1087. *Mechanism and Steric Course of Octahedral Aquation. Part VIII.* Aquation of* cis- *and* trans-*Bromochloro-, -Dibromo-, and -Bromohydroxobisethylenediaminecobalt*(III) *Salts.*

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The first-order rate constants for the aquation of *cis-* and *trans-* $[Co\ en_2ClBr]^+$, *trans*-$[Co\ en_2Br_2]^+$, and *cis-* and *trans*-$[Co\ en_2(OH)Br]^+$ have been measured over a range of temperature. The Arrhenius parameters are reported and briefly discussed. The steric course of the reaction has been determined in each case and is explained in terms of a unimolecular reaction with a trigonal-bipyramidal intermediate into which water enters at positions that are determined, not only by the five ligands bound to the cobalt, but also by the released halide ion which remains in the vicinity of the intermediate during its subsequent reaction.

Determinations of the steric courses of aquation of complexes of the type, *cis-* and *trans-* $[Co\ en_2(A)Cl]^+$, where A = OH, Cl, N_3, and NCS have been complicated by subsequent isomerisation of the product, $[Co\ en_2(A)H_2O]^{2+}$ at rates which were between 2 and 15 times greater than those of aquation.[1] It was possible to correct the observed product compositions for the subsequent isomerisation and thus determine the kinetic product ratio, but it remained desirable to study complexes with a more labile replaceable ligand, not only to obtain steric courses without undue interference from product isomerisation, but also to gain information about the effect of the departing ligand on the steric course of substitution in these unimolecular reactions. The necessary requirement that the rate of aquation be faster than, or of the same order of magnitude as, the rate of isomerisation of the product limits the choice of leaving group to Cl, Br, NO_3, and H_2O. The replacement of chlorine has been studied extensively and one bromo-complex, $[Co\ en_2(NCS)Br]^+$, has been reported.[1a,b] The appropriate nitrato-complexes are still under investigation and the steric course of water exchange in aquo-complexes has been reported in outline.[2]

In this paper we report aquation of $[Co\ en_2(A)Br]^+$, where A = Cl, Br, or OH. In addition to providing information about the displacement of bromine under the influence of a *cis-* or a *trans*-chlorine atom, the complexes, *cis-* and *trans*-$[Co\ en_2(Cl)Br]^+$ allow, at the same time, a determination of the rates and steric courses of the displacement of chlorine under the influence of a *cis-* or *trans*-bromine atom.

(1) *Isomerisation of* cis- *and* trans-*Aquobromobisethylenediaminecobalt*(III) *Salts.*—Preliminary studies of solutions containing, initially, only *cis-* or *trans*-$[Co\ en_2(Br)H_2O]^{2+}$ salts showed that, provided the solution was sufficiently acid (pH < 2), the reaction,

$$cis\text{-}[Co\ en_2(H_2O)Br]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[Co\ en_2(H_2O)Br]^{2+}$$

could be studied spectrophotometrically with little interference from the accompanying aquation, the rate of which is inversely proportional to the hydrogen-ion concentration. The relation between the spectra of these isomers[3] is very similar to that between the spectra of the corresponding chloro-complexes[1d] and the same method was used to determine the specific first-order rate constants for approach to equilibrium ($k_1 + k_{-1}$), differing only in the means used to determine D_∞ which was measured after six half-lives instead of the usual ten. The error introduced was less than that which would have arisen from aquation of the product. Optical-density changes were measured at 5300 Å, where the

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* Part VII, *J.*, 1963, 514.

[1] (*a*) Ingold, Nyholm, and Tobe, *J.*, 1956, 1691; (*b*) Baldwin and Tobe, *J.*, 1960, 4275; (*c*) Staples and Tobe, *J.*, 1960, 4803; (*d*) Baldwin, Chan, and Tobe, *J.*, 1961, 4637.

[2] Kruse and Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 1280.

[3] Chan and Tobe, *J.*, 1962, 4531.

molar extinction coefficients of the *cis*- and the *trans*-isomer are 90·3 and 10·0 l. mole^{-1} cm.$^{-1}$, respectively. The rate constants are reported in Table 1 together with the composition of the equilibrated product. The temperature-dependence of these constants can be expressed by

$$k_1 + k_{-1} = 1{\cdot}6 \times 10^{16} \exp(-27{,}000/\boldsymbol{R}T) \text{ sec.}^{-1}.$$

(2) *Kinetics of Aquation.*—In all cases, the progress of the reaction was followed by titrating halide ions in solution with silver nitrate after removing the complex cations by means of a cation-exchange resin. The techniques did not differ significantly from those used in the study of the corresponding chloro-complexes.[1d] In the studies of the *cis*- and *trans*-[Co en$_2$(Cl)Br]$^+$ cations, which released chloride and bromide to a total of one mole of halide (Cl$^-$ + Br$^-$) per mole of complex ion aquated, the reactions were followed and the rate constants computed by methods similar to those described for the base hydrolysis of these complexes.[3] As in that case, the complex offered two modes of aquation, (*a*) the displacement of bromine under the influence of co-ordinated chlorine, and (*b*) the displacement of chlorine under the influence of co-ordinated bromine, and both could be studied simultaneously. The kinetics, in all cases, are of the first order and the rate constants are collected in Table 2.

TABLE 1.

Isomerisation of aquobromobisethylenediaminecobalt(III) cations in aqueous nitric acid (0·01N).

(The *trans*-isomer was supplied as *trans*-[Co en$_2$(OH)Br]Br,H$_2$O, which was instantly converted into the aquo-complex when dissolved in the acid. The *cis*-compound was supplied as *cis*-[Co en$_2$(H$_2$O)Br]Br$_2$,H$_2$O.)

Temp.	Initial config.	Initial [complex] (mmole/l.)	$k_1 + k_{-1}$ $\times 10^4$ (sec.$^{-1}$)	Equilib. compn. (% *cis*)
0·0°	*trans*	4·04	0·0329	77
,,	,,	5·06	0·0327	
,,	,,	7·08	0·0327	
,,	,,	8·01	0·0329	
25·0	,,	4·00	2·14	76
,,	,,	5·06	2·14	
,,	,,	7·04	2·14	
,,	,,	8·05	2·14	
,,	*cis*	4·06	2·13	
34·6°	*trans*	4·05	9·2	76
,,	,,	5·08	9·1	
,,	,,	7·09	9·2	
,,	,,	8·02	9·2	

TABLE 2.

First-order rate constants for the reactions:

$$[\text{Co en}_2(\text{A})\text{X}]^+ + \text{H}_2\text{O} \xrightarrow{k_1} [\text{Co en}_2(\text{A})\text{H}_2\text{O}]^{2+} + \text{X}^-.$$

(Each entry for k_1 is the mean of four values covering a three-fold range of concentration of complex.)

A	X	Temp.	10^5k_1 (sec.$^{-1}$)
* *trans*-Cl	Br	0·0°	0·178
,,	,,	25·0	11·2
,,	,,	34·6	44·7
* *trans*-Br	Br	0·0	0·266
,,	,,	10·1	1·44
,,	,,	25·4	14·7
trans-OH	Br	0·0	21·6
,,	,,	10·0	106
,,	,,	25·0	950
* *trans*-Br	Cl	0·0	0·091
,,	,,	25·0	4·5
,,	,,	34·6	16·6
* *cis*-Cl	Br	0·0°	1·38
,,	,,	9·8	6·3
,,	,,	25·0	57
† *cis*-OH	Br	0·0	162
,,	,,	10·2	740
,,	,,	25·4	6300
* *cis*-Br	Cl	0·0	0·40
,,	,,	9·8	1·74
,,	,,	25·0	14·0

* Aquation studied in 0·01N-HNO$_3$. † Complex provided as *cis*-[Co en$_2$(H$_2$O)Br]Br$_2$,H$_2$O and converted into the hydroxo-complex at the beginning of the reaction by adding slightly less (96%) than the required amount of sodium hydroxide solution.

(3) *Steric Course.*—The relatively fast isomerisation of the aquo-products makes it impossible to determine the kinetically formed isomer ratio from the composition of the product at the end of the reaction. However, by analysing the mixture from time to time during the reaction, it was possible to measure the isomer ratio of the product and plot this against the fraction of reaction completed. The correction was then applied by extrapolating these values to zero reaction by using the known rates of isomerisation to guide the curve.[1a] The dibromo- and hydroxobromo-complexes were treated in the same way as the corresponding dichloro- and hydroxochloro-complexes [1d] and it was necessary, once again, to use a combination of spectrophotometric and titrimetric analysis to estimate the three complex species.

TABLE 3.

Isomeric distribution in the product of the reaction
cis- or *trans*-[Co $en_2(A)X]^+ + H_2O \longrightarrow$ *cis*- and *trans*-[Co $en_2(A)H_2O]^{2+} + X^-$
expressed as a percentage of product having a *cis*-configuration.

A	X	Temp.	*cis*-Product (%)	A	X	Temp.	*cis*-Product (%)
trans-Cl	Br	25·0°	20 ± 5	*cis*-Cl	Br	25·0°	>95
trans-Br	Br	25·4	30 ± 2	*cis*-OH	Br	0·0	96 ± 4
trans-OH	Br	0·0	73 ± 2	*cis*-Br	Cl	25·0	>95
trans-Br	Cl	25·0	50 ± 5				

The analyses of the reaction mixtures obtained from the bromochloro-complexes were greatly complicated by the presence of five light-absorbing species since the complex, on aquation, could produce either [Co $en_2(Br)H_2O]^{2+}$ or [Co $en_2(Cl)H_2O]^{2+}$ depending upon whether the chlorine or the bromine was displaced. A complete spectrophotometric analysis being impossible, the following procedure was adopted. At the required time, a sample of the reaction mixture was withdrawn and cooled to 0°. A portion of this was placed in a spectrophotometer cell which was warmed in the hand until there was no further condensation on the windows (temperature = *ca.* 12°). The absorption spectrum

TABLE 4.

Rates, Arrhenius parameters, and steric courses of aquation of
[Co $en_2(A)X]^+$, $k_1 = B \exp(-E/\boldsymbol{R}T)$ (sec.$^{-1}$).

A	X	10^5k_1 at 25° (sec.$^{-1}$)	E (kcal./mole)	$\log_{10} B$	Product compn. (% *cis*)	A	X	10^5k_1 at 25° (sec.$^{-1}$)	E (kcal./mole)	$\log_{10} B$	Product compn. (% *cis*)
trans-OH	Cl	160	26·2	16·4	75 [1d]	*cis*-OH	Cl	1200	23·1	15·0	100 [1d]
trans-OH	Br	950	25·0	16·3	73	*cis*-OH	Br	6000	23·3	15·8	100
trans-Br	Cl	4·5	25·2	14·1	50	*cis*-Br	Cl	14·0	23·1	13·1	100
trans-Br	Br	13·9	25·6	14·9	30	*cis*-Cl	Cl	24·0	22·2 *	12·5	100 [1d]
trans-Cl	Cl	3·5	27·5 *	15·9	35 [1d]	*cis*-Cl	Br	57	23·9	14·3	100
trans-Cl	Br	11·2	26·6	15·6	20	*cis*-NCS	Cl	1·1	20·8	10·3	100 [1b]
trans-NCS	Cl	0·005	30·4	14·9	50—70 [1a,b]	*cis*-NCS	Br	2·3	23·1	12·3	100 [1b]
trans-NCS	Br	0·05	30·1	15·3	45 [1a]						

* It has recently been suggested that the activation energies for the aquation of these two complexes are nearly equal (~28 kcal./mole).[4] The results given for the *cis*-isomer are too widely scattered to give reliable Arrhenius parameters, and comparison with Mathieu's data [5] indicates agreement at four temperatures and wide disagreement at the highest temperature studied. There is therefore no reason to revise the activation energy assigned by Mathieu. The aquation of the *trans*-isomer has now been studied over a temperature range by three sets of workers,[4–6] and results are available over the range 15—50°. The best straight line, which fits all the results moderately well, gives an activation energy of 27·5 kcal./mole, significantly higher than that given by Mathieu [5] (24·2) but very close to that calculated by Basolo *et al.*[6] from more widely scattered data. There is no doubt that this reaction is in need of very careful study over as wide a temperature range as possible.

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[4] Panasyuk, Solomko, and Reiter, *J. Inorg. Chem. U.S.S.R.*, 1961, **6**, 1033.

[5] Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 2152.

[6] Basolo, Boston, and Pearson, *J. Amer. Chem. Soc.*, 1953, **78**, 2678.

between 6500 and 4500 Å was measured as rapidly as possible (7 minutes), and then a known volume of the solution was analysed quantitatively for chloride and bromide. The amount of aquation occurring during this treatment was negligible. From these results it was possible to calculate the amount of unchanged chlorobromo-complex present and the concentration of the chloroaquo- and the bromoaquo-complexes, but there still remained the two unknown isomeric compositions of the two aquo-products. By applying Beer's law to the known spectra of the pure components,[1d,3] a series of spectra was calculated for solutions of the known composition in which the *cis* : *trans* ratios of the chloroaquo- and the bromoaquo-complex were varied independently. Only one pair of ratios gave satisfactory agreement between the calculated and the measured spectrum over the entire wavelength range studied and it was thus possible to obtain the fraction of each component with the *cis*-configuration to within better than 5% of the total amount of the component. These analyses were made periodically during the reaction, and the kinetically produced isomer ratio in the aquo-product was determined by extrapolating these values to zero reaction. The values are reported in Table 3.

Discussion.—The results obtained in this work are summarised in Table 4, together with those for the analogous chloro-complexes. The original hope, that, by using a more labile ligand, it would be possible to separate the formation of the aquo-isomers from their subsequent isomerisation, has been fulfilled, but, in the case of the bromochloro-complexes, this advantage has been counterbalanced to some extent by the similar labilities of the chlorine and the bromine and the consequent reduction in the accuracy of analysing a five-component system.

The results throw light on three separate issues: (i) the labilising and directing influences of co-ordinated bromine on the replacement of other ligands in the complex; (ii) the effect of changing the nature of the displaced group on the rates and Arrhenius parameters of aquation; and (iii) the dependence, if any, of steric course of the reaction on the nature of the leaving group.

Changing the non-participating group from chlorine to bromine has only a small effect on the rate of aquation. When the ligand in question is *trans* to the leaving chlorine, the rate at 25° is increased by a factor of 2·6 and when it is *cis* the increase is only about 15%. In order to make this comparison, the rate constants for the aquation of the dichloro-complexes have been halved to take account of the statistical effect of the two equivalent chlorine atoms. The activation energies for aquation of the *trans*-complexes appear to be more affected by the change in the nature of the non-participating ligands than are the rate constants. This is not unusual and it has already been pointed out that, in complexes of this type, an increase in the activation energy is generally accompanied by an increase in the frequency factor.[1d] In view of the uncertainty of the activation energy for aquation of the *trans*-$[\mathrm{Co\ en_2Cl_2}]^+$ complex, there is little point at the moment in attempting to draw any conclusion from the differences that are observed.

An observation that is general for all complexes of the type, $[\mathrm{Co\ en_2(A)X}]^{n+}$, is that when X is changed from Cl to Br, the rate of aquation is increased. This increase is usually 5—6-fold, but there are exceptions, *e.g.*, A = *cis*-NCS [1b] and *trans*-Br. Once again, when such relatively small effects on rate are in question, the study of Arrhenius parameters may not be of great significance until they can be determined with considerably more precision; nevertheless, in all but one of the cases listed in Table 4, the *trans*-bromo-complex has a lower activation energy for aquation of bromide than the corresponding *trans*-chloro-complex has for aquation of chloride. This is in direct contrast to the ions *cis*- and *trans*-$[\mathrm{Co\ en_2(NH_3)X}]^{2+}$ (ref. 7) and *trans*-$[\mathrm{Co\ en_2(NO_2)X}]^+$ (ref. 8), where the change from X = Cl to Br is accompanied by an increase in activation energy of about 1 kcal./mole, which is then overcompensated by a more favourable entropy of activation.

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[7] Tobe, *J.*, 1959, 3776.

[8] Langford and Tobe, *J.*, 1963, 506; Ašperger and Ingold, *J.*, 1956, 2862.

It is also of interest that, in aquation of the complexes, [Co(DMG)$_2$(H$_2$O)X] (DMG = dimethylglyoximato-ion), changing X from Cl to Br also increases the activation energy by about 2 kcal./mole, but here the entropy change does not compensate and the rate of replacement of chlorine is somewhat greater than that for bromide.[9] All the complexes listed in Table 4 are aquated by a unimolecular mechanism, whereas the halogenoammine and the halogenonitro-complexes are believed to be aquated bimolecularly. However, inspection of the activation energies of the *cis*-complexes in Table 4 shows that any general correlation of the activation-energy changes with the mechanism of the aquation is unjustified.

The aquation of the *cis*-complexes still appears to be stereospecific and, within experimental error, in every case, only the *cis*-isomer of the product is obtained. The *trans*-isomers are all aquated with steric change; replacement of bromine leads to less steric change than the replacement of chlorine. This dependence of the steric course of a unimolecular reaction on the nature of the leaving group is not an unusual phenomenon. The general stereochemical rule for an $S_{\text{N}}1$ substitution at an asymmetric carbon atom is that substitution involves racemisation, usually together with an excess of inversion, except when a configuration-holding group is present.[10] Since the intermediate is a trigonal-planar species, and therefore has a plane of symmetry, it might be expected to lead to complete racemisation and the fact that it does not is explained by saying that the leaving group, although no longer bonded to the reaction centre, is sufficiently close when the intermediate undergoes further reaction, to influence attack adjacent to itself, usually repelling the entering reagent. This reasoning can be applied to the five-co-ordinate intermediate of unimolecular aquation which must react with one of the adjacent water molecules long before the released halide ion has left its immediate environment. The stereochemical consequences of substitution and the way in which they are affected by the departing ligand are readily understandable in terms of a trigonal-bipyramidal intermediate (Fig. 1).[1b,11] This is formed by extension of the Co–X bond until it is broken, the extension being accompanied by the movement of a pair of ligands that were *cis* to ligand X and *trans* to one another. Since there are two such pairs, two intermediates, which have the relationship of mirror images, are formed. Entry of water into these intermediates should follow, in its symmetry, the reverse of the path taken by X and should

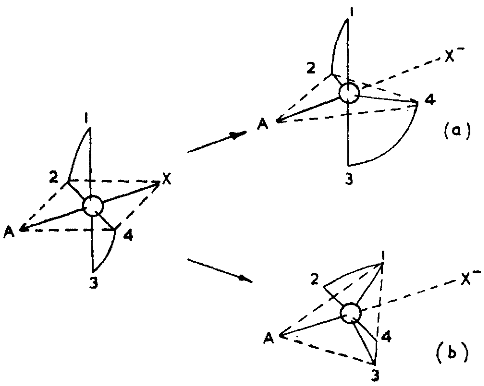

FIG. 1.

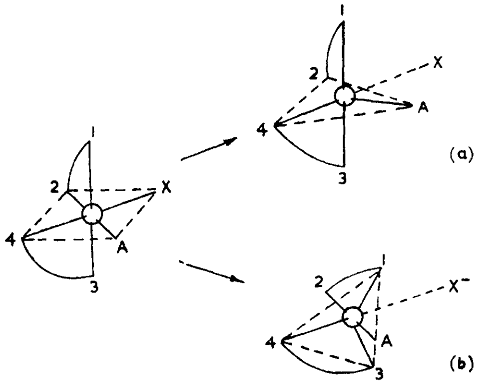

FIG. 2.

FIGS. 1 and 2. Five-co-ordinate intermediates and their formation.

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[9] Ablov and Sychev, *J. Inorg. Chem. U.S.S.R.*, 1959, **4**, 1143.

[10] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953, p. 386.

[11] Basolo and Pearson, " Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958, p. 216.

therefore take place at the edge of the trigonal plane. There are three such paths and they are not stereochemically equivalent. In (1a), entry at 2,4 leads to a *trans*-product, whereas entry at A.2 and A.4 will lead to one enantiomorphic form of the *cis*-product. In (1b), entry at 1,3 leads to a *trans*-product, whereas entry at A,1 or A.3 yields a *cis*-product of opposite configuration to that obtained from (1a). Although there are good reasons to believe that the chances of entry of a water molecule at any of the six possible positions are not statistically equivalent, it can be reasoned from symmetry that, in the absence of asymmetric reagents and other asymmetric conditions, forms (1a) and (1b) are produced and consumed in equal amounts and that both yield the same *cis* : *trans* ratio of the product. The *cis*-form, therefore, is always the racemate. The *cis* : *trans* ratio of the product will depend on the relative ease of entry of water adjacent to and opposite to ligand A. The intermediate lives in an environment of water molecules that form the inner solvation shell, and it is one of these that becomes attached to the cobalt. It is suggested that the conformation of the solvation shell, and hence the ability of a particular water molecule in it to become attached, is affected, not only by the ligands that remain attached to the metal in the intermediate, but also by the halide ion that has just been expelled. In the series of complexes under discussion, the two ethylenediamine ligands exert a constant effect and can be ignored in any comparison within the series. The process can conveniently be looked upon as a competition between A and X^- to introduce a water molecule into the co-ordination shell of the cobalt. Taking the steric courses listed in Table 4, it is possible to write ligands A and ions X^- in a series representing their ability to introduce a water molecule, OH $>$ Br^- $>$ NCS $>$ Cl^- $\sim$ Br $>$ Cl, where the ions in italics are not bonded to the cobalt.

The retention of configuration during aquation of *cis*-complexes in this series has been explained in terms of a square-pyramidal intermediate.[12] However, it is known that, in solvents other than water, the *cis*-$[\mathrm{Co\,en_2Cl_2}]^+$ cation can undergo unimolecular substitution with considerable steric change [13] and, although this could be explained by saying that the square-pyramidal intermediate has a long enough life in a non-aqueous environment to undergo rearrangement before the entering group is bonded, it is simpler to postulate that, just like the *trans*-isomer, the *cis*-isomer forms a trigonal-bipyramidal intermediate. It can be seen in Fig. 2 that the *cis*-isomer is able to form two different intermediates, (2a) which has A in the trigonal plane, and (2b) which has A in an axial position. Since it is postulated that these unimolecular processes occur most easily when A stabilises the intermediate of lower co-ordination number by donating a second pair of electrons to the cobalt,[14] it is necessary to discard intermediate (2b) because, when A is in an axial position, the relevant orbitals are orthogonal. Intermediate (2a), however, is identical with the intermediate (1b) that is derived from the *trans*-isomer and it is therefore necessary to explain why reactions of the *cis*- and *trans*-isomer have such completely different steric courses. The retention of configuration in aquation of the *cis*-complexes can be understood, once again, in terms of the abilities of A and X^- to introduce an adjacent water molecule into the intermediate. When this intermediate is derived from a *trans*-complex, A and X^- are on opposite sides of the cobalt atom and therefore compete against one another; but when, as in (2a), the intermediate is derived from a *cis*-complex, A and X^- are adjacent to one another and combine to place the water molecule into positions that lead to the formation of a *cis*-product with a retained configuration. In the reactions studied in non-aqueous solution the entering reagent is, not a solvent molecule, but an anion, and so repulsion between this anion and X^- leads to steric change.

Experimental.—Preparations. The salts, *trans*-$[\mathrm{Co\,en_2(OH)Br]Br,H_2O}$, *cis*-$[\mathrm{Co\,en_2(H_2O)Br]Br_2,H_2O}$, *trans*-$[\mathrm{Co\,en_2(Cl)Br]ClO_4}$, and *cis*-$[\mathrm{Co\,en_2(Cl)Br]NO_3}$ were from

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[12] Ingold, Nyholm, and Tobe, *Nature*, 1960, **187**, 477.
[13] Brown and Nyholm, *J.*, 1953, 2693; Tobe and Watts, *J.*, 1962, 4614, and unpublished results.
[14] Pearson and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 4878.

batches whose preparation and analyses have been reported before.[3] *Trans*-Dibromobisethylenediaminecobalt(III) bromide was prepared by Werner's method,[15] whereby carbonatobisethylenediaminecobalt(III) bromide was warmed with concentrated hydrobromic acid. The crude product was dried and freed from acid by heating it at 110° and was purified by recrystallisation from anhydrous methanol {Found: Co, 13·9; co-ordinated Br, 37·9; Br^-, 19·0. $[Co(C_2H_8N_2)_2Br_2]Br$ Co, 14·0; co-ordinated Br, 38·2; Br^-, 19·1%}.

Kinetics.—The preparation, sampling, and analysis of reaction mixtures was carried out by the methods described previously.[1d] When chloride and bromide ions were both released in the course of the reaction, they were estimated by potentiometric titration. Spectrophotometric measurements were made with a Unicam S.P. 500 spectrophotometer. Thermostats were accurate to ±0·05°. Light was excluded as a routine precaution.

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[15] Werner, *Annalen*, 1912, **386**, 111.