336. *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part V.* Bimolecular Basic Hydrolysis and Aquation of Some Halogeno- and Nitrato-amminobis(ethylenediamine)cobalt*(III) *Ions.*

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This paper continues the report on the steric course, in kinetically controlled conditions, of bimolecular nucleophilic substitution at octahedral cobalt. The present examples relate to the displacement by attacking hydroxide ions in solvent water of halogeno- or nitrato-ligands from halogeno- or nitrato-amminobis(ethylenediamine)cobalt(III) ions. The reactions are bimolecular, totally and with respect to each of the partial reactions leading to the stereoisomeric products, which underwent neither isomeric change nor further substitution under the conditions of their formation. At 0° the *trans*-chloro-cation gave 76%, the *cis*-chloro-cation 84%, the *cis*-bromo-cation 85%, and the *cis*-nitrato-cation 86% of *cis*-isomer, in the mixture of *cis*- and *trans*-hydroxy-isomers formed. When the *d-cis*-chloro-cation was employed the hydroxy-product contained 60% of the *d-cis*-isomer of like configuration, and 24% of its optical enantiomer, besides 16% of the *trans*-isomer. With the *d-cis*-bromo-cation the proportions of the same three products were 58%, 26%, and 15%, respectively. With the *l-cis*-bromo-cation the proportions were 27%, 58%, and 15%, respectively; and it is now the second of the three isomers which has a configuration resembling that of the initial halogen compound. Apart from the additional particulars furnished by the use of optically active compounds in the present series, these stereochemical findings, applying to reactions of a number of cations characterised by the presence of the ammonia ligand, closely resemble those reported in the preceding paper for reactions of a series of cations characterised by the presence of the *iso*thiocyanato-ligand. The directing effects of these two ligands on the substitutions are, therefore, either negligible or equal; and so the question of the degree of importance attaching to orienting effects, by ligands present already, on bimolecular octahedral substitutions is brought into the foreground.

The rates of the aquations which the above halogeno- and nitrato-cations undergo in aqueous acidic solutions have been measured, though these reactions are detectably reversible in the conditions used.

THIS paper describes an investigation of the kinetics and stereochemistry of some further bimolecular substitutions, in which an attacking hydroxide ion replaces a ligand in various

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* Part IV, preceding paper.

bis(ethylenediamine)cobalt(III) cations, containing a characteristic unreplaced group. The latter group is the ammonia ligand in the present examples. The displaced groups are the chloro-, bromo-, and nitrato-ligands. The complex cations were examined in *trans*-, *DL-cis*, or *D*- or *L-cis*-forms.

(1) *Kinetics and Products of the Reaction of Hydroxide Ion with the* trans-*Chloroamminobis(ethylenediamine)cobalt*(III) *Ion in Water*:

$$OH^- + trans\text{-}[Co\ en_2NH_3Cl]^{2+} \longrightarrow cis\text{- and } trans\text{-}[Co\ en_2NH_3(OH)]^{2+} + Cl^-$$

(1.1) *Basic Chemistry*.—The *cis*- and the *trans*-series of salts of chloroamminobis(ethylenediamine)cobalt(III) are well characterised, and their configurations are made certain by the optical resolution of the *cis*-salts.[1]

There are a number of chemical differences of analytical importance between the ammino-cations and the *iso*thiocyanato-cations discussed in the preceding paper. The ammino-ligand does not interact with silver ions. This makes available the method of following halogen displacement by silver titration of the produced halide ion, in acidified samples of the reaction solution. Actually, this method is not convenient for following the alkaline hydrolysis of the *trans*-chloroammino-cation, because of the high reaction rate; but it was used in the study of the more slowly reacting *cis*-chloroammino-cation.

The ammino-ligand is not displaced at all in dilute aqueous alkali at 0°, the conditions in which we have investigated the kinetics of displacement of the halogen; *i.e.*, there is no detectable second step of hydroxylation in these conditions. This meant that, in following the kinetics of the chlorine displacement by the spectrophotometric method, we were able to use the " infinite-time " reading. Another important advantage is that, provided we prove that the *cis*- and *trans*-hydroxy-products are formed primarily, simultaneously, and in constant ratio, and that they suffer no subsequent interconversion in the conditions of their formation, we can deduce the steric course of the substitution directly from the proportions in which the hydroxy-isomers are present at the completion of the process, without needing to trace their proportions throughout the reaction. It happens that, on account of the character of the spectra concerned, the latter method would have been difficult to apply.

In following kinetics by the spectrophotometric method, the reaction in alkaline solution is stopped by the addition to withdrawn samples of excess of acid, which also protonates the hydroxyammino-products, to give aquoammino-products. The resulting spectrum thus depends on three coloured substances, the original *trans*-chloroammino-cation and the produced *cis*- and *trans*-aquo-cations. The " infinite-time " samples were also examined after acidification: their spectra depended only on the *cis*- and *trans*-aquo-cations.

Certain questions of stability required to be investigated. By means of spectrophotometric measurements with pure *trans*-chloroammino-salts and pure *cis*- and *trans*-aquoammino-salts, prepared as described in Section 7, it was established (*a*) that the *cis*- and the *trans*-hydroxy-cations in alkaline solution undergo no isomerisation or other reaction at the temperature at which the chlorine displacement was conducted; (*b*) that no isomeric change accompanies the protonation of either hydroxy-cation by acidification to give the corresponding aquo-cation; (*c*) that the *trans*-chloro-cation is stable in acid solution at the temperature of the optical measurements; and (*d*) that the pure *cis*- and *trans*-aquo-cations both remain unchanged in acid solution under the conditions of the analytical measurements. On the other hand, in aqueous acid at higher temperatures than those used in the study of the alkaline hydroxylation, the *trans*-chloro-cation undergoes aquation, as will be described in Section 5.

(1.2) *Kinetics*.—The spectrophotometric method was used, water being the solvent; and the spectra on which it depends are shown in Fig. 1. They have the peculiarity that the absorption curves of the chloro-cation and the two aquo-cations do not differ strongly throughout the visible and near-ultraviolet regions, until near 3000 Å, at which the chloro-cation suddenly becomes strongly absorbing, and both aquo-cations weakly absorbing. At this wavelength then, we can conveniently follow the progress of the hydroxylation,

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[1] Werner, *Ber.*, 1911, **44**, 1887.

without concerning ourselves with the stereoisomeric composition of the hydroxy-products, which can have no appreciable influence on the measurements.

It is necessary to be particularly careful about the applicability of Beer's law when working at a wavelength near 3000 Å, because this is not very far from where some of the anions used show appreciable absorption, and near-lying absorption bands of cations and anions are liable to be mutually broadened by the electrostatic interaction of the ions. This upsets Beer's law, because the extent of such interaction depends on concentration. An examination showed that the disturbance was actually inappreciable for the *trans*-chloroammino-salts throughout the range of concentrations over which we used them, but that it began to be appreciable for the *cis*- and *trans*-aquoammino-salts in the concentrations in which they were built up towards the end of some of our runs. If the effect is indeed one of electrostatic interaction, it appears plausible that it should become noticeable at lower concentrations of the triply charged aquo-cations than of the doubly charged chloro-cation. Its influence on the apparent kinetics was to cause a drift in the rate-constants towards the ends of certain runs. That this was an analytical, and not a kinetic, disturbance was confirmed in corresponding experiments with the *cis*-chloroammino-cation, in which it was observed with the spectrophotometric, but not with the titrimetric, method of analysis.

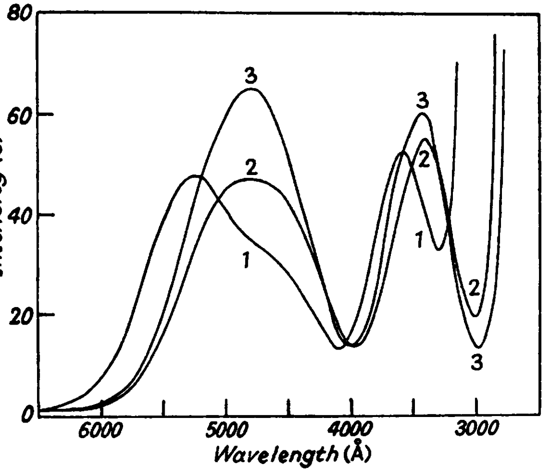

FIG. 1. *Spectrophotometric curves o extinction coefficients for halogeno- and aquo-amminobis(ethylenediamine)-cobalt*(III) *ions in water :*

(1) *trans*-[Co en$_2$(NH$_3$)Cl]$^{2+}$;
(2) *trans*-[Co en$_2$(NH$_3$)(OH$_2$)]$^{3+}$;
(3) *cis*-[Co en$_2$(NH$_3$)(OH$_2$)]$^{3+}$.

Good second-order rate-constants could be calculated for the major parts of all runs, and for almost the whole of some. It is a result of the doubled charge on the chloro-cation that the negative primary salt effect on reaction rate is noticeable. For ionic strengths up to 0·02, the slope of the plot of the logarithm of the rate constant against the square root of the ionic strength approaches the theoretical slope for point-ions, though at greater ionic strengths the slope falls off, as it should theoretically for space-occupying ions.

Our rate constants, given in Table 1, show this salt effect. The most important thing they show, however, is that, at ionic strengths from 0·02 downwards, these second-order rate constants show only such small variation as is quantitatively required by electrostatic theory, despite a 4-fold variation in the initial concentration of the *trans*-chloro-cation and a 20-fold variation in the initial concentration of hydroxide ion. This leaves no doubt that a bimolecular reaction is under observation.

(1.3) *Steric Course.*—The absorption curves of the chloro- and of the two aquo-cations are ill-adapted for accurate analyses of mixtures of all three coloured materials, because either all three curves, or two of them, follow one another too closely. But the solution at the end of reaction contains no chloro-cation, and, being stable under the conditions of measurement, it can be analysed, after acidification, for the ratio in which the two aquo-cations are present, by using the wavelength at which these cations have the greatest difference of absorption, *viz.*, 4800 Å.

It is then necessary to show that the ratio in which the stereoisomeric products are

TABLE 1. *Spectrophotometric second-order rate-constants for the substitution of hydroxyl for chlorine by hydroxide-ion attack on* trans-*chloroamminobis(ethylenediamine)cobalt*(III) *ion in water at* 0°.

[The complex cobalt cation was supplied as its chloride perchlorate, and the hydroxide ion as sodium hydroxide. In some experiments sodium perchlorate was added in order further to raise the ionic strength. The indicator of reaction progress was the optical density of acidified samples at 3000 Å. Initial and final extinction coefficients were taken as $\varepsilon_0 = 312{\cdot}4$ and $\varepsilon_\infty = 13{\cdot}0$. Rate constants were calculated with the equation $k_2 = \{2{\cdot}303/t(b - a)\} \log_{10} \{a(b - x)/(b(a - x)\}$ sec.$^{-1}$ mole^{-1} l.]

Run no.	Initial concns. (mmole/l.) [Co salt]	Initial concns. (mmole/l.) [NaOH]	Ionic strength	k_2
11	1·52	0·55	0·0051	1·43
4	0·94	4·17	0·0070	1·22
24	1·66	4·03	0·0091	1·19
25	1·64	7·96	0·0129	1·20
28	0·84	11·80	0·0143	1·18
29	1·65	11·80	0·0168	1·10
44	2·80	12·12	0·0205	1·10

Run no.	Initial concns. (mmole/l.) [Co salt]	Initial concns. (mmole/l.) [NaOH]	Initial concns. (mmole/l.) [NaClO$_4$]	Ionic strength	k_2
26	1·66	16·04	—	0·0210	1·05
30	3·35	11·80	—	0·0219	1·03
31	5·59	11·80	—	0·0286	1·00
32	8·36	11·80	—	0·0369	0·94
42	2·77	12·12	20	0·0404	0·79
41	2·79	12·12	40	0·0605	0·73

found at the end of reaction is also the constant ratio in which they appear in the course of it. The proof of this lies in the four common intersections of the curves in Fig. 2, which are the absorption curves of acidified samples of reaction solution, withdrawn at different times during a run. The common intersections mean either that the one original coloured substance is being replaced by only one coloured product (and we know that this is not true), or that it is being replaced by more than one, under the condition that these are formed in a strictly constant ratio, and, once formed, undergo no further change. Taking account of the overall kinetics, we must conclude that the two hydroxy-isomers are formed in simultaneous reactions, each of the second order.

The proportions of the isomers formed at 0°, the only temperature for which kinetic control has been applied, are in Table 2. The Table includes some similar measurements of the isomer ratio, which have been made at higher temperatures, where, however, the reaction is too fast to allow of rate measurements by our method.

TABLE 2. *Proportions in which* cis- *and* trans-*hydroxyamminobis(ethylenediamine)cobalt*(III) *ions are formed in the bimolecular reaction of hydroxide ions in water with* trans-*chloroamminobis(ethylenediamine)cobalt*(III) *ions.*

[Spectrophotometric measurements were made on acidified samples at 4800 Å. The extinction coefficients of the pure aquo-isomers, as determined for this wavelength, were $\varepsilon_{cis} = 65{\cdot}2$ and $\varepsilon_{trans} = 47{\cdot}7$.]

Temperature	0·0°	10·5°	25·0°
Extinction coefficient	61·0	61·6	62·3
cis-Isomer (%)	76	79	83

(2) *Kinetics and Products of the Reaction of Hydroxide Ion with the* d-cis-*Chloroamminobis(ethylenediamine)cobalt*(III) *Ion in Water:* *

$$\mathrm{OH^-} + d\text{-}cis\text{-}[\mathrm{Co\,en_2NH_3Cl}]^{2+} \longrightarrow d\text{-}cis\text{-} + l\text{-}cis\text{-} + trans\text{-}[\mathrm{Co\,en_2NH_3(OH)}]^{2+} + \mathrm{Cl^-}.$$

(2.1) *Basic Chemistry*.—All this is as described for the *trans*-chloro-isomer in Sub-section (1.1), except that here the optically active *cis*-chloro-, *cis*-hydroxy-, and *cis*-aquo-cations are optically stable (as well as being stable in the other ways considered in that Sub-section), under conditions relevant to the determination of the kinetics and steric course of the reaction of hydroxide ion with the chloro-cation.

An assumption is necessary concerning the relative configurations of optically active chloro-, hydroxy-, and aquo-cations. The last two are, of course, related by their mutual interconvertibility without stereo-change: in fact, we examine the hydroxy-cation in the form of its protonated derivative, the aquo-cation. As to the relation between optically

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* Concerning the configurational labelling of optically active cobalt ions, pending determination of their absolute configurations, see footnote in Part I (*J.*, 1953, 2675). In the present paper we provisionally label as *d* that enantiomer of *cis*-chloro-, -bromo-, or -aquo-amminobis(ethylenediamine)-cobalt(III) which is dextrorotatory for sodium-D light.

active chloro- and aquo-cations, Mathieu[2] concluded from his study of the circular dichroism of the active absorption bands of these cations, that the isomers which are dextrorotatory towards sodium-D light have corresponding configurations. We have accepted this highly probable conclusion.

(2.2) *Kinetics.*—These have been followed by the spectrophotometric method, and checked by titrimetric, and also, though only roughly, by polarimetric examination.

The absorption curve for the *cis*-chloroammino-cation is contained in Fig. 3: it has to be compared with the curves for the *cis*- and *trans*-aquo-cations, given in Fig. 1. The comparison shows that, although, as before, an accurate spectrophotometric determination of the three coloured substances simultaneously in acidified reaction samples is not possible, one can use the optical density at 3000 Å to give the concentration of surviving *cis*-chloro-cation, without needing to know the isomer ratio of the produced aquo-cations; and, at the end of reaction, when the chloro-cation has disappeared, one can use the optical density at 4800 Å to find the ratio of the aquo-isomers. In following the kinetics of the chlorine displacement by means of the optical density of acidified samples at 3000 Å, care was taken to work within the ascertained range of validity of Beer's law, although this meant excluding some readings in the presence of relatively large concentrations of the aquo-cations. Within these wide limits, good second-order rate-constants could be calculated. They are listed in Table 3.

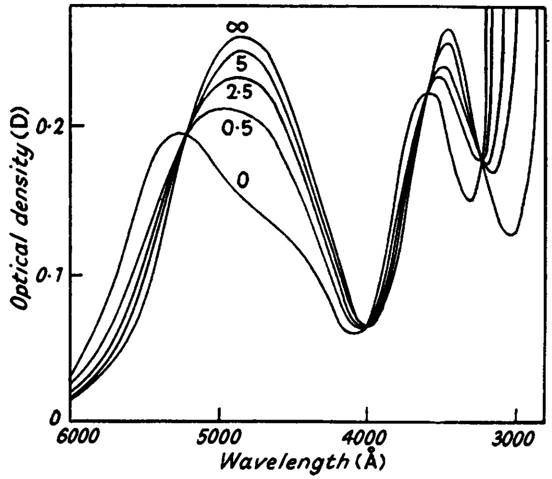

FIG. 2. *Spectrophotometric curves of optical density in a 4-cm. cell of samples from run 3, acidified at various times, given in minutes by the figures associated with the curves. The four common intersections show that the products are being formed in constant proportions.*

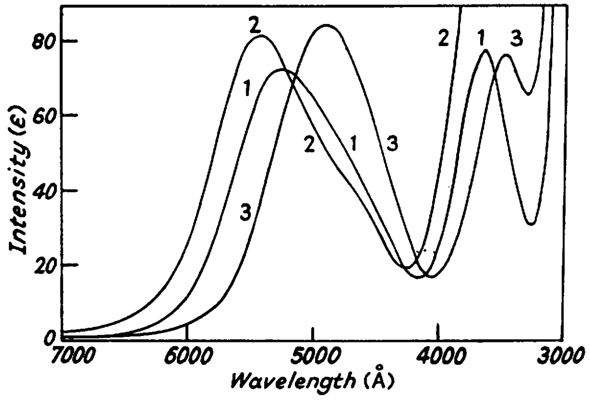

FIG. 3. *Spectrophotometric curves of extinction coefficients for halogeno- and nitrato-amminobis(ethylenediamine)cobalt*(III) *ions in water:*

(1) *cis*-$[Co\ en_2(NH_3)Cl]^{2+}$;
(2) *cis*-$[Co\ en_2(NH_3)Br]^{2+}$;
(3) *cis*-$[Co\ en_2(NH_3)(NO_3)]^{2+}$.

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[2] Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 476.

A few runs were followed by measuring the liberated chloride ion in acidified samples by titration with silver nitrate using a silver electrode. As the complex cation was taken in the form of its bromide, the titration curve showed two equivalence points, one in a constant position, corresponding to the end of the precipitation of silver bromide, and a second one in a varying position, representing the completed precipitation of silver chloride: the measurement of chief interest was the separation of these equivalence points. The second-order rate-constants thus obtained are also given in Table 3.

The polarimetric method of following the kinetics was inaccurate, owing to the difficulty of getting enough light, of such wavelength that the rotation underwent sufficient change, through the absorbing solutions. This difficulty was especially great near the beginning of a run, when a considerable proportion of the chloro-cation was present. Having regard to all the limitations and difficulties, we chose to work with sodium-D light. It was of some help that linearity could be proved, as Sub-section (2.3) describes, between optical rotation and the spectrophotometrically determined percentage of reaction. This linearity enabled initial and final rotations to be fixed fairly accurately by extrapolation. For the variation of the rotation between these limits, second-order rate-constants were calculated to give the mean value entered in Table 3.

The main result here is that the spectrophotometric values of the second-order rate-constant do not change by more than 10% over an 8-fold change in the initial concentration of the complex cation, and a 4-fold change in that of the hydroxide ion. It is therefore clear that a second-order reaction is being observed. One can just discern the expected negative salt effect, but the ionic strength was carried neither low enough nor high enough to establish it clearly. The titrimetric rate-constants seem to be a little higher than the spectrophotometric. On account of the difficulties mentioned, the polarimetric value is only rough.

TABLE 3. *Spectrophotometric, titrimetric, and polarimetric rate-constants for the substitution of hydroxyl for chlorine in* d-cis-*chloroamminobis(ethylenediamine)cobalt*(III) *ion in water at* 0°.

[The complex cation was supplied as its bromide. In the spectrophotometric method of analysis, the optical density of acidified samples at 3000 Å was used, the initial and final extinction coefficients being taken as ε_0 = 189 and ε_∞ = 13·3. The titrimetric method employed silver titration of chloride ion. The polarimetric readings were made at 5893 Å, initial and final molecular rotations being taken as $[M]_0$ = +525° and $[M]_\infty$ = +157°. Rate constants were caclulated as noted in Table 1.]

Run	Initial concns. (mmole/l.)			Ionic	
no.	Method	[Co salt]	[NaOH]	strength	k_2 *
14	Spec.	1·76	3·85	0·0091	0·48
16	,,	1·83	7·74	0·0132	0·50
20	,,	0·90	10·84	0·0135	0·47
17	,,	2·97	7·74	0·0166	0·50
18	,,	1·86	14·29	0·0199	0·50
22	,,	3·70	10·87	0·0220	0·47
19	Spec.	4·51	14·29	0·0278	0·43
23	,,	7·11	10·87	0·0322	0·45
35	Titr.	6·38	11·87	0·0310	0·49
40	,,	7·61	12·12	0·0350	0·52
36	,,	9·43	11·87	0·0402	0·50
Several	Polar.	(———Various———)			~0·5 (mean)

* In sec.$^{-1}$ mole^{-1} l.

(2.3) *Steric Course*.—The ratio in which the alkaline hydrolysis of the *d-cis*-chloroammino-cation produces *cis*- and *trans*-hydroxy-cations was determined essentially as described in Sub-section (1.2): it was first shown that the *cis*- and *trans*-aquo-cations appear in a constant ratio on acidification of samples taken at various stages of the reaction; and then the value of that ratio was determined in acidified samples, taken after completion of the reaction, as can then be done by measurement of optical density at 4800 Å.

The new feature of the experiments now described is the determination of the ratio in which the original *d-cis*-chloro-cation produces *d-cis*- and *l-cis*-hydroxy-cations. The type of procedure was broadly similar. It was necessary to show that the enantiomers are produced in a constant ratio, and that, once produced, they suffer no further change: then, the ratio in which they are formed could be equated to the ratio in which they finally appear.

The constancy of the ratio of the formed enantiomers was established by measuring, in a series of acidified examples taken at various times during the progress of reaction, (*a*) the optical density at 3000 Å and (*b*) the optical rotatory power at 5893 Å. The first measurement gave the proportion in which reaction had occurred at the time of sampling, and so the second measurement enabled a relation to be set up between the molecular rotatory power of total complex cations in the acidified solution, and the extent of reaction. This relation proved to be linear, as shown in Fig. 4; and the linearity shows that the *d-cis-* and *l-cis*-hydroxy-cations are appearing in a constant ratio. Their optical stability, once formed, was established by measuring the optical rotatory power at 5893 Å of a series of acidified samples, taken during reaction and long after it had been completed. It was found that the rotatory power changed while reaction continued, but then remained constant for at least 50 half-lives.

The straight line of Fig. 4 can be extrapolated to $[M]_D = +157°$ at 100% reaction. It follows that the *d-cis-*, *l-cis-*, and *trans*-aquo-isomers are then present in such proportions that collectively they have this molecular rotatory power. We may also conclude that, throughout reaction, the *d-cis-*, *l-cis-*, and *trans*-hydroxy-isomers are produced in just the same, constant, proportions. We know the proportion of *trans*-isomer in these isomer mixtures from the spectrophotometric measurements at 4800 Å. Thus the only figure still required in order to complete the analysis is the molecular rotatory power of a pure *cis*-aquo-enantiomer.

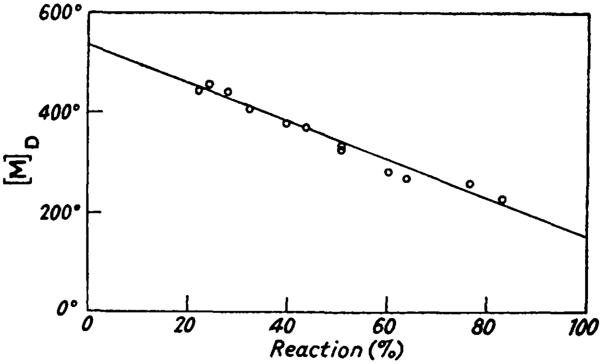

FIG. 4. *Change of rotatory power for* Na-D *light of acidified samples withdrawn at intervals during the reaction of* d-cis-*chloroamminobis(ethylenediamine)cobalt*(III) *ion with hydroxide ion in water at* 0°.

The *cis*-aquo-ammino-series of salts has not yet been optically resolved, and the best available figure for the maximal rotatory power of this cation is due to Mathieu.[2] He prepared it by allowing an aqueous solution of three equivalents of silver nitrate to react with fully resolved *d-cis*-bromoamminobis(ethylenediamine)cobalt(III) bromide. The rotation of the resulting solution was equivalent to $[M]_D$ +450°. A study of the circular dichroism of this solution led to the conclusion that the configuration of the aquo-cation corresponded to that of the bromo-cation from which it had been derived, and, furthermore, that little if any racemisation accompanied the aquation. We therefore use this figure in order to complete the isomer analysis, as shown in Table 4.

TABLE 4. *Proportions in which* d-cis-, l-cis-, *and* trans-*hydroxyamminobis(ethylenediamine)-cobalt*(III) *ions are formed in the bimolecular reaction of hydroxide ions with* d-cis-*chloroamminobis(ethylenediamine)cobalt*(III) *ions in water at* 0°.

	ε_{4800}		$[M]_D$
cis-Aquo-cation	65·2	*d-cis*-Aquo-cation	+450°
trans- ,,	47·7	Aquo-cation mixture	+157°
Aquo-cation mixture	62·4		

Formed hydroxy-isomers ≡ Final aquo-isomers =	*d-cis*	59·5%
	l-cis	24·5%
	trans-	16%

(3) *Kinetics and Products of the Reaction of Hydroxide Ion with the* d- *and* l-cis-*Bromoamminobis(ethylenediamine)cobalt*(III) *Ions in Water:*

$$\mathrm{OH^-} + d\text{- or } l\text{-}cis\text{-}[\mathrm{Co\,en_2NH_3Br}]^+ \longrightarrow d\text{-}cis\text{-} + l\text{-}cis\text{-} + trans\text{-}[\mathrm{Co\,en_2NH_3(OH)}]^{2+} + \mathrm{Br^-}$$

(3.1) *Basic Chemistry.*—The *trans*- and *d*- and *l*-*cis*-series of bromoamminobis(ethylenediamine)cobalt(III) salts are all well characterised: we had available both enantiomeric forms of the *cis*-salts.[1] The same questions of stability were checked as are mentioned in Sub-sections (1.1) and (2.1), by the same methods, and with the same results.

In order to be able fully to specify the steric course of the reaction, we have to make an assumption as to the configurational relation between a bromoammino-cation and an aquoammino-cation having signs of rotation related in a given way. Again we accept Mathieu's conclusion,[2] based on his study of circular dichroism in these materials, that those bromo- and aquo-cations which have the same sign of rotation for sodium-D light have corresponding configurations.

(3.2) *Kinetics.*—The reaction is very fast, and therefore, to give time for sampling, reactant concentrations had to be kept so low as to render inaccurate the titrimetric and the polarimetric method of following the kinetics. The latter method was excluded for the further reason that light absorption by the bromo-cation is inconveniently great. The kinetics of this reaction were therefore investigated by the spectrophotometric method only.

The absorption curve of the *cis*-bromo-cation is in Fig. 3, whilst those of the *cis*- and *trans*-aquo-cations, which the reaction product gives on acidification, are in Fig. 1. It is an advantage that the *cis*-bromo-cation begins to absorb light much more strongly than either aquo-cation already at 3700 Å, so that the kinetics of the disappearance of the bromo-cation can be followed very conveniently at 3400 Å, which is sufficiently removed from the shorter-wave region, in which the cations and anions begin to perturb each other's absorption bands, with a consequential breakdown of Beer's law. Thus, good second-order rate-constants could be calculated, over a sufficient range of reactant concentrations

TABLE 5. *Spectrophotometric second-order rate-constants for the substitution of hydroxyl for bromine in* d- *and* l-cis-*bromoamminobis(ethylenediamine)cobalt*(III) *ion in water at* 0°.

[Both enantiomeric bromo-cations were supplied as their bromides. Optical densities of acidified samples at 3400 Å were measured, the initial and final extinction coefficients being taken as $\varepsilon_0 = 405$ and $\varepsilon_\infty = 57{\cdot}3$. Rate constants were calculated as in Table 1.]

Run no.	Initial confign.	Initial concns. (mmole/l.) [Co salt]	[NaOH]	k_2 *		Run no.	Initial confign.	Initial concns. (mmole/l.) [Co salt]	[NaOH]	k_2 *	
110	*d*-	0·73	1·43	3·22	3·26	111	*l*-	0·72	1·43	3·25	3·38
112	,,	1·33	5·49	3·40		113	,,	1·39	5·49	3·55	
114	,,	1·55	9·30	3·29		115	,,	1·55	9·30	3·51	
108	,,	1·61	2·96	3·15		109	,,	1·65	2·95	3·22	

* In sec.$^{-1}$ mole^{-1} l.

TABLE 6. *Proportions in which* d-cis-, l-cis-, *and* trans-*hydroxyamminobis(ethylenediamine)cobalt*(III) *ions are formed in the bimolecular reaction of hydroxide ions with* d-cis- *and with* l-cis-*bromoamminobis(ethylenediamine)cobalt*(III) *ion in water at* 0°.

	ε_{4800}	$[M]_D$
d- or *l*-*cis*-Aquo-cation	65·2	± 450°
trans-Aquo-cation	47·7	—
Aquo-cation mixture from *d*-*cis*-bromo-cation	62·5	+149
,, ,, *l*-*cis* ,,	62·6	−141

From *d*-*cis*-bromo-cation	Formed hydroxy-isomers ≡ final aquo-isomers =	*d-cis*	59%
		l-cis	26%
		trans	15%
From *l*-*cis*-bromo-cation	Formed hydroxy-isomers ≡ final aquo-isomers =	*d-cis*	27%
		l-cis	58%
		trans	15%

to establish the second-order form of the reaction. Such measurements, some on *d-cis*- and some on *l-cis*-bromo-salts, are recorded in Table 5.

(3.3) *Steric Course.*—The method followed closely the lines sketched in Sub-section (2.3). The results are in Table 6.

(4) *Products of the Reaction of Hydroxide Ion with* dl-cis-*Nitratoamminobis(ethylenediamine)cobalt*(III) *Ion in Water.*

The reaction of this cation with hydroxide ion at 0° in water was too fast to permit kinetic investigation. Thus we have no proof of mechanism, but the high rate itself is an argument in favour of the bimolecular nature of the substitution process.

In the circumstances, we were able to determine only the isomer ratio in the hydroxy-cations formed when the *cis*-nitrato-cation, supplied as nitrate, interacts with sodium hydroxide in water at 0°. The analysis was made, as usual, by measurement of the extinction coefficient at 4800 Å, of the acidified product of the completed reaction. The mean value obtained was 62·8. The composition of the formed hydroxy-substitution product is therefore : *cis* = 86%, *trans* = 14%.

The absorption curve of the *cis*-nitrato-cation was useful in the experiments described in the next Section, and is shown in Fig. 3.

(5) *Rate and Equilibrium in the Aquation of* trans-*Chloro-*, cis-*Chloro-*, cis-*Bromo-*, *and* cis-*Nitrato-amminobis(ethylenediamine)cobalt*(III) *Ions.*

Examination (pp. 1708, 1710, 1714) of the stabilities of the above cations in acidified aqueous solution at temperatures near those at which their alkaline hydrolysis was investigated showed that no changes occurred in these conditions; but these experiments led us to observe that in acid aqueous solution at raised temperatures the cations undergo an aquation, in which the halogeno- and the nitrato-ligand become replaced by a water molecule. We took the opportunity to make approximate measurements of the rate of these changes. We could not measure their steric course, because, as will be explained, that would have required measurements of the isomer ratio of the *cis*- and *trans*-aquo-products near the commencement of reaction, and, as noted already, we have no method of measuring this ratio in the presence of the halogeno-ions. This is equally true for the nitrato-ion.

However, the rates were measured, sometimes with an optically active *cis*-isomer, or with a racemic *cis*-, or a *trans*-salt; and usually by the spectrophotometric, but occasionally by the titrimetric, method. The reactions were found to be approximately of first order, and some rate constants are given in Table 7.

TABLE 7. *First-order rate-constants* (k_1 *in* $sec.^{-1}$), *and equilibrium extent of aquation of halogeno- and nitrato-amminobis(ethylenediamine)cobalt*(III) *cations in* 0·17N-*aqueous perchloric acid.*

Run no.	Method	Initial salt	$[Salt]_0$ (mmole/l.)	Temp.	$10^5 k_1$	Aquo-formed (%)
47	Spec.	*trans*-$[Co\,en_2NH_3Cl]^{2+}Cl^-ClO_4^-$	3·92	62·6°	3·01	83·3
48	,,	,, ,,	2·42	,,	2·90	85·4
1	,,	,, ,,	3·82	89·9	43·1	83·3
5	Titr.	*dl-cis*-$[Co\,en_2NH_3Cl]^{2+}(Br^-)_2$	11·01	62·6	4·08	88·1
45	Spec.	*d-cis*- ,, ,,	5·28	,,	3·80	86·0
46	,,	,, ,,	4·12	,,	3·97	86·0
119	Spec.	*l-cis*-$[Co\,en_2NH_3Br]^{2+}(Br^-)_2$	3·98	44·8	1·60	92·2
120	,,	,, ,,	1·84	,,	1·76	96·1
117	,,	,, ,,	3·64	62·6	11·6	96·2
118	,,	,, ,,	1·90	,,	12·0	97·7
102	Titr.	*dl-cis*- ,, ,,	8·74	,,	12·0	92·2
	Spec.	,, ,,	,,	,,	13·1	90·1
103	Titr.	,, ,,	10·86	,,	12·5	93·3
203	Spec.	*dl-cis*-$[Co\,en_2NH_3NO_3]^{2+}(NO_3^-)_2$	5·29	44·8	11·2	97
204	,,	,, ,,	3·06	,,	11·1	98
201	,,	,, ,,	3·45	62·6	84·5	99

In their detail, the experimental methods were just as for the investigation of the alkaline reactions of the same halogeno- and nitrato-cations, except, of course, that the samples for analysis had to be chilled and did not require to be acidified. In the spectrophotometric method, the extinction coefficients for completed aquation were taken to be those observed on acidification after the corresponding completed alkaline hydroxylation. Any difference in the isomer ratio of the aquo-cations, as formed by aquation and through alkaline hydrolysis, was thus neglected in the optical calibration; but at the operative wavelengths, 3400 Å in the aquation of the bromo-cation, and 3000 Å in all other cases, the absorption of either aquo-cation is so weak relatively to that of the original halogeno- or nitrato-cation that an uncertainty in the ratio of aquo-isomers makes no practical difference.

It appears that the aquations do not go quite to their stoicheiometric completion: the extents to which the forward reaction was realised are entered in Table 7. One effect of this appreciable reversibility was that, in the absence of an investigation of the kinetics of the retrograde reaction, we had not an exact formula with which to calculate the rate-constants of the forward process. We therefore first calculated a specific rate of approach to equilibrium by means of the formula for a reversible reaction of first order in both directions, and then we multiplied this by the fractional extent to which the aquation goes forward, accepting the resulting first-order rate-constants of the forward process until they began to drift near the equilibrium point. Such drift is an indication that the retrograde reaction is beginning to attain a sufficient relative importance to require a more accurate representation of its kinetic form: but before the onset of drift, the forward rate-constants should be free from error due to an incorrect treatment of the back-reaction.

Another consequence of the reversibility of the aquation is that, whether or not the *cis*- and *trans*-aquo-cations would, at the temperature of the aquations, undergo reversible isomeric change in the absence of disturbance by attacking anions, they are certain to do so, under the influence of the anions present, by the mechanism of reversible anion attack. In some cases more than one kind of anion is present, either from the outset, or at least after anions have been liberated by the aquation; and in these cases parallel attacks, all reversible, by more than one anion could occur. Whether this further complication arises or not, it is clear that the ratio in which the *cis*- and *trans*-aquo-cations are present during aquation will not be constant and equal to the ratio in which they are originally formed, but will drift away from that ratio towards one determined by the thermodynamic situation. Hence the steric course of any of these aquations could be determined only by an extrapolation to zero time of *cis*–*trans* ratios measured at various times near the commencement of reaction; and that, as already explained, is a measurement for which the absorption curves of the substances involved do not provide a method.

It appears from Table 7 that both kinetics and thermodynamics favour aquation in the ligand order $NO_3 > Br > Cl$.

(6) *Summary and Discussion.*

The main results of stereochemical interest reported in the foregoing Sections are brought together in Table 8. Only the reactions of alkaline hydrolysis are included; for the corresponding reactions of aquation were not studied stereochemically, and the kinetic data relating to them are in Table 7.

As noted in previous Parts, there is only partial correlation in these octahedral substitutions between the incidence of stereo-change in the individual molecular acts of substitution and the experimentally observed stereochemical course of the substitutions. The degree of the correlation, optical isomerism being taken into account, is as follows. An initial *trans*-compound, substituted by molecular acts which preserve configuration, will give a *trans*-product, and by molecular acts which involve stereo-change will yield a *cis*-product. An initial *D*-*cis*-compound, if substituted by molecular processes without stereo-change will yield a *D*-*cis*-product, but substituted by molecular processes involving stereo-change may give a *trans*-, or an *L*-*cis*-, or even a *D*-*cis*-product; and similarly for an initial *L*-*cis*-compound.

We can therefore translate the experimental results in Table 8 for the *trans*-chloro-cation into molecular terms quite precisely: at 0°, 76% of the molecular acts of substitution involve stereo-change, and 24% do not. As to the *cis*-chloro- and *cis*-bromo-cations, we can say only that at least 40—41% of the molecular processes involve stereo-change, and we cannot say whether any individual transactions occur which lead to substitution with retention of configuration. For the *cis*-nitrato-cation, at least 14% of the molecular acts involve stereo-change, and again we do not know whether any occur which retain configuration.

TABLE 8. *Rate and steric course of reactions with hydroxide ion in water of bis(ethylenediamine)cobalt*(III) *ions containing the ammonia ligand.*

d-cis-, *l-cis-*, or *trans-*[Co en$_2$NH$_3$X]$^{2+}$ + OH$^-$ $\longrightarrow$ *d-cis-*, *l-cis-*, and *trans-*[Co en$_2$NH$_3$(OH)]$^{2+}$ + X$^-$.

(All reactions kinetically of second order.)

Displaced group (X)	Temp.	Rate constant k_2 (sec.$^{-1}$ mole^{-1} l.)	Product ratios (%) *d-cis*	*l-cis*	*trans*
trans-Cl	0·0°	1·25	76		24
,,	10·5	—	79		21
,,	25·0	—	83		17
d-cis-Cl	0·0	0·50	60	24	16
d-cis-Br	,,	3·26	59	26	15
l-cis-Br	,,	3·38	27	58	15
dl-cis-NO$_3$	,,	—	86		14

As to mechanism, there can be no doubt that all the reactions of Table 8 are bimolecular nucleophilic substitutions S_N2.[3] In substitutions at tetrahedral carbon by this mechanism, stereo-change is always complete; and therefore, the most striking result of Table 8 is the evidence it contains that, in substitution at octahedral cobalt by the same mechanism, stereo-change is not complete. The extent to which it is not is known precisely in the case of the *trans*-chloroammino-cation, and, whether the fact is significant or not, it is noticeable that the proportion in which configuration is retained is in the same neighbourhood for this cation as for the *trans*-chloro*iso*thiocyanato- and *trans*-bromo*iso*thiocyanato-cations, the investigation of which is described in the preceding paper. There is also an approximate correspondence between the stereochemical results obtained with the present *cis*-chloroammino- and *cis*-bromoammino-cations, and with the *cis*-chloro*iso*thiocyanato-cation of the preceding paper. If the ammino- and *iso*thiocyanato-ligands, $-NH_3^+$ and –N⁚C⁚S, have any considerable orienting effects on substitution, it is remarkable that such effects should be so similar, considering how different the ligands are with respect to both formal charge and unsaturation. For the present, these comparisons have their main significance as an incentive to examine other ligands, with a view to determining whether orienting effects are important in octahedral substitutions by the S_N2 mechanism.

There is a certain indication in the data of the preceding paper and of this one that the type of orientation found in bimolecular substitutions by hydroxide ions in octahedral complexes is not fundamentally altered when the displaced group is changed within the range examined, comprising chloro-, bromo-, and nitrato-groups. The invariance suggested is, of course, only an indication, again one requiring further experimental pursuit.

(7) *Preparations.*

trans-Chloroamminobis(ethylenediamine)cobalt(III) chloride perchlorate was prepared by decomposition of *trans*-chloro*iso*thiocyanatobis(ethylenediamine)cobalt(III) perchlorate with 30% hydrogen peroxide, as Werner describes,[4] except for a difference in method of isolation. After reaction, the mixture was evaporated with concentrated hydrochloric acid, and some green crystals of *trans*-dichlorobis(ethylenediamine)cobalt(III) perchlorate, which separated first, were removed. At a later stage red crystals of the desired chloride perchlorate of the

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[3] Cf. Part IV, preceding paper.

[4] Werner, *Annalen*, 1912, **386**, 1.

trans-chloro-ammine series separated and were collected. They were recrystallised once from concentrated hydrochloric acid with addition of ethyl alcohol, and then twice from water with added alcohol (Found: C, 13·1; H, 5·2. Calc. for $C_4H_{19}O_4N_5Cl_3Co$: C, 13·1; H, 5·2%). If the last two crystallisations are omitted the salt contains an extra molecule of hydrogen chloride.

cis-Chloroamminobis(ethylenediamine)cobalt(III) salts were prepared from *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride and aqueous ammonia, and the bromide was isolated first and was then converted into the (+)-α-bromocamphor-π-sulphonate for optical resolution, all as described by Werner.[1] From the less soluble diastereoisomer, *d-cis*-chloroamminobis(ethylenediamine)cobalt(III) bromide was obtained, with the aid of concentrated aqueous hydrobromic acid. It was crystallised from warm water with addition of ethyl alcohol (Found: Br, 40·8. Calc. for $C_4H_{19}O_5ClBr_2Co$: Br, 40·7%).

cis-Bromoamminobis(ethylenediamine)cobalt(III) bromide was prepared from diaquotetrahydroxybis(ethylenediamine)cobalt(II)-dicobalt(III) sulphate[5] and ammonium bromide as described by Werner,[4] and was resolved by Werner's method[1] by way of the (+)-α-bromocamphor-π-sulphonates. The less soluble of these, on treatment with concentrated hydrobromic acid, gave *d*-bromoamminobis(ethylenediamine)cobalt(III) bromide (Found: C, 11·2; H, 4·7; N, 16·1; ionic Br, 36·8; total Br, 53·6. Calc. for $C_4H_{19}N_5Br_3Co$: C, 11·0; H, 4·4; N, 16·1; ionic Br, 36·7; total Br, 55·0%). The solution containing the more soluble (+)-α-bromocamphor-π-sulphonate was then fractionally precipitated with sodium dithionate. At first, the racemic dithionate separated, and was removed, but later the optically active dithionate crystallised; and this was converted with concentrated hydrobromic acid into *l*-bromoamminobis(ethylenediamine)cobalt(III) bromide, which was recrystallised from aqueous hydrobromic acid (Found: C, 11·6; H, 4·5; N, 16·1; ionic Br, 36·7%).

The isomeric aquoamminobis(ethylenediamine)cobalt(III) salts were produced together by the action of concentrated aqueous lithium hydroxide on *cis*-bromoamminobis(ethylenediamine)cobalt(III) bromide, much as Werner described for the analogous experiment using potassium hydroxide.[4] The bromides were fractionally crystallised from aqueous hydrobromic acid, the process being followed by means of the absorption spectrum. *trans*-Aquoamminobis(ethylenediamine)cobalt(III) bromide separated first as its monohydrate, and was finally purified by crystallisation to constant absorption spectrum from water with additions of ethyl alcohol (Found: Br, 50·9. Calc. for $C_4H_{23}O_2N_5Br_3Co$: Br, 50·8%). It was converted into the corresponding nitrate by treatment with nitric acid (Found: C, 11·6; H, 5·1. Calc. for $C_4H_{21}O_{10}N_8Co$: C, 12·0; H, 5·3%). The *cis*-aquoamminobis(ethylenediamine)cobalt(III) bromide wa obtained from the more soluble fractions in the hydrobromic acid crystallisations, and was crystallised to constant spectrum from aqueous ethyl alcohol (Found: Br, 51·0%). It also was converted into the nitrate. An attempt was made optically to resolve it through the α-bromocamphor-π-sulphonates, but these proved to be too soluble.

cis-Nitratoamminobis(ethylenediamine)cobalt(III) nitrate was prepared by evaporating *cis*-aquoamminobis(ethylenediamine)cobalt(III) nitrate with concentrated nitric acid according to Werner's description.[4] The product was crystallised from aqueous ethyl alcohol until its absorption spectrum was constant, but analysis by combustion was frustrated by the violence of pyrolysis of the salt.

(8) *Methods of Measurement.*

The methods of starting and stopping kinetic runs, both of alkaline hydrolysis, and of aquation, were generally as described in the preceding paper, as also was the technique of analysis by absorption spectrophotometry.

Titrimetric analysis was now concerned with halide-ion content, rather than pH, and, in preparation for these determinations, reaction samples were run into dilute nitric acid. They were titrated electrometrically, a silver wire electrode, the usual agar–salt bridge and calomel half-cell being used.

Reaction samples were prepared for polarimetric measurement exactly as for spectrophotometric.

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[5] Werner and Jantsch, *Ber.*, 1907, **40**, 4430.