press.

was determined colorimetrically by Ridd's method,[11] which is very suitable for concentrations of azide in the range 10^{-6}—10^{-3}M.

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[11] Ridd, Thesis, London, 1951.