878. *Base Hydrolysis of Dichloro-, Chlorobromo-, Chlorohydroxo-, and Bromohydroxo-bis(ethylenediamine)cobalt(III) Salts.*

By S. C. CHAN and M. L. TOBE.

The kinetics and steric course of the replacement, by hydroxide, of the chlorine or bromine in *cis-* and *trans-*$[\mathrm{Co\,en_2Cl_2}]^+$, $[\mathrm{Co\,en_2ClBr}]^+$, $[\mathrm{Co\,en_2(OH)Cl}]^+$, and $[\mathrm{Co\,en_2(OH)Br}]^+$ cations have been studied and the Arrhenius parameters calculated. The considerable differences in the reactivity of these complexes are due largely to differences in the entropies of activation, and the steric course of the reaction depends very much upon the nature and the position of the non-participating ligand.

THE reaction between *cis-* and *trans-*$[\mathrm{Co\,en_2Cl_2}]^+$ and hydroxide ions was studied by Pearson *et al.*[1] who also interpreted departures from a simple second-order kinetic rate law at the later stages of the reaction as due to replacement of the second chlorine atom and ascribed a rate constant to the reaction of an unspecified hydroxochloro-isomer with hydroxide ions. In an attempt to obtain information about the steric course of hydroxide substitution * in *trans-*$[\mathrm{Co\,en_2(OH)Cl}]^+$ salts, it was noticed that the rate of the reaction was very much slower than that reported by Pearson *et al.*,[1] and the work described in this paper is an attempt to discover the reasons for the large difference in the reactivity of the *trans-*$[\mathrm{Co\,en_2Cl_2}]^+$ and *trans-*$[\mathrm{Co\,en_2(OH)Cl}]^+$ towards hydroxide substitution.

METHODS

(1) *Kinetics.*

$$cis\text{- or } trans\text{-}[\mathrm{Co\,en_2AX}]^+ + \mathrm{OH^-} \longrightarrow cis\text{- and } trans\text{-}[\mathrm{Co\,en_2AOH}]^+ + \mathrm{X^-}$$

The kinetics of these reactions follow a simple second-order rate law, $d[\mathrm{X^-}]/dt = k_2[\mathrm{Complex}][\mathrm{OH^-}]$, which may be complicated slightly by a slower replacement of group A (when A = Cl or Br) from the product, either by further reaction or by aquation. In addition, when A = OH or $\mathrm{NO_2}$, it is necessary to correct for the simultaneous replacement of X by aquation. In all cases, the rate of the reaction was determined by measuring the concentration of free halide ions in the solution after the reaction had been stopped by acidification. The techniques used to initiate reaction and sample the mixture depended upon the rate. For relatively slow reactions the reagents were mixed in a flask and samples were withdrawn at suitable times by pipette and run into an excess of acid. For reactions of intermediate rate a thermostat-controlled automatic sampling-pipette was used with which samples could be removed at intervals of 15 seconds. The fast reactions were followed with an apparatus where the reagents were mixed in a three-way tap and reacted while passing along a tube. The reaction was stopped almost instantaneously when the solution emerged and ran into a considerable excess of acid. When the starting compound was readily aquated, it was

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* In this paper, " hydroxide substitution " denotes replacement of a ligand by OH, in this case replacement of Cl by OH. It does not denote replacement of an OH ligand already present by some other ligand.

[1] Pearson, Meeker, and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 709.

TABLE 1.

Second-order rate constants (l. mole^{-1} sec.$^{-1}$) for the reaction.

$$[\mathrm{Co\,en_2AX}]^+ + \mathrm{OH}^- \longrightarrow [\mathrm{Co\,en_2AOH}]^+ + \mathrm{X}^-$$

Constants were determined from titrimetric data. Unmarked entries report complexes where the background aquation could be neglected and the constants were calculated from the expression, $k_2 = x/[at(a - x)]$, where a = initial [Complex] = initial [OH$^-$] and $x = [\mathrm{X}^-]_t - [\mathrm{X}^-]_0$, concentrations being measured at times $t = t$ and $t = 0$ sec., respectively. The values of k_2 given for each run represent the average of seven determinations over a wide range of time. The complexes marked with an asterisk are aquated at a rate comparable with their reaction with hydroxide and it was necessary to apply a correction. The apparent second-order rate constant, k_2^*, determined from the expression,

$$k_2^* = \frac{2{\cdot}303}{t(b - a)} \log_{10} \frac{a(b - x)}{b(a - x)},$$

where b = initial [OH$^-$], is related to the true second-order rate constant, k_2, by the expression, $k_2 = k_2^* - k_1/(b - x) + t\,.\,\mathrm{d}k_2^*/\mathrm{d}t$, where k_1 is the first-order rate constant for the complicating aquation and is known in all cases.[2,3] The third term, $t\,.\,\mathrm{d}k_2^*/\mathrm{d}t$, made only an insignificant contribution under the experimental conditions and could be ignored. The complexes of the type, [Co en$_2$ClBr]$^+$ lost chloride and bromide during the reaction in a way such that [Cl$^-$]/[Br$^-$] remained constant and at the end of the reaction [Cl$^-$] + [Br$^-$] = initial [Complex]. The rate constant, k_2, obtained by using x = total [Halide], is equal to the sum of the constants for the displacement of chloride, k_2^{Cl}, and the displacement of bromide, k_2^{Br}. Since the constant ratio, [Br$^-$]/[Cl$^-$] = $k_2^{\mathrm{Br}}/k_2^{\mathrm{Cl}}$, the two constants can be evaluated in the same experiment.

A	X	Temp.	k_2	A	X	Temp.	k_2
trans-Cl	Cl	0·8°	95	cis-Cl	Cl	0·8°	17·4
,,	,,	10·2	386	,,	,,	10·2	77·6
,,	,,	25·4	3160	,,	,,	25·4	710
trans-Cl	Br	0·8	306	cis-Cl	Br	0·8	80
,,	,,	10·2	1310	,,	,,	10·2	313
,,	,,	25·4	12,100	,,	,,	25·4	2640
trans-Br	Cl	0·8	125	cis-Br	Cl	0·8	27
,,	,,	10·2	570	,,	,,	10·2	104
,,	,,	25·4	5300	,,	,,	25·4	840
*trans-OH	Cl	0·0	0·0167	*cis-OH	Cl	0·0	0·368 ‡
,,	,,	10·2	0·072	,,	,,	10·2	1·63 ‡
,,	,,	25·0	0·56	,,	,,	25·4	11·9 ‡
*trans-OH	Br	0·0	0·168	*cis-OH	Br	0·0	2·66 ‡
,,	,,	10·2	0·813	,,	,,	10·2	11·4 ‡
,,	,,	25·4	7·0	,,	,,	25·4	86 ‡
*trans-NO$_2$	Cl	0·0	0·080 †	*cis-NO$_2$	Cl	0·0	0·032 †
,,	,,	10·2	0·387	,,	,,	10·2	0·146
,,	,,	25·4	3·67	,,	,,	25·4	1·18

* Corrections made for simultaneous aquation. † Values quoted are from Ašperger and Ingold.[7]
‡ Complexes supplied as aquo-complex so that one equivalent of hydroxide is used instantaneously in their conversion into the hydroxo-complex.

necessary to prepare a fresh solution for each determination. The second-order rate constants for all these reactions are listed in Table 1. The value given for each complex at each temperature represents the average of four constants, determined from separate runs, which agree to better than ±1%. The initial hydroxide concentration varied between 10^{-3} and 10^{-2}M, and the initial concentration of the complex between 5 × 10^{-4} and 5 × 10^{-3}M. The fastest reactions were studied under conditions such that the concentrations of the complex and the hydroxide were equal.

(2) *Steric Course.*—The products of the reaction were measured by spectrophotometric methods which, in many cases, were extremely simple because the products of the reaction neither reacted further nor isomerised in the time required for the first reaction to become

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[2] Baldwin, Chan, and Tobe, *J.*, 1961, 4637.
[3] Chan and Tobe, unpublished results.

complete. Solutions of the hydroxochloro- and the hydroxobromo-bis(ethylenediamine)-cobalt(III) complex, acidified at the completion of the hydroxide reaction, contain only the diaquo-complexes in the same isomeric ratio as the dihydroxo-complexes produced by this reaction. The isomeric ratio was determined by the usual methods from the known extinction coefficients of the pure isomers at the appropriate wavelengths. Pearson *et al.*[4] found that, when equivalent amounts of the dichloro-complex and hydroxide ions were mixed, the product contained a considerable amount of dihydroxo-product as well as an equal amount of the unchanged dichloro-complex. In view of the considerable difference in the rates of reaction of the dichloro- and monochloro-species, this seemed surprising, but, on adding the alkali rapidly to a solution of the complex, we obtained the same result. However, when the alkali was added drop by drop to a well-stirred solution of the complex at 0°, the local excess of alkali was eliminated and the first stage of the reaction could be separated from the second. The spectrum of a solution that was acidified immediately after addition of the calculated amount of alkali, then corresponded exactly to that of a mixture of *cis*- and *trans*-aquochloro-isomers, with no significant quantity of any other species that absorbed light in the region studied. In the case of the *trans*-dichloro-complex, the analysis was checked by stopping the reaction before it was complete, by means of the flow apparatus, and analysing the mixture, now containing unchanged dichloro-complex in addition to the aquochloro-isomers, by the combined titrimetric and spectrophotometric technique used in the aquation studies.[2] The results of the two methods are in complete agreement.

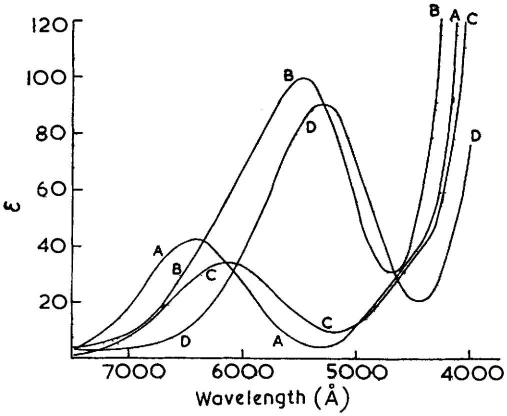

FIG. 1. Visible absorption spectra of complexes (A) *trans*-[Co en$_2$BrCl]$^+$, (B) *cis*-[Co en$_2$BrCl]$^+$, (C) *trans*-[Co en$_2$(H$_2$O)Br]$^{2+}$, and (D) *cis*-[Co en$_2$(H$_2$O)Br]$^{2+}$.

Measurement of the steric course of the reaction between hydroxide ions and the chlorobromo-complexes was greatly complicated by simultaneous release of chloride and bromide ions. When the solution that had been treated slowly with one equivalent of alkali was acidified, it contained four light-absorbing species, namely, *cis*- and *trans*-[Co en$_2$(H$_2$O)Cl]$^{2+}$ and *cis*- and *trans*-[Co en$_2$(H$_2$O)Br]$^{2+}$. The analysis was carried out as follows. The spectrum of the acidified reaction product was measured as soon as possible after acidification. The concentration of free chloride and bromide ions was calculated from the rate constants of the two simultaneous hydroxide substitutions and checked by independent experiments (see above). Then [Cl$^-$] = [Aquobromo-species], and [Br$^-$] = [Aquochloro-species]. The isomeric distribution was determined by a trial-and-error method whereby spectra were calculated on the basis of the known extinction coefficients of the pure components (Fig. 1) for various isomeric ratios within the limits of the known ratio of chloroaquo- to bromoaquo-cations. Only one combination gave a spectrum agreeing over the whole visible wavelength range with that obtained experimentally, but, because of the overlapping character of the spectra used, the figures quoted are reliable only to ±5% of the *cis*-product. The product analyses are collected in Table 2.

In the cases of the *cis*-[Co en$_2$Cl$_2$]$^+$ and the *cis*-[Co en$_2$(OH)Cl]$^+$ cation, the steric course of hydroxide substitution was studied in greater detail by using optically active complexes. The reactions with hydroxide were carried out in the same way as those involving the racemates and the optical rotation of the acidified reaction product at the sodium-D line was measured.

[4] Pearson, Meeker, and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 2675.

TABLE 2.

Isomeric composition of the products of the reaction
$[\mathrm{Co\ en_2AX}]^+ + \mathrm{OH}^- \longrightarrow [\mathrm{Co\ en_2A(OH)}]^+ + \mathrm{X}^-$
in aqueous solution at 0°.

A	X	*cis*-Product (%)	A	X	*cis*-Product (%)	A	X	*cis*-Product (%)
trans-Cl ...	Cl	5 ± 2	*trans*-OH ...	Cl	94 ± 2	*cis*-Br	Cl	40 ± 5
,, ...	Br	5 ± 5	,, ...	Br	90 ± 2	**cis*-OH ...	Cl	97 ± 2
trans-Br ...	Cl	$\not>5$	*cis*-Cl	Cl	37 ± 2	* ,, ...	Br	96 ± 2
			,, ...	Br	30 ± 5			

* Provided as the aquo-complex.

Since these measurements are made within the region of anomalous rotatory dispersion of the complex, no regular relation can be expected between the absolute configuration of the complex and the sign of the rotation. However, in the case of dichloro-, chloroaquo-, and diaquobis(ethylenediamine)cobalt(III) cations, it has been shown [5] that those enantiomorphs that have the same sign of rotation for the sodium-D line have the same relative configuration. It should be pointed out that although the sign of the rotation for this line is positive, the dichloro-complex used is referred to as the lævo-enantiomorph in order to conform to the previous usage of Werner [6] who measured the rotation at longer wavelengths, where it is negative. In order to maintain this convention, the chloroaquo- and diaquo-complexes that have positive rotations for the sodium-D line will be referred to as the lævo-forms. The data were treated in the following way:

(*A*) *l-cis*-$[\mathrm{Co\ en_2Cl_2}]^+$ cation.

cis-Product = 37%: *l-cis*-$[\mathrm{Co\ en_2(H_2O)Cl}]^{2+}$, $[M]_\mathrm{D} = +980°$;
aquochloro-product, $[M]_\mathrm{D} = +49°$.

Hydroxy-isomers formed = Final aquo-isomers: *l-cis* (confign. retd.) 21%;
d-cis (confign. invd.) 16%;
trans. 63%.

(*B*) *l-cis*-$[\mathrm{Co\ en_2(OH)Cl}]^+$ cation.

cis-Product = 97%: *l-cis*$[\mathrm{Co\ en_2(H_2O)_2}]^{3+}$, $[M]_\mathrm{D} = +100°$;
diaquo-product, $[M]_\mathrm{D} = +25°$.

Hydroxy-isomers formed = Final aquo-isomers: *l-cis* (confign. retd.) 61%;
d-cis (confign. invd.) 36%;
trans. 3%.

DISCUSSION

The second-order kinetic form of the base hydrolysis of complexes of the type $[\mathrm{Co(AA)_2AX}]^{n+}$ and $[\mathrm{Co(NH_3)_5X}]^{n+}$ where AA is a diamine chelate, A is another non-participating ligand, and X is the displaced group, has been explained by two mechanisms. One requires a single-stage bimolecular attack by a hydroxide ion on the cobalt atom ($S_\mathrm{N}2$), while the other requires a pre-equilibrium in which the hydroxide ion functions as a base that removes a proton from an amine-nitrogen atom to form a small equilibrium concentration of the amido-conjugate base which is assumed to expel group X very rapidly as a result of the labilising power of the amido-group. The latter mechanism ($S_\mathrm{N}1cb$), will give the observed kinetic form if only a small fraction of the complex is present as the conjugate base. In spite of the many experimental results available, it has been impossible to decide unequivocally which mechanism is correct. Both mechanisms require that the electron-displacing properties of group A have no large effect on the rate of the reaction. In a bimolecular process in which bond-making and bond-breaking are of equal importance, the electron displacements which assist the former hinder the latter, and *vice-versa*. In

[5] Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 476; 1937, **4**, 687.
[6] Werner, *Ber.*, 1911, **44**, 3279.

a similar way, electron-withdrawal increases the concentration of conjugate base in equilibrium with a given amount of base, but, at the same time, reduces the lability of group X.

Results for the rate and steric course are summarised in Table 3, together with the appropriate Arrhenius parameters. The study of the base hydrolysis of the chloronitrobis(ethylenediamine)cobalt(III) complexes made by Ašperger and Ingold[7] at 0° has been extended to other temperatures and other published data for the bis(ethylenediamine) cobalt(III) system are included for comparison, together with the Arrhenius parameters, when known.

On comparing the data for the complexes where X = Cl it is apparent that, with a few exceptions, the rates are not very dependent upon the nature of group A. The low rates for the complexes where A = NO_2 have been explained in terms of the strong electron-withdrawing properties of the nitro-group,[7] but the marked reduction of reactivity on changing A from *trans*-Cl (or Br) to *trans*-OH is surprising. In view of the general similarity of the rates of the other members of this series, it is difficult to explain the 5000-fold differences in rate in terms of the electron-displacing properties of group A, whichever of the two mechanisms is invoked, and it is therefore necessary to look further afield. The rate differences are due, almost entirely, to a factor of 10^4 in the *B* value, which corresponds to a difference of 19 e.u. in the entropies of activation. The activation energies collected in Table 3, which are reliable to ±0·3 kcal./mole, show no systematic relation with the nature and position of ligands A and X; nor do they appear to differ very much from one another in comparison with those for the aquation (acid hydrolysis) of the same compounds, where the extremes represent a range of 10 kcal./mole. The

TABLE 3.

Second-order rate constants, Arrhenius parameters, and products of the base hydrolysis of $[Co\ en_2AX]^{n+}$ at 0°:

$k_2 = B \exp(-E/\boldsymbol{R}T)$ (l. mole^{-1} sec.$^{-1}$)

A	X	k_2	*E* (kcal./mole)	$\log_{10} B$	*cis*-Product (%)
trans-Cl	Cl	85	23·2	20·5	5
,, ...	Br	269	24·2	21·8	5
trans-Br	Cl	110	24·9	21·9	0
trans-OH	Cl	0·017	22·8	16·4	94
,, ...	Br	0·168	23·7	18·2	90
trans-NCS[8]	Cl	0·35	23·2	18·7	76
,, [8]	Br	1·95	—	—	81
trans-NH_3[9]	Cl	1·25	—	—	76
trans-N_3[10]	Cl	0·41	—	—	13
trans-NO_2[7]	Cl	0·080	24·4	18·4	6
cis-Cl	Cl	15·1	24·6	20·8	37 (21) *
,, ...	Br	71	23·1	20·3	30
cis-Br	Cl	23	22·7	19·5	40
cis-OH	Cl	0·37	22·4	17·4	97 (61)
,, ...	Br	2·7	22·5	18·4	96
cis-NCS[8, 11]	Cl	1·40	—	—	80 (56)
cis-NH_3[9]	Cl	0·50	—	—	84 (60)
,, [9]	Br	3·3	—	—	85 (59)
cis-N_3[10]	Cl	0·17	—	—	51
cis-NO_2[7]	Cl	0·032	23·1	17·0	67 (46) †

* Figures in parentheses indicate the amount of *cis*-product with the same configuration as the starting material. † Optical activity data deduced from ref. 12.

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[7] Ašperger and Ingold, *J.*, 1956, 2862.
[8] Ingold, Nyholm, and Tobe, *J.*, 1956, 1691.
[9] Nyholm and Tobe, *J.*, 1956, 1707.
[10] Staples and Tobe, *J.*, 1960, 4803.
[11] Baldwin and Tobe, *J.*, 1960, 4275.
[12] Basolo and Pearson, " Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 233.

steric results are also difficult to explain in terms of a simple S_N2 or S_N1cb mechanism, especially for the dihalogeno-complexes.

These results lead us to propose a mechanism which retains, as its basis, a bimolecular reaction between the hydroxide ion and the complex, but is modified mainly in the way by which the reagents come together. The unique high reactivity of the hydroxide ion towards these cobaltammine complexes in aqueous solution has been explained in terms of its mobility through the solvent shell of the complex ion.[13] Any other anionic reagent would require some desolvation in order to enable the reagents to come into contact, but the hydroxide ion can pass through the solvent shell by a Grotthus proton-transfer mechanism and appear in a position suitable for substitution without occurrence of desolvation. The hydroxide ion will have a similar mobility around the complex ion, although the Grotthus chain may also include the amine protons and those on the co-ordinated hydroxide group. This mobility of the hydroxide ion about the complex may be visualised as a " sticky " collision whereby the reagents are kept together longer than is usual, even in solution, and are able to change their relative orientations. It is possible that such an association may be indistinguishable from ion-pair formation, but the introduction of that concept will not add anything to the argument. As a result of this mobility, it is possible to consider the probability of finding the hydroxide ion in a particular position; such a function represents the likelihood that a Grotthus chain terminates at the point in question and depends on the nature and the arrangement of all the ligands in the complex. In order to explain the rates and steric courses of these reactions it is necessary to combine this function with another, representing the probability that an attack from the point in question results in replacement.

Two postulates have been made in order to assess these probabilities. First, that the probability of finding the hydroxide ion in a particular place about the complex will be greatest in the regions experiencing the most positive charge (or least negative charge). This appears logical on electrostatic grounds and also from the point of view that, in a Grotthus chain, the hydroxide ion will always have a bias to move in the direction of highest positive charge, this being the path of increasing polarisation of the participating water molecules. The second postulate is that attack adjacent to the outgoing group is easier than attack remote from it, on the grounds that (*a*) the strong near-neighbour interaction between the incoming $OH^{\delta-}$ and the outgoing $X^{\delta-}$ will assist reaction, and (*b*) there is least disturbance to the other five ligands and the surrounding solvent shell.

In applying these principles to the individual complexes it is convenient to discuss the *cis*- and *trans*-isomers separately and to start with the *trans*-dichloro-complex. In this case groups A and X are identical and lie on an axis of symmetry of the complex ion. If the attack by the hydroxide ion is bimolecular, the hydroxide ion, on commencing its bonding, will always be adjacent to one chlorine and opposite to the other, and the departing chlorine will be the one most labilised by the hydroxide. This replacement will have a steric course that differs from that involving complexes with only one labile group because these allow a distinction to be made between attack from the front and from the back. If, on the other hand, the mechanism involves dissociation of the conjugate base, the position of re-entry is controlled by the remaining chlorine only, and the steric course should not differ fundamentally from those of the other complexes of the type $[\text{Co en}_2\text{ACl}]^{n+}$; this, second consideration applies equally to both *cis*- and *trans*-isomers. The very unusual steric courses for the dichloro-complexes are thus more compatible with a bimolecular than a unimolecular mechanism. The steric course of substitution for the *trans*-dichloro-isomer indicates that the chlorine displaced is nearly always that adjacent to the incoming hydroxide ion; this is in accord with the second of the above postulates. The similar behaviour of the *trans*-chlorobromo-complex supports this idea since, although either ligand can be displaced, the products are almost entirely *trans*.

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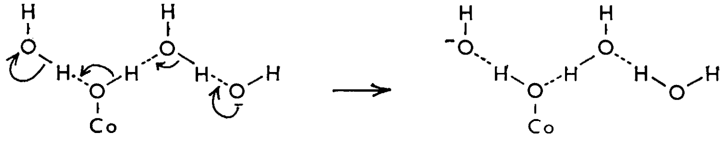
[13] Tobe, *Sci. Progr.*, 1960, **48**, 485.

The fast reaction of the *trans*-dihalogeno-complexes is due, at least in part, to the absence of other sites, attractive to the hydroxide ion, that would reduce the probability of finding this reagent adjacent to a labile ligand. These complexes are two of the very few examples where there is a large probability that the hydroxide ion will be in a position of high reactivity.

In the second series of *trans*-complexes to be considered, the group A is NCS, NH_3, or OH. Here the probability of finding the hydroxide ion in the vicinity of ligand A is much greater than that of finding it in the vicinity of ligand X. When A = NH_3 or NCS the attraction comes from the residual positive charge, *e.g.*, $-\mathrm{NH_3}^{\delta+}$ or $^{-}\overset{+}{\mathrm{N}}{\equiv}\mathrm{C}{\cdot}\overset{-}{\mathrm{S}}$ (one of the two canonical forms). The hydroxyl group owes its apparent attraction to the presence of one or more solvent molecules bound strongly to it by hydrogen bonds. These form part of a Grotthus chain which also includes the co-ordinated hydroxyl group, which participates as a result of its residual basicity. In this group of complexes much of the attack takes place adjacent to ligand A and opposite to ligand X, resulting in a mainly *cis*-product formed at a slower rate. When group A is OH, the probability of finding the reagent adjacent to it appears to be greatest since the product is almost entirely the *cis*-isomer. The unusually slow rate may be due to the hydroxide ion's being held away from the cobalt.



The case where A = NO_2 requires special consideration. Here, the probability of finding the hydroxide ion near the nitro-group is high, but the reaction from this position is hindered by the feed-back of electrons into the ligand as the reaction proceeds.[7] This leads to major attack adjacent to X, but since the probability of finding the hydroxide ion there is small the rate is slow. The case where A = N_3 is intermediate in that the probability of finding the hydroxide ion near the azide group is less than that of finding it near a nitro-group.

cis-Complexes differ from their *trans*-isomers in their lower symmetry. The four amine-nitrogen atoms no longer occupy equivalent positions relative to ligands A and X, and the stereochemical consequences of attack at various positions of the complex are therefore more complicated.[14] Two new types of location are present in a *cis*-isomer that are not found in the *trans*-form, namely, that adjacent to ligands A and X (faces 1,A,X and 2,A,X in Fig. 2) and that remote from ligands A and X (faces 1,3,4 and 2,3,4 in Fig. 2). That remote from both A and X is a favourable location when both these ligands repel the hydroxide ion, *e.g.*, in the dihalogeno-complexes. When group A has some attraction for the hydroxide ion, *e.g.*, is NH_3, NCS, OH, NO_2, or N_3, there must be competition between 1,3,4 and 2,3,4 on the one hand and 1,3,A and 2,3,A on the other.

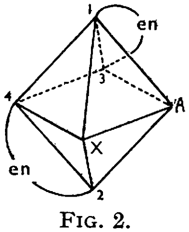


FIG. 2.

Applying these remarks to the complexes studied we would expect to find that, when A = Cl or Br, attack occurs mainly from faces 1,3,4 and 2,3,4. If one uses the hypothesis of edge displacement [14] to predict the steric consequences of the attack, entry from these positions should produce *trans*- and inverted *cis*-products in the statistical ratio 2 : 1. Attack from all other faces will be adjacent to at least one labile ligand, whose displacement results in a *cis*-product with retained configuration owing to substitution without rearrangement. The unusually large amount of *trans*-product is thus accounted for.

When group A is NH_3, NCS, or OH, a considerable amount of the attack is at faces

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[14] Brown, Ingold, and Nyholm, *J.*, 1953, 2674.

1,3,B and 2,3,B. The stereochemical consequences of these attacks are the formation, in the statistical ratio of 1 : 2, of the *cis*-product with inverted configuration and the *cis*-product with retained configuration resulting from edge-displacement of ligand A. The amount of *trans*-product will be greatly decreased, but there will be a concomitant increase in the amount of *cis*-product with a retained configuration. The difference in the behaviour of complexes where A = OH, on the one hand, and A = NH_3 or NCS, on the other, arises from the greater apparent attractive power of the hydroxyl ligand, which causes the attack from faces 1,3,4 and 2,3,4, which was minor but significant in the latter complexes, to be almost negligible in the former.

When group A is NO_2 or N_3, the probability of finding the reagent adjacent to this ligand is high. However, as was explained for the corresponding *trans*-isomers, attack is difficult from this position. The attack therefore comes from faces 1,3,4 and 2,3,4, giving *trans*- and inverted *cis*-products, and from faces X,1,4 and X,2,4, which give a *cis*-product with a retained configuration.

Work is in progress in order to obtain data over a wider range of groups A and X, so that this hypothesis can be tested more thoroughly.

EXPERIMENTAL

Preparations.—The salts, *trans*-[Co en_2Cl_2]Cl, *trans*-[Co en_2(OH)Cl]Cl,H_2O, *cis*-[Co en_2Cl_2]Cl,H_2O, and *cis*-[Co $en_2(H_2O)Cl]SO_4,1\frac{1}{2}H_2O$, were from the batches whose preparation and analyses were reported previously.[2]

trans-Bromochlorobis(ethylenediamine)cobalt(III) perchlorate was prepared by a method similar to that used by Werner [15] for the nitrate, perchloric acid being used as precipitant instead of ammonium nitrate. The salt was purified by dissolving it (2 g.) in water (200 ml.), filtering the solution rapidly, and adding solid sodium perchlorate to the filtrate {Found: Co, 14·8; Br, 20·4; Cl, 8·9. Calc. for $[Co(C_2H_8N_2)_2BrCl]ClO_4$: Co, 14·9; Br, 20·3; Cl, 9·0%}.

cis-Bromochlorobis(ethylenediamine)cobalt(III) nitrate was prepared by Werner's method,[15] by treating a cold saturated solution of the bromide with solid ammonium nitrate. It was purified by dissolving 9 g. in water (200 ml.) at room temperature and adding solid ammonium nitrate to the rapidly filtered solution {Found: Co, 16·4; Br, 22·5; Cl, 9·8. Calc. for $[Co(C_2H_8N_2)_2BrCl]NO_3$: Co, 16·4; Br, 22·4; Cl, 9·95%}.

trans-*Hydroxobromobis*(*ethylenediamine*)*cobalt*(III) *bromide* The bromide, *trans*-[Co en_2Br_2]Br (18 g.), was powdered and cooled in ice and to this was added, with stirring, a mixture of diethylamine (3·6 g.) and ice (13 g.). After 10 min. at 0°, the solid was filtered off and was washed successively with 7 : 3 v/v ethanol–water, ethanol, and ether. The crude product (10 g.) was placed on a sintered-glass funnel fitted to a Buchner flask that contained ethanol (100 ml.) cooled to 0° and surrounded by an ice-bath. Ice-cold water (40 ml.) was poured on to the solid which dissolved and, as suction was applied, passed through the filter and immediately crystallised when the solution met the ethanol. The crystals were filtered off as soon as possible, washed with ethanol and ether, and air-dried {Found: Co, 15·6; Br^-, 21·4; co-ordinated Br, 21·4. Calc. for $[Co(C_2H_8N_2)_2Br(OH)]Br,H_2O$: Co, 15·7; Br^-, 21·4; co-ordinated Br, 21·4%}.

cis-Aquobromobis(ethylenediamine)cobalt(III) bromide was prepared and purified from *trans*-[Co en_2Br_2]Br by Werner's method [16] {Found: Co, 12·9; Br^-, 34·8; co-ordinated Br, 17·4. Calc. for $[Co(C_2H_8N_2)_2(H_2O)Br]Br_2,H_2O$: Co, 13·0; Br^-, 35·1; co-ordinated Br, 17·6%}.

trans-Chloronitrobis(ethylenediamine)cobalt(III) nitrate was prepared and purified by Werner's method [17] {Found: Co, 18·2; co-ordinated Cl ,10·9; Cl^-, 0. Calc. for $[Co(C_2H_8N_2)_2(NO_2)Cl]NO_3$: Co, 18·2; co-ordinated Cl, 11·0%}.

cis-Chloronitrobis(ethylenediamine)cobalt(III) chloride was prepared and purified by Werner and Gerb's method [18] {Found: Co, 19·8; Cl^-, 11·9; co-ordinated Cl, 11·9. Calc. for $[Co(C_2H_8N_2)_2(NO_2)Cl]Cl$: Co, 19·9; Cl^-, 12·0; co-ordinated Cl, 12·0%}.

[15] Werner, *Annalen*, 1912, **386**, 118.
[16] Werner, *Annalen*, 1912, **386**, 127.
[17] Werner, *Ber.*, 1901, **34**, 1734.
[18] Werner and Gerb, *Ber.*, 1901, **34**, 1739.

l-cis-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared from the racemate through the (+)-α-bromocamphor-π-sulphonate.[19] Repetition of the resolution did not increase $[M]_D = 2190°$.

l-cis-Aquochlorobis(ethylenediamine)cobalt(III) bromide, prepared from the racemate through the (+)-α-bromocamphor-π-sulphonate by Fischlin's method,[20] had $[M]_D + 980°$.

Kinetics.—The following method was used for the slower reactions. Appropriate amounts of the complex and aqueous sodium hydroxide solution of the desired concentration were brought to reaction temperature in separate flasks. The alkali solution was then poured on the solid, which dissolved immediately. This time was taken as zero and samples were withdrawn from time to time with a fast-running pipette and delivered into cooled vessels containing an excess of nitric acid. The " killed " solutions were then passed down a column containing Amberlite IR-120 resin (H^+ form). The effluents contained the anionic components together with an equivalent amount of hydrogen ions, and the halide-ion concentrations were determined by Volhard's method when only one type was present, or by potentiometric titration when chloride and bromide were present together. This method of sampling became inaccurate for reactions whose first half-life was less than 45 sec., and a fast sampling apparatus was used for some of these. This was essentially a thermostat-controlled, fast-running, automatic sampling pipette. The aliquot portion, measured by the volume between a capillary tip and the tap, was removed and delivered by compressed air. The limit of this apparatus was reached with reactions whose first half-life was less than 15 sec., and a flow method was developed to study the fastest reactions. This apparatus consisted of two thermostat-controlled reservoirs which could be connected, by turning a three-way tap, to a thermostat-controlled tube, 3 mm. in diameter. Equal volumes of solutions of complex and of alkali (5·00 or 10·00 ml.) were placed in the reservoirs and, when thermal equilibrium was established, the tap was opened and the solutions forced, by compressed air, into the reaction tube. Experiment indicated that mixing was complete within the tap and the reagents reacted while passing along the tube; on emerging from the other end, they were run into an excess of nitric acid which immediately stopped the reaction.

It was possible to measure the time interval (T) between the opening of the tap and the completion of the flow, the volume of each of the reagent solutions (V), and the volume (v) of the reaction tube. In order to measure the rate of the reaction it was necessary to know the actual time of reaction, τ, which is related to the other quantities by the expression,

$$\tau = \left(\frac{v}{2V + v} + \phi\right) T = mT,$$

where ϕ is a term arising from the volume of mixing within the tap, the volume within which the reaction is stopped, and other indeterminable causes. The time T depends on the applied pressure (p), and the first step in the calibration of the apparatus was the construction of a p–T curve, for each of the reaction tubes, so that it was possible, when the runs were made, to select a particular value for T by pre-setting the applied pressure.

The calibration of the apparatus, which was, effectively, the determination of m for each of the three tubes, was made at 25·4°. Runs were carried out in the apparatus for reactions of a similar nature to those under examination and having known, independently measured, rate constants. The " killed " solutions were analysed as described above, and T was plotted against $\log_{10}(a - x)$, when $[OH^-] \gg [\text{Complex}]$ or against $1/(a - x)$ when $[OH^-] = [\text{Complex}]$ (a and x have the significance given in Table 1). In all cases a straight line was obtained, indicating that m, and therefore ϕ, was independent of pressure over the range studied. The slopes of these plots are related to the second-order rate constants, k_2, by the expressions, $k_2 = 2{\cdot}303(\text{slope})/m[OH^-]$, when $[OH^-] \gg [\text{Complex}]$, or by $k_2 = \text{slope}/m$ when $[OH^-] = [\text{Complex}]$; thence m can be calculated. It was found that the correction ϕ was negligible for all but the smallest tube. The long and the medium tube ($v = 5{\cdot}47$ and $2{\cdot}55$ ml., respectively) were calibrated for the reaction between hydroxide and *cis*-$[\text{Co en}_2(\text{OH})\text{Cl}]^+$ (k_2, determined with the fast sampling apparatus, $= 13{\cdot}8$ l. mole^{-1} sec.$^{-1}$); the short tube ($v = 0{\cdot}14$ ml.) was calibrated for the reaction between hydroxide and *trans*-$[\text{Co en}_2\text{Cl}_2]^+$ (k_2, determined with the flow apparatus and the medium-length calibrated tube, $= 3{\cdot}16 \times 10^3$ l. mole^{-1} sec.$^{-1}$).

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[19] Bailar and Rollinson, *Inorg. Synth.*, 1946, **2**, 224.

[20] Fischlin, Diss., Zürich, 1919.

Identical procedures were used to determine the unknown rate constants, m being treated as the known and k_2 as the unknown constant.

Spectrophotometric measurements were made with a Unicam S.P. 500 quartz spectrophotometer and silica cells. Thermostats were accurate to ±0·05° but temperature control was less reliable for the fastest reactions.

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William Ramsay and Ralph Forster Laboratories,
University College, Gower Street,
London, W.C.1.

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