335. *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part IV.* Bimolecular Basic Hydrolysis and Aquation of Some Halogeno*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *Ions.*

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This paper reports the beginning of an investigation of the steric course in kinetically controlled conditions of bimolecular nucleophilic substitutions at octahedral cobalt. In the present group of experiments an attacking hydroxide ion in solvent water displaces halogen from a halogeno*iso*thiocyanatobis(ethylenediamine)cobalt(III) ion. The reactions are bimolecular, not only overall, but also with respect to the formation of each of the stereoisomeric products, which thus appear in constant ratios. The products suffer no reversible interconversion in the conditions of their formation, although at late times a further stage of substitution sets in with displacement of the *iso*thiocyanato-group. At 0°, the *trans*-chloro-cation gives 76%, the *trans*-bromo-cation 81%, and the *cis*-chloro-cation 82% of *cis*-isomer in the mixture of *cis*- and *trans*-hydroxy-cations formed. Thus stereo-change in bimolecular nucleophilic substitution at octahedral cobalt is not exclusive, as it is at tetrahedral carbon.

Rates of aquation in dilute aqueous acid of the *trans*-chloro- and *trans*-bromo-cations have been measured. The products formed are here to be distinguished from the products found, because the *cis*- and *trans*-aquo-isomers undergo reversible interconversion in the conditions of their formation. Because of this complication the stereochemistry of the aquation of the chloro-cation could not be adequately determined, but the aquation products formed from the bromo-cation were shown by a kinetic analysis to contain 43—46% of the *cis*-aquo-isomer at 63—90°. It is thus clear that aquation can pursue a course involving stereo-change.

The rates of interconversion of the *cis*- and *trans*-aquo-isomers have been measured. At 63—90°, some 81—84% of the *cis*-isomer is present at equilibrium.

IN Parts I and II * it was shown that the two mechanisms, S_N1 and S_N2, of nucleophilic substitution, which have long been familiar in organic chemistry, both participate in the ligand substitutions of octahedrally co-ordinated atoms, in particular of cobalt(III). In Part II kinetic criteria for the recognition of these mechanisms were developed. These results prepared the way for an investigation of the spatial orientation of octahedral substitution, under each of the two mechanisms, by a combined study of products and kinetics. In Part III,* this investigation was commenced on the side of the unimolecular

* Part I, *J.*, 1953, 2674; Part II, *ibid.*, p. 2680; Part III, *ibid.*, p. 2696.

mechanism of substitution, S_N1, using a cobalt(III) octahedral centre; and now, the more fully to launch our programme, we report in these papers our first results on spatial orientation in the bimolecular mechanisms of substitution, S_N2, again at octahedral cobalt(III).

We have studied bimolecular substitution in bis(ethylenediamine)cobalt(III) complexes containing one displaced group, and one characteristic non-replaced group, both groups being treated as variable features of the structure. Up to the present, our displaced groups have been the chloro-, bromo-, and nitrato-ligands. As characteristic retained groups, we now report on the *iso*thiocyanato- and ammino-ligands. The other possible constitutional variable, the introduced group, has not yet been made to vary, inasmuch as the work to be reported is concerned only with hydroxide ion as substituting agent, in solvent water. Water itself is highly active in cobalt substitutions: we know that it cannot be used as solvent in the study of unimolecular substitutions by weakly nucleophilic substituting agents, because it then usurps the functions of substituting agent: and the price one pays for the convenience of using water in the study of bimolecular substitutions is that one is practically limited to the hydroxide ion as reagent, since this is the only stable anion that is sufficiently highly nucleophilic to attack the cobalt atom much faster than the water can, thereby securing that the substitution proceeds directly, and does not go, as many substitutions by anions in aqueous solutions do go, through the route of a preliminary aquation.

Most of the earlier literature of kinetic and stereochemical studies of octahedral substitutions is cited in Part I. In none of this work are the two methods of investigation so combined that an observed stereochemical outcome of substitution can be related to an established mechanism. Some further stereochemical results for cobalt(III) substitutions have since become available,[1] but they too are unassociated with kinetic evidence of mechanism. Parts II and III of this series described an integrated kinetic and stereochemical study of substitutions in the cobalt(III) complex, but only for unimolecular substitutions S_N1.

In the present paper we report a combined kinetic and stereochemical examination of three substitutions in the cobalt(III) system, all proceeding by the bimolecular mechanism S_N2. In each, the hydroxide ion, attacking in aqueous solution, displaces a halogen as halide ion from a bis(ethylenediamine)cobalt(III) ion containing a retained *iso*thiocyanato-ligand. We also report a kinetic and stereochemical study of the aquations of the same complex ions, and a kinetic study of a reversible isomerisation of their stereoisomeric aquo-derivatives.

(1) *Kinetics and Products of the Reactions of Hydroxide Ion with* trans-*Chloro*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *Ion in Water:*

$$OH^- + \textit{trans}\text{-}[Co\ en_2(NCS)Cl]^+ \longrightarrow \textit{cis-}\text{ and }\textit{trans}\text{-}[Co\ en_2(NCS)OH]^+ + Cl^-$$

(1.1) *Basic Chemistry.*—The *cis*- and *trans*-series of salts of chloro*iso*thiocyanatobis(ethylenediamine)cobalt(III) are both well characterised. Their stereochemistry is made certain by the optical resolution of salts of the *cis*-series; and equally by the conversion of the *trans*-salts, without rupture of the cobalt–nitrogen bond, into *trans*-salts of the chloroamminobis(ethylenediamine) series, which are known as to configuration, because the isomeric *cis*-chloroammino-salts have been resolved.[2]

When a dilute aqueous solution of a *trans*-salt, such as the bromide, perchlorate, thiocyanate, or dithionate, is treated with dilute sodium hydroxide, the colour changes slowly from purple to orange-pink. This is a visible sign of the reaction formulated above. This reaction can at any stage be stopped by the addition of acid, which also instantaneously protonates the formed *cis*- and *trans*-hydroxy*iso*thiocyanato-cations to give the *cis*- and *trans*-aquo*iso*thiocyanatobis(ethylenediamine)cobalt(III) ions; and it is by way of these protonated derivatives that the immediate products of the substitution have been examined.

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[1] Basolo, Stone, and Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 819.

[2] (*a*) Werner, *Annalen*, 1912, **386**, 1; (*b*) Tupizina, Diss., Zürich, 1915; (*c*) Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 484.

It is necessary to have some knowledge of the stabilities of the substances involved under the alkaline and acidic conditions employed. At the temperatures used in the study of the hydroxylation process, 0—20°, and in solutions of an acidity at least of pH 5, the *trans*-chloro-cation and the *cis*- and *trans*-aquo-cations are all stable for periods much longer than those of our hydroxylation experiments. This was established by spectrophotometric examination of solutions of pure salts of these cations prepared as described in Section (8). However, changes occur at higher temperatures, such as 50—90°, in the acidic aqueous solutions. The *trans*-chloro-cation then undergoes direct aquation, at a rate which we have measured, to give aquo*iso*thiocyanato-cations; and the *cis*- and *trans*-aquo-cations themselves undergo reversible isomerisation, the rate of which we have likewise measured. We have also measured the equilibrium attained in this balanced reaction. These and similar measurements are described in Sections (4)—(6) of this paper.

The actual process of acidification, with protonation of the *cis*- and *trans*-hydroxy-cations to give their conjugate acids, the corresponding aquo-cations, induces no stereoisomeric change. This was shown by spectrophotometric examination of solutions of pure *cis*- and *trans*-aquo-salts after repeated alternate basifications and acidifications.

In dilute alkaline solution, at the temperatures used for the displacement of chlorine by hydroxide ion from the *trans*-chloro*iso*thiocyanato-cation, the *cis*- and *trans*-hydroxy*iso*thiocyanato-cations, show no signs of isomerisation. This conclusion followed from a spectrophotometric examination of basified and kept solutions of *cis*- and *trans*-aquo*iso*thiocyanato-salts. However, the two hydroxy*iso*thiocyanato-cations were found to undergo, in these conditions, a relatively slow second stage of hydroxylation, involving displacement of the *iso*thiocyanato-group, and the formation of dihydroxybis(ethylenediamine)cobalt(III) cations. Such displacements of the *iso*thiocyanato-group were, however, slow enough not to be more than slightly troublesome in our study of the displacement of chlorine by the attack of hydroxide ion.

The *cis*- and *trans*-series of salts of aquo*iso*thiocyanatobis(ethylenediamine)cobalt(III) are themselves quite well characterised, and the isomeric cations have distinctive spectra. The assignment to them of their respective stereochemical structures was originally made by Werner on slightly dubious grounds, but correctly, as was established by the subsequent work of Mathieu.[2c, 3b] From the optically active *cis*-chloro*iso*thiocyanato-cation, he obtained, by a direct and completed aquation, an optically active solution of an aquo*iso*thiocyanato-cation; and this agreed in its spectrum with the *cis*-aquo-cation to within the toleration demanded by its partial isomerisation, of which we now report the rate and equilibrium.

A number of the reactions which we have studied kinetically are appreciably accelerated by light. We, therefore, ran all rate processes in darkened vessels.

(1.2) *Kinetics.*—The rate of the alkaline hydroxylation of the *trans*-chloro*iso*thiocyanato-cation has been measured titrimetrically in aqueous methyl alcohol, and in water, at 0°, and spectrophotometrically in water only at 0°, 10°, and 20°.

The obvious titrimetric method of following liberated chloride ion with the aid of a silver electrode was unavailable, since, as Mathieu originally noted,[3b] silver ions combine with complex cobalt ions containing the *iso*thiocyanato-group. However, the aquo-*iso*thiocyanato-cations, which the formed hydroxy*iso*thiocyanato-cations produce on acidification of the reaction samples, are weak acids, and, after neutralisation of any excess of strong acid, can be titrated as such. Thus, the titration curve, as obtained by the use of a glass hydrogen electrode, shows two equivalence points, the separation of which measures the concentration of aquo-cations. The method tends to give somewhat high reaction rates, because any temporary local alkalinity during titration leads to some further hydroxylation of still undecomposed chloro-cation, and thus to high estimates of the amount of reaction at the time of sampling.

It was not possible to secure a good analytical measurement for the completed displacement of chlorine, because of the incursion at late times of the second step of hydroxylation, with displacement of the *iso*thiocyanato-group. Infinite-time values were therefore

[3] (*a*) Werner, *Arch. Sci. phys. nat. Genève*, 1911, **32**, 457; (*b*) Mathieu, *Bull. Soc. chim. France*, 1937, **4**, 695.

calculated from weights of material taken. Good second-order rate-constants were calculated for the first 80% of chlorine displacement. These constants are in the left-hand part of Table 1.

TABLE 1. *Second-order titrimetric and spectroscopic rate-constants, and spectrophotometric product-compositions for the substitution of hydroxyl for chlorine by hydroxide-ion attack on the* trans-*chloro*iso*thiocyanatobis*(*ethylenediamine*)*cobalt*(III) *ion in aqueous methyl alcohol or in water.*

[" Titr." means by pH titration, and " Spec." means by spectrophotometry. In the rate measurements by spectrophotometry the optical density at 4900 Å was used, and the extinction coefficients, $\varepsilon_0 = 40$ and $\varepsilon_\infty = 187$ in water, were taken as calibration points. The latter figure is calculated for aquo*iso*thiocyanato-products containing 76% of the *cis*-isomer. Rate-constants were calculated for the first 80% of reaction from the formula $k_2 = \{2{\cdot}303/t(b - a)\} \log_{10} \{a(b - x)/(b(a - x)\}$ sec.$^{-1}$ mole^{-1} l., or in case $b = a$, the formula $k_2 = x/ta(a - x)$ sec.$^{-1}$ mole^{-1} l., where a is the initial concentration of the complex cobalt ion, and b that of the hydroxide ion. The complex chloro-cation was supplied as bromide for the measurements in aqueous methyl alcohol, and as perchlorate for the measurements in water. Hydroxide ions were introduced as carbonate-free sodium hydroxide. The measurements of product-composition during the progress of the runs, as given in the last column of the Table, involved determinations of optical density at three wavelengths, 5800, 5300, and 4900 Å (cf. Sub-section 1.3).]

Run no.	MeOH (%) in solv.	a (mmole l.$^{-1}$)	b (mmole l.$^{-1}$)	k_2
Method, Titr.	*Temp.,* 0·00°.			
10	87	3·02	5·85	0·098
11	86	2·77	6·57	0·104
9	85	2·84	8·23	0·110
7	83	3·07	6·12	0·113
6	82	3·34	4·10	0·116
17	0	3·15	5·93	0·347
30	,,	2·46	3·48	0·350
29	,,	2·35	6·69	0·368
31	,,	2·49	7·92	0·374
32	,,	2·45	9·60	0·365
34	,,	2·45	11·11	0·349
			Mean	0·359

Run no.	MeOH (%) in solv.	a (mmole l.$^{-1}$)	b (mmole l.$^{-1}$)	k_2	Products, *cis* (%)
Method, Spec.	*Temp.,* 0·00°.				
37	0	2·08	2·08	0·357	79
38	,,	1·91	1·83	0·352	75
60	,,	1·76	2·69	0·371	75·5
59	,,	1·76	5·26	0·378	74
61	,,	1·77	10·90	0·311	75
62	,,	1·76	21·72	0·348	76
63	,,	0·94	8·11	0·323	77
64	,,	1·77	8·11	0·349	76
65	,,	2·61	8·11	0·324	75·5
66	,,	3·55	8·11	0·328	75
			Mean	0·339	75·8
Method, Spec.	*Temp.,* 10·05°.				
68	0	2·29	6·05	1·41	74·5
69	,,	4·02	6·05	1·28	75
71	,,	6·06	6·05	1·49	73
72	,,	1·86	3·86	1·54	72
73	,,	1·97	1·96	1·53	75
74	,,	1·95	8·74	1·55	76
			Mean	1·47	74·2
Method, Spec.	*Temp.,* 20·00°.				
81	0	3·92	3·92	6·11	73
82	,,	3·24	3·24	6·65	72
			Mean	6·38	72·5

The spectrophotometric method depends on differences in the absorption spectra of the *trans*-chloro-cation, and of the *cis*- and *trans*-aquo-cations —aquo- and not hydroxy-cations, because reaction was followed by means of the spectra of acidified samples. These three spectra are among those shown in Fig. 1. Salts of the three cations, individually, and as binary pairs, were shown to obey the Beer–Lambert law at the relevant wave-lengths and concentrations.

The initial spectrum of the reaction is the spectrum of the *trans*-chloro-cation. It is not possible directly to observe a final spectrum corresponding to the completed displacement of chlorine, because of the commencement, at late times, of the second stage of hydroxylation. However, as the next Sub-section shows, we know the proportions in which the *cis*- and *trans*-aquo-cations are produced, and therefore can calculate, from the observed spectra of the separate cations, a spectrum corresponding to the completion of chlorine displacement. It is thus found that the greatest change in optical density between the *trans*-chloro-cation and the produced mixture of *cis*- and *trans*-aquo-cations occurs at

4900 Å, and therefore optical density at this wavelength was adopted as the indication of reaction progress.

As before, good second-order rate-constants were calculated for the first 80% of reaction. These constants are entered in Table 1. The spectrophotometric constants for 0° are slightly lower than the titrimetric constants for solvent water at that temperature, but, as mentioned above, we must expect the titrimetric method to give high values. The errors in the spectrophotometric method seem to be random. We must assume that they obscure the theoretically expected negative salt effect, which would, however, be small at the concentrations used. Nevertheless, the spectrophotometric constants have been determined over a range of reagent concentration great enough to leave no doubt that the alkaline hydrolysis is indeed a second-order reaction.

Most of the rates are not inconveniently high at 0°; but at 10° the general accuracy begins to be affected by errors of timing, and at 20° these are much the most serious errors. The Arrhenius equation which best fits the rate data for these three temperatures is $k_2 = B_2e^{-E/RT}$ with $B_2 = 6{\cdot}6 \times 10^{13}$ sec.$^{-1}$ mole^{-1} l., and $E = 23{\cdot}2$ kcal./mole. But because of the low accuracy of the measured rates at 20°, these parameters must be regarded as only roughly evaluated.

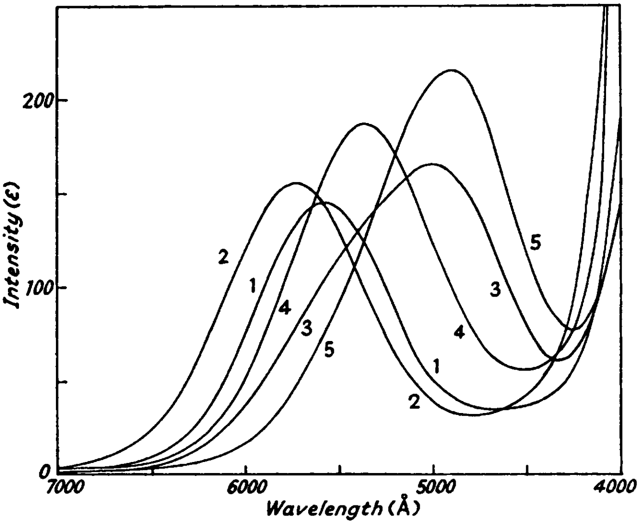

FIG. 1. *Spectrophotometric curves of extinction coefficients for halogeno- and aquo-*isothiocyanatobis*(ethylenediamine)cobalt*(III) *ions in water:*

(1) *trans*-$[Co\ en_2(NCS)Cl]^+$.
(2) *trans*-$[Co\ en_2(NCS)Br]^+$.
(3) *cis*-$[Co\ en_2(NCS)Cl]^+$.
(4) *trans*-$[Co\ en_2(NCS)OH_2]^{2+}$.
(5) *cis*-$[Co\ en_2(NCS)OH_2]^{2+}$

(1.3) *Steric Course.*—Werner preparatively converted the *trans*-chloro-cation, as thiocyanate, by means of concentrated potassium hydroxide, into the *trans*-hydroxy-cation, and, as dithionate, by means of concentrated aqueous ammonia, into the *cis*-hydroxy-cation,[2a] thereby making the stereochemistry of the formed hydroxy-cation apparently depend either on the anion of the complex cobalt salt or on the cation of the alkali. We therefore began our stereochemical investigation by allowing dilute solutions of the bromide, perchlorate, thiocyanate, and dithionate of the *trans*-chloro-cation to interact with dilute potassium and ammonium hydroxide. We found that, when the displacements of chlorine were substantially complete, the spectra of the solutions were practically identical. It has to be concluded that some condition is present in Werner's preparations which does not apply in our dilute solutions.*

When the absorption spectra of acidified reaction samples taken at different times are

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* This is not simply that the thiocyanate of the *trans*-aquo-cation is the less soluble of the stereoisomeric thiocyanates, whilst the dithionate of the *cis*-aquo-cation is the less soluble of the isomeric dithionates, because a more than 50% yield is obtained in either type of preparation. It is possible that, in the concentrated alkali a bimolecular OH-exchange, with hydroxide ion as substituting agent, leads to reversible stereo-change between the hydroxy-cations, and a subsequent disturbance of the balance of the isomers by separation of one or the other, according to the available anion. We have left this matter undecided, but report the incidental observation that Werner's preparation of the *cis*-hydroxy-salt can be repeated with the modification of using lithium in place of ammonium hydroxide.

plotted together, all the curves go through a single point, as shown in Fig. 2, with the exception of the curve applying to " infinite time." This means that, except at late times, the one original coloured substance is being replaced, either by only one other, or by more than one under the condition that these are being formed in a strictly constant ratio. In other words, if both *cis*- and *trans*-hydroxy-products are being formed, then they are arising as primary products, and simultaneously, in reactions of identical kinetic order.

With our knowledge of the spectra of the separate substances involved, curves such as these can be analysed to give the ratio in which the reaction of the *trans*-chloro-cation is yielding the *cis*- and *trans*-hydroxy-cations. A particularly sensitive form of analysis, and one which we like to apply when the optical results are good enough, is to read, for each reaction sample, the optical density at three wavelengths, and then to solve the three simultaneous linear equations that should, by Beer's law, give these optical densities in terms of the unknown concentrations of the three coloured substances. The coefficients in the equations are obtained by measuring the extinction coefficients of the three pure substances at the same three wavelengths, the partial optical density due to any absorbing component being the product if its concentration, its extinction coefficient, and the path-length. The equations being solved for the concentrations, we have a check upon the method, inasmuch as the sum of the three concentrations should be the same for all reaction samples. The concentrations will give additionally the proportion of reaction which has occurred, and the ratio in which *cis*- and *trans*-hydroxy-products are present, in each of the samples taken. The extinction coefficients, which we have determined with pure salts and used in this way, are in Table 2; and, as an illustration of the method, its application to one run is set out in Table 3.

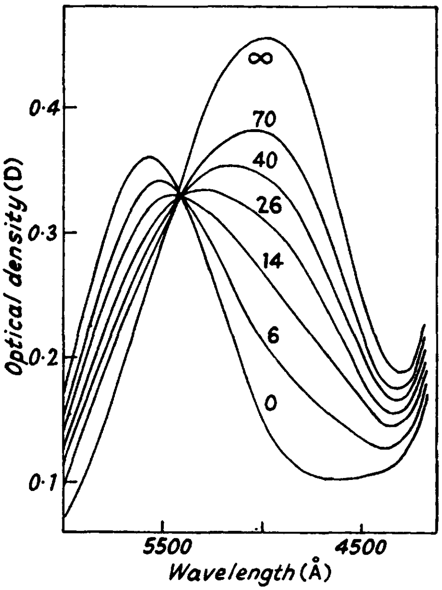

FIG. 2. *Spectrophotometric curves of optical density, in a cell of length* 4 *cm., of samples from Run* 38, *acidified at various times, given in minutes by the figures associated with the curves.* The common intersection shows that the products are being formed in constant proportions, and the deviation of the infinite-time curve that a subsequent reaction enters at late times.

It was confirmed quite generally by this analysis that the *cis*- and *trans*-hydroxy-products are formed in constant ratio throughout reaction. The mean values thus obtained for the stereoisomeric compositions of the products of all the runs which were thus followed spectrophotometrically are collected in the last column of Table 1. The

TABLE 2. *Extinction coefficients* (ε *in* $cm.^{-1}$ $mole^{-1}$ *l.*) *as determined for pure salts in water at* 0°, *and used for the spectrophotometric measurement of composition.*

λ (Å)	5800	5300	4900
ε of *trans*-[Co en_2(NCS)Cl]$^+$	122·6	110·3	40·0
ε of *cis*-[Co en_2(NCS)OH_2]$^{2+}$	37·7	145·3	216·2
ε of *trans*-[Co en_2(NCS)OH_2]$^{2+}$	100·3	185·1	99·6

TABLE 3. *Spectrophotometric analysis of run* 62.

{Solvent: water. Temp.: 0°. Initial concn. of *trans*-[Co en_2(NCS)Cl]$^+$ = 0·00176M, and of NaOH = 0·02172M. Samples were acidified, and made up to a 2-fold dilution with water, before measurement in a cell of length 4 cm. The observations are in the first four columns. In following columns, the calculated concentrations of *trans*-[Co en_2(NCS)Cl]$^+$, *cis*-[Co en_2(NCS)OH_2]$^{2+}$, and *trans*-[Co en_2(NCS)OH_2],$^{2+}$ called [A], [B], and [C], respectively, are in units 10^{-4} mole/l. The figures in the last two columns are 100([B] + [C])/([A] + [B] + [C]) and 100[B]/([B] + [C]), respectively.}

Time	Optical density			Calcd. concns.				Reactn.	*cis*
(sec.)	D_{5800}	D_{5300}	D_{4900}	[A]	[B]	[C]	Sum	(%)	(%)
77·2	0·320	0·450	0·353	4·78	2·68	1·12	8·58	44·3	71
94·2	0·311	0·461	0·390	4·53	3·21	1·01	8·75	48·2	76
112·2	0·299	0·468	0·412	4·07	4·37	1·17	8·70	53·2	75
131·0	0·289	0·470	0·429	3·79	3·72	1·16	8·67	56·3	76
153·2	0·270	0·480	0·462	3·08	4·12	1·40	8·60	64·2	75
174·2	0·259	0·491	0·498	2·73	4·62	1·37	8·72	68·7	77
209·4	0·240	0·502	0·533	2·02	5·05	1·61	8·68	76·9	76
249·0	0·232	0·520	0·573	1·63	5·54	1·69	8·86	81·6	77
319·2	0·216	0·521	0·602	1·28	6·01	1·55	8·84	85·5	79
								Mean *cis*-product:	76

essential result is that, in this definitely bimolecular substitution, the *trans*-chloro-cation is converted into 76% of the *cis*-hydroxy-cation, and 24% of its *trans*-isomer, at 0° in water. At higher temperatures the figures seem to move slightly towards each other, but further experiments on the temperature effect are desirable.

(2) *Kinetics and Products of the Reaction of Hydroxide Ion with* trans-*Bromo*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *Ion in Water:*

$$OH^- + trans\text{-}[Co\ en_2(NCS)Br]^+ \longrightarrow cis\text{- and } trans\text{-}[Co\ en_2(NCS)OH]^+ + Br^-$$

(2.1) *Basic Chemistry*.—The *cis*- and *trans*-series of bromo*iso*thiocyanatobis(ethylenediamine)cobalt(III) salts are both well characterised. Apart from close analogies with corresponding salts of the two chloro*iso*thiocyanato-series, the configurational identity of the *trans*-bromo*iso*thiocyanato-salts is proved by their conversion, without rupture of the cobalt–nitrogen bond, into *trans*-bromoamminobis(ethylenediamine) salts, which are known as to configuration, because their isomers of the *cis*-series have been optically resolved.[2a]

The rest of the basic chemistry of the reaction forming the subject of Section (2) is as described in Sub-section (1.1).

(2.2) *Kinetics*.—This reaction of the *trans*-bromo-cation is faster than the corresponding reaction of the *trans*-chloro-cation. Consequently, we have not been able to use the titrimetric method for following the reaction of the bromo-compound, because of the increased error due to reaction in the course of titration. On the other hand, the spectrophotometric method, by reason of the increased spectral differences, is a little more accurate than before. The high rates of reaction of the bromo-cation precluded measurements at temperatures other than 0°.

The absorption curves on which the spectrophotometric method depends are in Fig. 1. The usual checks were made as to the applicability of Beer's law. For the determination of rate constants, we again used, as our index of the amount of reaction, the optical density at 4900 Å of acidified samples of the solution. The initial optical density was simply that due to the employed bromo-cation. Owing to the high rate of hydroxylation with bromine displacement, and the consequently reduced relative importance of the second stage of hydroxylation with displacement of the *iso*thiocyanato-group, a final optical density, to correspond to completion of displacement of the bromine, could be directly measured with fair accuracy; but we preferred to calculate it, from our knowledge of the spectra of the stereoisomeric aquo-cations, and of the proportions in which they are produced, as recorded in Sub-section (2.3).

Good second-order rate-constants, showing only a random scatter, presumably due to errors in timing the samples of these fast runs, could be calculated for the first 90% or so of reaction. The constants for a number of runs are in Table 4. As they remain nearly the same over a 4-fold change in the initial concentration of each reactant, there can be no doubt that this hydroxyl substitution is a second-order process.

TABLE 4. *Second-order spectrophotometric rate-constants and product-compositions for the substitution of hydroxyl for bromine by hydroxide-ion attack on the* trans-*bromo*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *ion in water at* 0°.

[See explanation at the head of Table 1. The complex bromo-cation was supplied as perchlorate, and the hydroxide ion as sodium hydroxide. Rate measurements were based on the optical density at 4900 Å, with the calibrating extinction coefficients $\varepsilon_0 = 32$ and $\varepsilon_\infty = 194$, the latter figure being calculated for aquo*iso*thiocyanato-products containing 81% of the *cis*-isomer. The measurement of product-compositions during the progress of the runs was based on determinations of optical density at the wavelengths 5800, 5300, and 4600 Å.]

Run no.	*a* (mmole/l.)	*b* (mmole/l.)	k_2 (sec.$^{-1}$ mole^{-1} l.)	Mean (sec.$^{-1}$ mole^{-1} l.)	Products (%) *cis*	Products (%) Mean
101	2·47	3·26	1·84	1·95	81	81·4
102	1·43	1·62	1·76		83	
103	1·41	3·27	2·10		81	
104	1·42	4·94	1·96		81	
105	1·42	6·27	2·17		81	
106	0·68	3·30	1·90		—	—

(2.3) *Steric Course.*—The absorption curves of acidified reaction samples all go through a common point. This shows that, if several coloured substances are being formed, then they are being produced in constant proportions. The analysis which gives the proportions in which the *cis*- and *trans*-hydroxy-products are formed, was made by reading the optical densities of the samples at three wavelengths, and then setting up simultaneous equations for them in terms of the unknown concentrations of the three coloured substances, the coefficients in the equations being given by the extinction coefficients, recorded in Table 5, which were measured in the pure substances at the same wavelengths. The general consistency of the method is better than in the previous application, as illustrated by the specimen analysis in Table 6.

TABLE 5. *Extinction coefficients* (ε *in cm.*$^{-1}$ *mole*$^{-1}$ *l.*) *as determined for pure salts in water at* 0°, *and used in the spectrophotometric measurement of composition.*

	λ (Å)	5800	5300	4600
ε of	*trans*-$[\mathrm{Co\ en_2(NCS)Br}]^+$	154·6	84·4	36·3
	cis-$[\mathrm{Co\ en_2(NCS)OH_2}]^{2+}$	37·7	145·3	151·5
	trans-$[\mathrm{Co\ en_2(NCS)OH_2}]^{2+}$	100·3	185·3	57·7

TABLE 6. *Spectrophotometric analysis of run* 103.

{Solvent: water. Temp.: 0°. Initial concn. of *trans*-$[\mathrm{Co\ en_2(NCS)Br}]^+$ = 0·00141M, and of NaOH = 0·00327M. Further explanation is at the head of Table 3, except that Br must be read for Cl.}

Time	Optical density			Calcd. concns.				Reactn.	*cis*
(sec.)	D_{5800}	D_{5300}	D_{4600}	[A]	[B]	[C]	Sum	(%)	(%)
57·8	0·340	0·292	0·187	4·76	1·79	0·33	6·88	30·8	85
85·4	0·311	0·314	0·214	4·02	2·34	0·53	6·88	41·6	81
115·6	0·288	0·333	0·239	3·43	2·84	0·66	6·93	50·5	81
157·6	0·259	0·352	0·266	2·73	3·40	0·78	6·91	60·5	81
211·0	0·235	0·374	0·294	2·10	3·96	0·92	6·98	69·9	81
268·6	0·210	0·380	0·305	1·55	4·23	1·04	6·82	77·3	80
361·6	0·190	0·393	0·321	1·05	4·56	1·19	6·80	84·6	79
511·0	0·173	0·411	0·345	0·06	5·03	1·26	6·89	91·3	80
"∞"	0·148	0·431	0·368	−0·06	5·49	1·46	6·89	100·9	79
								Mean *cis*-product:	81

The mean values of the stereoisomeric proportions of the products of the five runs thus examined are included in Table 4. The results show that in this certainly bimolecular displacement of halogen by hydroxide ion from the *trans*-bromo-cation in water at 0°, there are formed 81% of the *cis*-hydroxy-cation and 19% of its *trans*-isomer.

(3) *Kinetics and Products of the Reaction of the Hydroxide Ion with* cis-*Chloro*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *Ion in Water* :

$$\mathrm{OH^-} + cis\text{-}[\mathrm{Co\ en_2(NCS)Cl}]^+ \longrightarrow cis\text{- and } trans\text{-}[\mathrm{Co\ en_2(NCS)OH}]^+ + \mathrm{Cl^-}$$

(3.1) *Basic Chemistry*.—This is as described in Sub-section (1.1).

(3.2) *Kinetics*.—This reaction is too rapid to be studied kinetically by the titrimetric method, and it is not an easy subject for the spectrophotometric method, because much of the absorption curve of the *cis*-chloro*iso*thiocyanato-cation lies about midway between the curves for the *cis*- and the *trans*-aquo*iso*thiocyanato-cations, with the result that the change of absorption during reaction is somewhat slight. However, the relevant absorption curves being as in Fig. 1, we have examined the kinetics of the reaction, using the optical density of acidified samples at 4700 Å as indicator of reaction progress. Owing to the large rate of chlorine displacement, the end of this process is not much overlapped by the beginning of thiocyanate liberation, and hence second-order rate-constants could be calculated over nearly the whole reaction. The mean rate-constants for several runs are in Table 7. Though they are not very precise, they apply to a sufficiently wide range of reactant concentrations to leave no doubt that a second-order reaction is under observation.

(3.3) *Steric Course*.—Owing to the smallness of the changes of absorption it was not possible in this case to carry out complete analyses during the course of reaction, based on the absorption at three wavelengths. The reaction was therefore run to completion at 0°, and the absorption was measured at a single wavelength, one favourable for distinguishing between the *cis*- and *trans*-aquo-isomers, *viz*., 4900 Å. The extinction coefficient of the acidified reaction solution at this wavelength was 193·2, and from this and the extinction coefficients, given in Table 2, for the separate aquo-salts, it can be calculated that the mixture of isomers produced contained 80·3% of the *cis*-form. This figure is slightly low, because, in the completed run, owing to the overlapping of reaction stages, a small proportion of the aquo*iso*thiocyanato-cations will become replaced by the less absorbing diaquo-cations. By noting the approximate rate of this slow further change, it is possible to make a rough allowance for its effect on our result. By doing so, we obtain an adopted value of 82% for the proportion of *cis*-hydroxy-isomer formed in the first stage of bimolecular hydroxylation of the *cis*-chloro-cation by hydroxide ions in water at 0°.

TABLE 7. *Second-order spectrometric rate constants for the substitution of hydroxyl for chlorine by hydroxide ion attack on* cis-*chloro*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *ion in water at* 0°.

[See explanation at the head of Table 1. The *cis*-chloro-cation was supplied as chloride, and the hydroxide ion as sodium hydroxide. For measurements of reaction progress based on optical densities at 4700 Å, the extinction coefficients ε_0 = 125·7 and ε_∞ = 159·8 were taken as providing end-values.]

Run no.	75	77	78	79	
a (mmole/l.)	2·25	2·24	3·12	4·54	
b („)	3·73	8·09	8·09	8·09	
k_2 (sec.$^{-1}$ mole^{-1} l.)	1·35	1·45	1·52	1·28	Mean : 1·40

(4) *Kinetics and Products of the Aquation of* trans-*Chloro*iso*thiocyanatobis(ethylenediamine)-cobalt*(III) *Ion in Water* :

$$\mathrm{H_2O} + trans\text{-}[\mathrm{Co\ en_2(NCS)Cl}]^+ \longrightarrow \left\{\begin{array}{c} cis\text{-}[\mathrm{Co\ en_2(NCS)OH_2}]^{2+} \\ \rightleftharpoons \\ trans\text{-}[\mathrm{Co\ en_2(NCS)OH_2}]^{2+} \end{array}\right\} + \mathrm{Cl^-}$$

As described in Sub-section (1.1), our examination of the stabilities of the complex salts, in the conditions concerned in the investigations on their alkaline hydroxylations, led us to study certain reactions which these salts undergo in water in the absence of alkali. These observations are described in Sections (4)—(6).

(4.1) *Kinetics*.—In water at raised temperatures the *trans*-chloro-cation undergoes aquation in two steps: first the chlorine is replaced by a water molecule, and then the *iso*thiocyanato-group is similarly replaced. The first step is the faster, and its rate is independent of hydrogen ions at pH values of less than 5. The second step, however, is considerably retarded by hydrogen ions; and so, by working with acidities approaching that of pH 2, it becomes possible to ignore this step completely.

In these conditions the products of the aquation are simply the *cis*- and *trans*-aquo*iso*thiocyanato-salts. But these do not appear in the ratio in which they are formed, because they undergo reversible interconversion. This reaction is rapid, but not instantaneous; and therefore the aquo-isomers do not immediately appear in their equilibrium ratio, though at late times they attain these proportions. In fact, they do not appear in any constant ratio during the progress of reaction, and we are consequently precluded from measuring reaction progress by the change of optical density at a fixed wavelength. What we have done, therefore, is, first, to follow the changes of optical density at the three wavelengths, 5800, 5300, and 4900 Å, then, with the aid of the constants in Table 2, to set up simultaneous equations for these optical densities in terms of the unknown concentrations of the three coloured substances, and, finally, to extract from these equations the one root of importance for the kinetics of the aquation, *viz.*, that representing the concentration of surviving chloro-cation.

The disappearance of the chloro-cation follows the first-order rate-law. Our rate-constants for this reaction are in Table 8. They fit the Arrhenius equation $k_1 = B_1 e^{-E/RT}$, with $B_1 = 8{\cdot}5 \times 10^{14}$ sec.$^{-1}$, and $E = 30{\cdot}4$ kcal./mole.

(4.2) *Steric Course.*—We failed to determine this for the reason that the specific rate of interconversion of the aquo-products (Section 6) is about 10—15 times greater than that of their collective formation. This means that only a somewhat small fraction of the material in any sample is causing a departure of the composition from the equilibrium composition. Thus the observed departures were too small, in relation to the errors of measurement, to justify the long extrapolation which would be required in order to give the composition of freshly formed aquation products.

TABLE 8. *First-order spectrophotometric rate constants (k_1 in sec.$^{-1}$) for the aquation of the* trans-*chloro*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *ion in* 0·0070N-*aqueous perchloric acid* (pH 2·16).

[The complex cation was supplied as perchlorate. Optical densities at 5800, 5300, and 4900 Å were measured, and concentrations were then calculated with the aid of the extinction coefficients of Table 2.]

Run no.	Initial Co salt (mmole/l.)	10^5k_1	Mean 10^5k_1	Run no.	Initial Co salt (mmole/l.)	10^5k_1	Mean 10^5k_1	Run no.	Initial Co salt (mmole/l.)	10^5k_1	Mean 10^5k_1
	At 45·0°				At 70·6°				At 89·9°		
53	1·97	0·106	0·113	45	2·27	3·93	4·04	51	2·00	40·3	42·8
54	2·82	0·114		48	3·06	4·00		52	2·97	43·4	
55	3·90	0·114		49	4·06	3·97		47	4·16	43·5	
56	4·96	0·118		46	4·98	4·28		50	5·09	43·7	

(5) *Kinetics and Products of the Aquation of* trans-*Bromo*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *Ion in Water*:

$$\mathrm{H_2O} + trans\text{-}[\mathrm{Co\ en_2(NCS)Br}]^{+} \longrightarrow \left\{ \begin{array}{c} cis\text{-}[\mathrm{Co\ en_2(NCS)OH_2}]^{2+} \\ \upharpoonleft\!\downharpoonright \\ trans\text{-}[\mathrm{Co\ en_2(NCS)OH_2}]^{2+} \end{array} \right\} + \mathrm{Br^-}$$

(5.1) *Kinetics.*—The general conditions applying to this aquation are as described above for the chloro-cation, except that the aquation of the bromo-cation goes about 4 times faster. Thus its rate, and that of the following isomerisation, are more nearly comparable; and therefore the proportions in which the aquo-products appear drift much more in the course of reaction. It is thus all the more necessary to use three wavelengths, rather than one, for following the disappearance of the bromo-cation.

From observed optical densities at 5800, 5300, and 4600 Å, good first-order rate constants for the aquation were obtained. These are given in Table 9. They agree with the formula $k_1 = B_1 e^{-E/RT}$ in which $B_1 = 2{\cdot}1 \times 10^{15}$ sec.$^{-1}$ and $E = 30{\cdot}1$ kcal./mole.

TABLE 9. *First-order spectrometric rate constants (k_1 in sec.$^{-1}$) for the aquation of the* trans-*bromo*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *ion in* 0·0070N-*aqueous perchloric acid* (pH 2·16).

[The complex cation was supplied as perchlorate. Optical densities at 5800, 5300, and 4600 Å were measured, and concentrations were then calculated with the aid of the extinction coefficients of Table 5.]

Run no.	Initial Co salt (mmole/l.)	10^5k_1	Mean 10^5k_1	Run no.	Initial Co salt (mmole/l.)	10^5k_1	Mean 10^5k_1	Run no.	Initial Co salt (mmole/l.)	10^5k_1	Mean 10^5k_1
	At 62·6°				At 70·6°				At 89·9°		
113	2·23	5·81	5·78	110	2·18	16·5	16·5	117	2·99	158	161
112	2·94	5·63		108	3·02	16·2		111	4·09	162	
114	4·29	5·74		109	4·28	16·7		116	4·80	164	
115	5·23	5·92									

(5.2) *Steric Course.*—The specific rate of aquation of the *trans*-bromo-cation, and the specific rate of approach to equilibrium of the formed aquo-isomers, are alike to within a factor of 3. It follows that, if the *cis*- and *trans*-aquo-cations are formed in one ratio, but finally come into equilibrium at a different one, we should be able to observe a substantial part of this drift from the one isomer ratio to the other, in the course of the aquation process.

This ratio does indeed drift. The spectrophotometric method of analysis, with which we follow the kinetics of aquation, has, because of the drift, to be so elaborated that it gives not only the concentrations of the surviving bromo-cation, but also those of the separate *cis*- and *trans*-aquo-cations; and thus the analysis shows the drift, as illustrated in Table 10.

The simplest way to use these drifts in the measured ratio of isomers present in order to deduce the ratio in which the *cis*- and *trans*-aquo-cations are initially *formed*, would be to extrapolate the measured ratios back to zero time. However, an extrapolation of the length involved, if made empirically, would be somewhat hazardous; and it is safer to "guide" it theoretically by fitting a curve of the right functional form to the data. This we can do with the aid of rate-constants given in Sections (5.1) and (6).

TABLE 10. *Spectrophotometric analysis of run* 116.

{Solvent: 0·0070N-aqueous perchloric acid (pH 2·16). Temp.: 89·9°. Initial concn. of *trans*-$[\text{Co en}_2(\text{NCS})\text{Br}]^+[\text{ClO}_4]^-$ = 0·00480M. Undiluted samples examined in cell of length 1 cm. See also explanation at head of Tables 3 and 6.}

Time	Optical density			Calc. concns.				Reactn.	*cis*
(sec.)	D_{5800}	D_{5300}	D_{4600}	[A]	[B]	[C]	Sum	(%)	(%)
112	0·658	0·459	0·228	38·8	4·2	3·6	46·6	16·8	54
195	0·620	0·488	0·261	34·8	6·8	4·9	46·5	25·3	58
281	0·559	0·515	0·305	29·2	10·7	5·8	45·8	36·2	65
378	0·520	0·545	0·343	25·2	13·8	6·8	45·8	45·0	67
481	0·470	0·568	0·381	20·7	17·1	7·5	45·3	54·4	70
589	0·432	0·599	0·423	16·8	20·5	8·3	45·6	63·1	72
705	0·396	0·607	0·448	14·0	22·9	8·0	45·0	68·9	74
860	0·359	0·624	0·484	10·9	26·1	7·8	44·9	75·7	77
1009	0·325	0·641	0·503	7·5	27·7	9·0	44·3	83·1	75
1199	0·306	0·659	0·540	5·9	30·8	8·4	45·0	86·8	79

Let f be the fraction of *cis*-aquo-isomer in the total aquo-isomers *present* at any time t. Then the precise way in which f will vary with time between its limits, f_0 at $t = 0$, and f_∞ at $t = \infty$, will depend on the rates of aquation and isomerisation, in particular on the specific rate k_a of total aquation of the bromo-cation and the total specific rate $k_1 + k_{-1}$ of the approach, by reversible interconversion of the aquo-isomers, to their equilibrium. The functional form of the variation with time of the isomer ratio present, as measured by f, is expressed in the following equation:

$$\frac{f - f_\infty}{f_0 - f_\infty} = \frac{k_a}{(k_1 + k_{-1}) - k_a} \cdot \frac{\exp(-k_a t) - \exp[-t(k_1 + k_{-1})]}{1 - \exp(-k_a t)}$$

The derivation of this formula is outlined below. While the composition of the isomers present, as measured by f, is changing thus, the fraction F_a, measuring the total progress of aquation, is increasing with time according to the formula

$$F_a = 1 - \exp(-k_a t)$$

By eliminating t between these equations we can treat f as a function of F_a, as is done in Fig. 3. The equation connecting f with F_a contains only rate constants, which we have measured, f_∞, which we can measure, and one adjustable parameter f_0. This f_0 measures the ratio of isomers initially *formed*, and is our real unknown : we choose it so as to make the theoretical curve for f fit the data as well as may be.

Experimental values of f are plotted against F_a for a number of runs in Fig. 3. Two temperatures are involved, but the scatter of points on account of analytical error is greater than the temperature effect. Theoretical curves are plotted, according to the above equations, for the two temperatures. (The flatter curve applies to the higher temperature, for which the isomerisation is less fast relatively to the aquation.) The experimental parameters used in the equations in order to construct these curves are derived from Sections (5.1) and (6), and are in the middle three columns of Table 11. The last column of this Table gives the results of these " guided extrapolations," *viz.*, the values of f_0 required to give the fit shown in Fig. 3. It would appear that there is considerable stereo-change in this aquation : at 63°, the *trans*-bromo*iso*thiocyanato-cation produces 43% of the *cis*-aquo*iso*thiocyanato-cation, and 57% of its *trans*-isomer.

FIG. 3. *Theoretical curves,* (——) *for* 62·6° *and* (- - -) *for* 89·9°, *and experimental values,* ○ *for* 62·6° *and* + *for* 89·9°, *for the percentage* 100f *of* cis-*aquo-isomer contained in the total aquo-isomers present at various percentage degrees of progress* 100F_a *of aquation of* trans-[Co en$_2$(NCS)Br]$^+$ *in dilute aqueous perchloric acid.* The intercepts on the f axis give the proportions in which the aquo-isomers are formed by aquation.

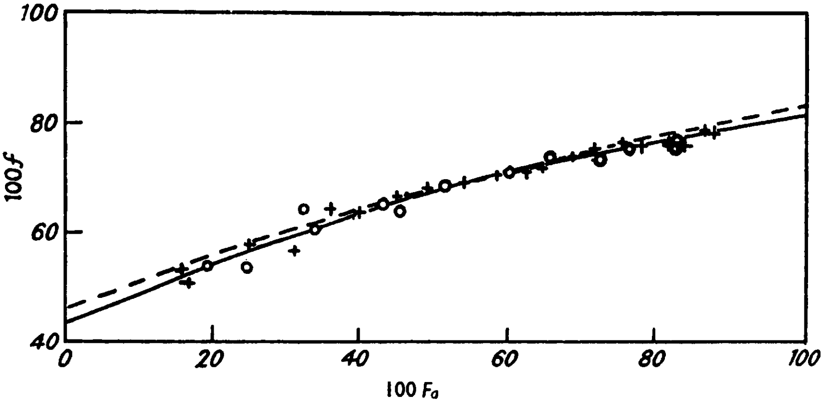

TABLE 11. *Rate data used to calculate the steric course of aquation of the* trans-*bromo*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *ion from analytical observations on aquation products undergoing isomerisation concurrently with production. Calculated steric course of the aquation.*

	Experimental			Calcd.
Temp.	k_a (sec.$^{-1}$)	$k_1 + k_{-1}$ (sec.$^{-1}$)	f_∞	f_0
62·6°	5·78 × 10^{-5}	16·4 × 10^{-5}	0·81	0·43
89·5	—	340 × 10^{-5}	0·84	—
89·9	161 × 10^{-5}	(356 × 10^{-5}) *	(0·84) *	0·46

* Extrapolated for temperature.

In order to derive the above equation for f, we first set down the concentration dx_1 of total aquo-products *formed* during an element of time dt_1 at t_1 :

$$dx_1 = k_a\,[\exp(-k_at_1)]dt_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The concentration of *cis*-isomer contained in this element of aquo-products, when freshly formed, will be f_0dx_1. But, on account of the reversible isomerisation, at a later time t, the concentration of *cis*-isomer in this element of formed material dx_1 will have changed to fdx_1, where

$$(f - f_\infty)/(f_0 - f_\infty) = \exp[-(k_1 + k_{-1})(t - t_1)] \quad . \quad . \quad . \quad . \quad (2)$$

This concentration fdx_1 must be expressed in terms of the differential dt_1 rather than of dx_1, by means of (1) and (2), and it must then be integrated from $t_1 = 0$ to $t_1 = t$, in order to obtain the total concentration of *cis*-isomer *present* at time t. We do not set down these steps as they are purely mechanical. The total concentration of aquo-isomers present at time t is given by (3) :

$$aF_a = a[1 - \exp(-k_at)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The ratio of these concentrations is f, the equation for which, given on p. 1701, contains f_0, because of the use of equation (2). In the application of this equation, f is treated as known, and f_0 as the unknown.

(6) *Rate and Equilibrium in the Reversible Isomerisation of the* cis- *and* trans-*Aquo*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *Ions in Water :*

$$cis\text{-} \rightleftharpoons trans\text{-}[Co\ en_2(NCS)OH_2]^{2+}$$

In warm aqueous solutions acidified with perchloric acid, each of the aquo*iso*thiocyanato-isomers undergoes conversion into the other. The composition thus tends to an equilibrium; but at late times this situation may be disturbed by a slow incursion of an aquation process in which a second water molecule enters the complex, with ejection of the *iso*thiocyanato-group. However, this aquation is retarded by hydrogen ions; and so, by working at acidities near 0·01N or higher, it can be made unimportant.

Using the pure salts *cis*-$[Co\ en_2(NCS)OH_2{}^{2+}S_2O_6{}^{2-},3H_2O$ and *trans*-$[Co\ en_2(NCS)OH_2]^{2+}(Br^-)_2,2H_2O$, we have measured spectrophotometrically the rate of isomerisation of either isomeric cation, and the ratio of their concentrations at equilibrium. The index of reaction progress was the optical density at 4800 Å. The incursion of a small amount of aquation at late times probably had no effect on the rate measurements. However, in the long-period runs, which were made in order to determine equilibrium composition, it may have led to low estimates of the proportion of the more absorbing *cis*-isomer, since the diaquo-cation is a relatively weak absorber at the wavelength used. Of these long-period experiments, those which started with the *trans*-isomer are expected to have produced the more accurate results.

The kinetics were those of a balanced reaction of first order in both directions. The sum $k_1 + k_{-1}$ of the rate constants of the opposing reactions, *i.e.*, the specific rate of approach to equilibrium, could be calculated directly from the optical densities, by means of the following equation :

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

The measured specific rate-sums $k_1 + k_{-1}$ are in Table 12. They show that the rate of isomerisation is independent of the concentration of hydrogen ions within the range of our measurements. The measured equilibrium compositions are also in Table 12. They show that the rate-ratio k_{-1}/k_1 is approximately 5.

This isomeric change may be intramolecular, or it may be a substitution with stereo-change; but we cannot know which it is, nor, if the latter alternative is correct, how much substitution simultaneously occurs without stereo-change, in the absence of measurements, which have not yet been made but are being undertaken, of the rate of water-exchange with isotopically labelled solvent water.

TABLE 12. *First-order rate-constants* ($k_1 + k_{-1}$ *in sec.*$^{-1}$) *of approach to equilibrium, and stereoisomeric composition at equilibrium, in the reversible interconversion of* cis- *and* trans-*aquo*iso*thiocyanatobis(ethylenediamine)cobalt*(III) *ions in dilute aqueous perchloric acid.*

Run no.	Temp.	pH	Initial confign.	Initial [Co salt] (mmole/l.)	Rate: 10^5 ($k_1 + k_{-1}$)		Equilm.: *cis* (%)	
58	62·6°	2·16	*trans*	3·63	16·1	16·4	83	82
67	,,	0·28	,,	3·62	16·7		83	
83	,,	1·70	*cis*	4·48	13·9		79	
84	,,	0·33	,,	4·68	16·4		79	
57	89·5	2·16	*trans*	3·66	340		84	

(7) *Summary and Discussion.*

The main results recorded in the foregoing are collected in Table 13.

As noted in Part I, it is a pecularity of the octahedral geometry of the complexes under discussion, that complete correlation does not exist between microchemical stereo-change associated with individual molecular acts of substitution, a form of stereo-change that can be reduced to the concept of "edge-displacement," and observable changes of stereochemical classification in actual experiments on substitution. If the compound substituted is a *trans*-isomer, then, and then only, the correlation is complete: all molecular acts of substitution that proceed without stereo-change then give a *trans*-product, and all those that involve stereo-change yield a *cis*-product. But if the compound substituted is the *cis*-isomer, then, although all molecular acts of substitution that proceed without stereo-change give the *cis*-product, those that involve stereo-change may give either *cis*- or *trans*-products; and thus the proportion of *cis*-product found macrochemically is only an upper limit to the proportion in which configuration is retained in the molecular transactions, whilst the proportion of *trans*-product found is a lower limit to the proportion in which stereo-change accompanies the molecular processes.

TABLE 13. *Rate and steric course of reactions in water of bis(ethylenediamine)cobalt*(III) *ions containing the* iso*thiocyanato-ligand.*

Reaction type	Kinetic order	Displaced group (X)	Temp.	Rate-constant	Product ratios (%)	
					cis	*trans*
(*A*) *cis*- or *trans*-[Co en$_2$(NCS)X]$^+$ + OH$^-$ $\longrightarrow$ *cis*- and *trans*-[Co en$_2$(NCS)OH]$^+$ + X$^-$						
				k_2 (sec.$^{-1}$ mole^{-1}/l.)		
S_N2	2	*trans*-Cl	0·0°	0·34	76	24
	,,	,,	10·0	1·47	74	26
	,,	,,	20·0	6·38	72·5	27·5
	,,	*trans*-Br	0·0	1·95	81	19
	,,	*cis*-Cl	0·0	1·40	82	18
(*B*) *trans*-[Co en$_2$(NCS)X]$^+$ + OH$_2$ $\longrightarrow$ *cis*- and *trans*- [Co en$_2$(NCS)OH$_2$]$^{2+}$ + X$^-$						
				k_1 (sec.$^{-1}$)		
Aquation	1	*trans*-Cl	45·0	0·113 × 10^{-5}	—	—
	,,	,,	70·6	4·04 ,,	—	—
	,,	,,	89·9	42·8 ,,	—	—
	,,	*trans*-Br	62·6	5·78 ,,	43	57
	,,	,,	70·6	16·5 ,,	—	—
	,,	,,	89·9	161 ,,	46	54
(*C*) *cis*- or *trans*-[Co en$_2$(NCS)X]$^{2+}$ $\longrightarrow$ *cis*- and *trans*-[Co en$_2$(NCS)X]$^{2+}$						
				($k_1 + k_{-1}$)(sec.$^{-1}$)		
Isomerisation	1	*cis*- or *trans*-OH$_2$	62·6	16·4 × 10^{-5}	81	19
	,,	*trans*-OH$_2$	89·5	340 ,,	84	16

Of the three types of reaction for which stereochemical results in kinetically definite conditions are here reported, the only one of which the mechanism is well established is the alkaline hydrolysis (*A*), which is certainly a bimolecular nucleophilic substitution S_N2.* Discussion in the remainder of this Section will be confined to reactions of this type. The aquation process (*B*) will be discussed in Part VI.

In carbon chemistry, S_N2 substitutions produce quantitative inversion of configuration, independently of the constitutional details of the system. If an analogous rigid rule held for cobalt substitutions, then, with all allowances made for the latitude with which, as recalled above, we must translate macroscopic stereochemical findings into molecular terms, it would still be true that a *trans*-halogeno-factor would give 100% of the *cis*-hydroxy-product in an S_N2 substitution. As Table 13 shows in two examples, this is not true. And the molecular interpretation of the actual results obtained in these examples is that, whilst most of the individual molecular encounters resulting in substitution do produce a stereo-change, a significant fraction of them effect substitution with retention of configuration.

It thus appears that in bimolecular octahedral substitutions no such sharp rule governs steric direction, as applies in the field of tetrahedral substitutions. Whether some less extreme form of the same rule applies, or, if not, what constitutional factors control the course of reaction, must be left for further experiment to determine.

(8) *Preparations.*

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride, the starting material for many of the following preparations, was obtained as described by Bailar,[5] and crystallised twice from aqueous hydrochloric acid. For some experiments it was further purified by extraction with, and crystallisation from, well-dried methyl alcohol in which the tris(ethylenediamine) salt, present as an impurity, is insoluble (Found: C, 16·7, 17·0, 17·1; H, 5·5, 5·5, 5·6; Cl, 37·7, 37·2. Calc. for $C_4H_{16}N_4Cl_3Co$: C, 16·8; H, 5·6; Cl, 37·3%).

Salts of *cis*- and *trans*-chloro*iso*thiocyanatobis(ethylenediamine)cobalt(III) were prepared as Werner describes.[2a] The bromide of the *trans*-series was crystallised from water when required only as starting point for further preparations, but was recrystallised from dry methyl alcohol when required for measurements (Found: C, 17·1, 17·1; H, 4·7, 4·9. Calc. for $C_5H_{16}N_5SClBrCo$: C, 17·0; H, 4·6%). On treatment of a saturated solution of the bromide in water with a small excess of 72% perchloric acid, the *trans*-perchlorate separated, which was recrystallised from aqueous ethyl alcohol, but could not be analysed by combustion, because of the violence of its pyrolysis. By mixing a saturated aqueous solution of the bromide with one of potassium thiocyanate, the thiocyanate of the *trans*-series was obtained; it was recrystallised from water. The crude chloride of the *cis*-series was converted into the *cis*-perchlorate by grinding it with 72% perchloric acid, and then triturating the salt which separated again with perchloric acid. This salt was reconverted into the *cis*-chloride by adding concentrated hydrochloric acid to its concentrated solution in warm water; the salt formed was crystallised from aqueous ethyl alcohol.

trans-Dibromobis(ethylenediamine)cobalt(III) bromide was prepared by Werner's method,[2a] and after trituration with concentrated hydrobromic acid was obtained as its hydrogen bromide adduct, from which the loosely bound hydrogen bromide was removed by washing the crystals

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* Interpretation of the second-order kinetics by an assumed extraction by the basic reagent of a nitrogen-bound proton of an ethylenediamine group, to give a more easily aquated complex ion, is considered to be excluded by the absence of a relation between bimolecular rate and base-strength (cf. Part II).

Our view that the second-order alkaline reaction is a bimolecular substitution S_N2, not dependent on preliminary conjugate-base formation, has very recently been contested by Pearson, Meeker, and Basolo,[4] on the ground that replacement, in cations such as *trans*-dichlorobis(ethylenediamine)cobalt(III), of the bis(ethylenediamine) by tetrapyridyl or bis-2 : 2′-dipyridyl ligands, which have no nitrogen-bound hydrogen, leads to a ready aquation which is unaccelerated by alkali up to pH 9·2. We think that a greatly increased prominence of unimolecular hydrolysis in the presence of the aromatic ligands is to be expected for the known reason for which one finds it on passing from a *n*-alkyl to a benzyl halide, *viz.*, participation of aromatic π-electrons. The high rates observed, especially with the dipyridyl complexes, strongly suggest that the above-named authors got their results by promoting a mechanism, rather than by suppressing one. Moreover, as will be shown in Part VI, they could have obtained at least as great a degree of alkali-independence by retaining the ethylenediamine residues and simply changing the *trans*-group (to a nitro-group moreover, which, by their mechanism, should favour alkali-sensitivity).

[4] Pearson, Mecker, and Basolo, *J. Inorg. Nuclear Chem.*, 1955, **1**, 341.

[5] See Fernelius, *Inorg. Synth.*, 1946, **2**, 233.

successively with water (a small amount), ethyl alcohol, and ethyl ether, and then heating at 110°. For some experiments, this salt was freed from its main impurity, the tris(ethylenediamine) salt, by extraction with, and crystallisation from, well-dried methyl alcohol.

Salts of the *trans*-bromo*iso*thiocyanatobis(ethylenediamine)cobalt(III) series were prepared by Werner's method [2a] from the above dibromo-bromide. The thiocyanate and the bromide were crystallised from water. The perchlorate was prepared from the thiocyanate by grinding the latter with concentrated perchloric acid. It was also prepared by treating a concentrated aqueous solution of the bromide with 72% perchloric acid, and crystallising from water the salt which separated (Found : C, 14·4; H, 4·0. Calc. for $C_5H_{16}O_4N_5SClBrCo$: C, 14·4; H, 3·9%).

Salts of the *trans*-hydroxy- and *trans*-aquo-series were also prepared by Werner's methods.[2a] *trans*-Chloro*iso*thiocyanatobis(ethylenediamine)cobalt(III) thiocyanate was dissolved in warm 25% aqueous potassium hydroxide, and the *trans*-hydroxy*iso*thiocyanatobis(ethylenediamine)-cobalt(III) thiocyanate, which separated slowly from the cooled solution, was washed with ethyl alcohol and ethyl ether, and recrystallised from a small amount of dilute aqueous potassium hydroxide (Found : C, 21·6, 21·6; H, 5·9, 5·6; H_2O, 6·6. Calc. for $C_6H_{17}ON_6S_2Co,H_2O$: C, 21·6; H, 5·8; H_2O, 5·5%). The absorption spectrum from 7000 to 3850 Å of an acidified aqueous solution of this salt was identical with that of a solution prepared in equivalent concentration from the aquo-salt next to be mentioned. A concentrated aqueous solution of the hydroxy-salt was mixed with one of bromine-free hydrogen bromide in very slight excess. On evaporation at low pressure over sulphuric acid, *trans*-aquo*iso*thiocyanatobis(ethylenediamine)cobalt(III) bromide separated as its dihydrate (Found: C, 13·0; H, 5·0; H_2O, 11·9. Calc. for $C_5H_{18}ON_5SBrCo,2H_2O$: C, 13·3; H, 4·9; H_2O, 12·0%).

Werner's method [2a] of preparing salts of the *cis*-hydroxy- and *cis*-aquo-series gave low and variable yields in our hands. He made the dithionate of the hydroxy-series by treating *trans*-chloro*iso*thiocyanatobis(ethylenediamine)cobalt(III) dithionate with concentrated aqueous ammonia; and from the hydroxy-salt he generated the dithionate of the aquo-series by addition of acetic acid. He mentions that, unless the original chloro-salt is very pure, the reaction takes an unwanted direction. Though we are not convinced that its formation has much to do with the final stages of purification of the chloro-salt, we confirm that a by-product is formed, often in large amount; and we have identified it, by analysis, and by its absorption spectrum, as *cis*-chloroamminobis(ethylenediamine)cobalt(III) dithionate. Because of the difficulties of this method, we have prepared *cis*-hydroxy- and *cis*-aquo-salts with the aid of an ion-exchange column [6] from *cis*-chloro*iso*thiocyanatobis(ethylenediamine)cobalt(III) chloride. A solution of this (5·5 g.) in water (115 ml.) was passed through a column, 60 cm. × 2 cm., of Amberlite IRA-400 in hydroxide form at a rate of 5 ml./min. The elutriant was acidified to pH 4 by addition of aqueous dithionic acid, freshly prepared from barium dithionate and sulphuric acid, and was evaporated under reduced pressure to 15—20 ml., and then set to crystallise after being warmed to 40° and having some ethyl alcohol added. The orange salt which separated was the nearly pure dithionate trihydrate of the *cis*-aquo-series, and by addition of more ethyl alcohol a further quantity of the same salt in a less pure form could be obtained from the purple solution, which contained the *trans*-isomeride. The first crop of the *cis*-salt was further purified by two more crystallisations from aqueous ethyl alcohol, the last of which produced no further change in the absorption spectrum (yield 2 g.; a further 1·8 g. were obtained by working up residues). The *salt* was dried in a vacuum over sulphuric acid, and then left in air to regenerate the trihydrate {Found: Co, 12·5, 12·4, 12·6, 12·6; S, 20·4; H_2O, 15·2. $[Co\,en_2(NCS)OH_2]S_2O_6,3H_2O$ requires Co, 12·9; S, 20·5; H_2O, 15·3%}. This salt on gentle dehydration loses only its $3H_2O$ of crystallisation, which it can recover by exposure to the air; but on stronger dehydration (as in the above analysis) it loses also its H_2O of constitution, and becomes converted into the dinuclear salt, *di*iso*thiocyanatotetrakis*(*ethylenediamine*)*dicobalt*(III) *dithionate*, which on exposure to air takes up half the total amount of water lost, to form its tetrahydrate {Found : Co, 13·5; H_2O, 8·6. $[Co_2\,en_4(NCS)_2](S_2O_6)_2,4H_2O$ requires Co, 13·6; H_2O, 8·3%}. The absorption spectrum of this salt is naturally quite different from that of the mononuclear parent. The latter was converted into the thiocyanate of the *cis*-aquo-series, which is an anhydrous salt, by treatment of a concentrated aqueous solution of the dithionate with ammonium thiocyanate, and crystallisation of the resulting thiocyanate from water.

(9) *Methods of Measurement.*

For the alkaline hydrolytic runs, the weighed complex salt, dissolved in the solvent, aqueous methyl alcohol, or boiled-out distilled water, and also carbonate-free standard aqueous sodium

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[6] Basolo and Steringer, *J. Amer. Chem. Soc.*, 1950, **72**, 5748.

hydroxide, and the water needed to adjust the volume of the reaction mixture, were separately brought to thermostat temperature, and then the reaction solution was made up. Timed samples, withdrawn by an appropriately jacketed, fast-running, 5 ml. pipette, were delivered into excess of aqueous perchloric acid.

In titrimetric analysis, this was a measured amount of standard acid, and the resulting solution was titrated with sodium hydroxide by using a glass electrode and calomel half-cell. In spectrophotometric analysis, the reaction samples were delivered into acid contained in 10 ml. standard flasks and, after making up to the marked volume, the absorption of light was measured, at one or more wavelengths, by means of a Unicam Quartz spectrophotmeter SP 500.

For the aquation runs the sealed-tube method was used. The reaction solution was made up, from the weighed salt, water, and aqueous perchloric acid, at room temperature, and the set of tubes was then charged and simultaneously put into the thermostat. As soon as thermal equilibrium had been reached, one tube, and after timed intervals other tubes, were withdrawn, and cooled in solid carbon dioxide and alcohol in order quickly to stop the reaction. Their contents were then brought up to room temperature and analysed spectrophotometrically.

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[*Received, November 10th*, 1955.]