907. *The Mechanism and Steric Course of Octahedral Aquation. Part IV.*[1] *The Aquation of* cis- *and* trans-*Dichloro- and* cis- *and* trans-*Chlorohydroxo-bis(ethylenediamine)cobalt*(III) *Salts.*

By M. E. Baldwin, S. C. Chan, and M. L. Tobe.

The rate constants of the solvolytic aquation of the *cis*- and *trans*-$[Co\ en_2Cl_2]^+$ and *cis*- and *trans*-$[Co\ en_2OHCl]^+$ cations have been determined over a range of temperature and the Arrhenius parameters calculated. The products of these reactions, $[Co\ en_2H_2OCl]^{2+}$ and $[Co\ en_2OH,H_2O]^{2+}$, isomerise to equilibrium mixtures at rates comparable with those of their formation. The rates of isomerisation and the positions of equilibrium are reported. When corrections are made for the isomerisation of the product, it is found that *trans*-$[Co\ en_2Cl_2]^+$ and *trans*-$[Co\ en_2OHCl]^+$ yield 35% and 75%, respectively, of the *cis*-aquo-product directly, whereas both the *cis*-isomers yield only *cis*-product.

THE dependence of the rates of aquation of complex ions of the type $[Co\ en_2ACl]^{n+}$ (where en = ethylenediamine) on the nature of the non-participating ligand A, has led to the postulation of two mechanisms for the process, a unimolecular (S_N1) mechanism when A = OH, Cl, N_3, or NCS, and a bimolecular (S_N2) mechanism when A = OH_2, NH_3, or NO_2.[2,3] Previous investigations of the steric course of aquation of the *trans*-isomers showed that the bimolecular aquations (A = NH_3 [4] or NO_2 [2]) lead to no steric change, whereas two unimolecular aquations (A = N_3 [1] or NCS [5]), result in considerable steric

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[1] Part III, Staples and Tobe, *J.*, 1960, 4803.

[2] Ašperger and Ingold, *J.*, 1956, 2862.

[3] Basolo and Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958, p. 166.

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

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

change. The work presented in this paper shows that in the other two cases where unimolecular aquation is expected (A = OH or Cl) the *trans*-isomer yields a considerable amount of *cis*-aquo-product.

(1) *The Isomerisation of* cis- *and* trans-*Aquochlorobis(ethylenediamine)cobalt*(III) *Salts*.—The colour of a freshly prepared acidified aqueous solution of *trans*-[Co $en_2H_2OCl]Cl_2$ slowly changes from green to violet at room temperature although the amount of free chloride ions in solution does not change. A study of the changes that take place in the spectrum of an acidified aqueous solution of the *trans*-isomer showed (Fig. 1) that the colour change is due to the isomerisation,

$$cis\text{-}[\mathrm{Co\ en_2ClH_2O}]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[\mathrm{Co\ en_2H_2OCl}]^{2+}$$

The specific rate constant, $(k_1 + k_{-1})$, for approach to equilibrium was determined spectrophotometrically by following the change of optical density at 520 mμ where there was a maximum difference between the extinction coefficients of the two isomers. The change obeyed a first-order rate law, the rate constant being obtained from the slope of the semilogarithmic plot of $\log_{10} (D_\infty - D_t)$ against time, where D_∞ was the optical density determined after ten half-lives. Provided that the solution was sufficiently acidic (0·01N-nitric acid), the subsequent replacement of co-ordinated chlorine did not interfere. The results are collected in Table 1 where it will be seen that the values obtained for $(k_1 + k_{-1})$ at 25° are the same whether equilibrium is approached from the *trans*- or the *cis*-side. Since equilibrium lies closer to the *cis*-side most of the data are derived from solutions originally containing the *trans*-isomer. The position of equilibrium does not change significantly between 0° and 40°, indicating that the activation energies of the *trans* to *cis*, and the *cis* to *trans*, change must be similar.

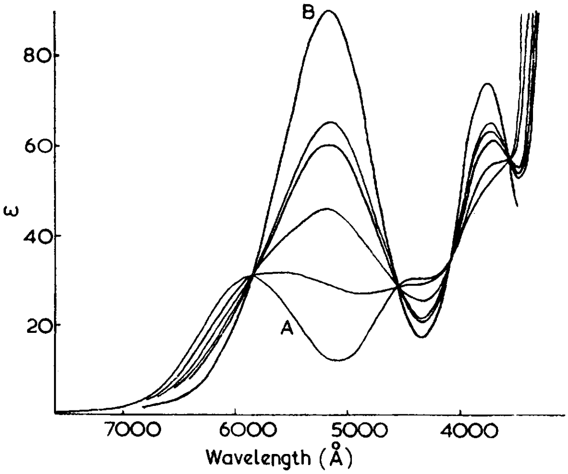

FIG. 1. Change in the spectrum of an acidified solution of *trans*-[Co $en_2OHCl]Cl,H_2O$.

A = *trans*-[Co $en_2H_2OCl]^{2+}$.
B = *cis*-[Co $en_2H_2OCl]SO_4$.

Intermediate curves, read upwards from A, are for 60, 143, 301 and 395 min., respectively, at 25°.

(2) *Isomerisation of* cis- *and* trans-*Hydroxoaquobis(ethylenediamine)cobalt*(III) *Cations*.—Kruse and Taube [6] recently studied the relation between the isomerisation and the water exchange of these isomers. Anticipating difficulties due to the acid–base relationship between the diaquo-, hydroxoaquo-, and dihydroxo-cations they studied the isomerisation of a self-buffered mixture of the diaquo- and hydroxoaquo-complexes where the major path of isomerisation was through the latter. The results are in very good agreement with this work when corrections are made for the difference in temperature.

We have found that the anticipated difficulties do not arise and that the solvolytic

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

disturbance due to dissolving the appropriate hydroxoaquo-complex in carbon dioxide-free water affects the rates of isomerisation less than the experimental error does. Although it is possible to measure the rate of isomerisation by studying the light-absorption changes of a solution of the hydroxoaquo-complex, it was found more convenient to take, and then acidify, samples of the reaction mixture, converting the labile hydroxoaquo-species into the relatively inert diaquo-species, which could then be examined spectrophotometrically. The specific rate constants for the approach to equilibrium ($k_1 + k_{-1}$) were determined in the usual way from the change in optical density of the acidified samples measured at 490 mμ and are given in Table 2, together with the isomeric composition at equilibrium. The value obtained by direct measurement (59% of *cis*) is in very good agreement with that calculated by Bjerrum and Rasmussen [7] from the equilibrium data for the diaquo-, hydroxoaquo-, and dihydroxo-bis(ethylenediamine)cobalt(III) cations (58·6% of *cis*).

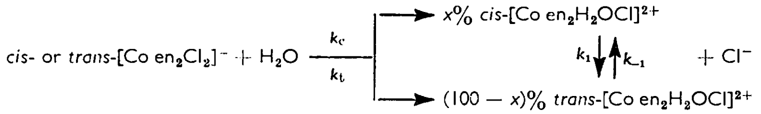
TABLE 1.

Isomerisation of the aquochlorobis(ethylenediamine)cobalt(III) cations in aqueous nitric acid (0·01N).

The *trans*-isomer was supplied as *trans*-[Co $en_2OHCl]Cl,H_2O$ which was converted instantly into the aquo-complex on dissolving in acid. The *cis*-isomer was supplied as *cis*-[Co $en_2H_2OCl]SO_4,1{\cdot}5H_2O$.

Temp.	Initial confign.	Initial [Complex] (mmole/l.)	($k_1 + k_{-1}$) × 10^4 (sec.$^{-1}$)	*cis*-Isomer (%) at equil.	Temp.	Initial confign.	Initial [Complex] (mmole/l.)	($k_1 + k_{-1}$) × 10^4 (sec.$^{-1}$)	*cis*-Isomer (%) at equil.
0·0°	*trans*	4·02	0·0162	73	35·0°	*trans*	4·04	4·4	74
,,	,,	5·08	0·0161	74	,,	,,	5·08	4·4	74
,,	,,	6·00	0·0161	73	,,	,,	6·07	4·3	74
,,	,,	7·04	0·0158	73	,,	,,	6·92	4·3	74
25·0	,,	4·00	0·97	73	40·1	,,	4·04	8·7	73
,,	,,	4·95	0·96	73	,,	,,	5·12	8·7	73
,,	,,	6·01	0·97	73	,,	,,	6·04	8·7	73
,,	,,	6·97	0·96	73	,,	,,	6·99	8·8	73
,,	*cis*	4·10	0·94	73					
,,	,,	5·04	0·95	74					
,,	,,	6·07	0·95	73					
,,	,,	7·06	0·96	73					

(3) *The Steric Course of Aquation of* cis- *and* trans-*Dichlorobis*(*ethylenediamine*)*cobalt*(III) *Salts*.—



The kinetics of these reactions have been thoroughly examined in the past and are repeated here only as far as is necessary to elucidate the steric course of the processes. The rates of aquation at 25° determined titrimetrically in 0·01N-nitric acid agree with those published by Mathieu [8] and Basolo *et al.*[9] The steric course of aquation of the *cis*-dichloro-complex has been determined by Mathieu [10] who studied the mutarotation of the optically active complex and showed that the product, when first formed, had the same specific molecular rotation as an independently resolved specimen of *cis*-[Co $en_2H_2OCl]^{2+}$. The spectrophotometric analysis described below confirms that no *trans*-product is initially formed.

The rate constant for the isomerisation of the product is about three times that for aquation of the *trans*-dichloro-isomer and about one-half of that of the *cis*. In neither case

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[7] Bjerrum and Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265.

[8] Mathieu, *Bull. Soc. chim. France*, 1936, **3**, (*a*) 2121, (*b*) 2152.

[9] Basolo, Boston, and Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 3089.

[10] Mathieu, *Bull. Soc. chim. France*, 1937, **4**, 687.

can the steric course be determined by analysing the solution when the aquation is complete since the composition will be controlled by the isomerisation equilibrium. However, by measuring the composition of the product at various stages of the reaction it was not difficult to correct for the isomerisation. In both cases, the composition of the product, expressed as % of *cis*-product, was plotted against % of reaction completed, and the extrapolation of these curves back to zero reaction gave the composition of the product as formed by aquation. These data are plotted in Fig. 2, where the extrapolations are guided by functions of the correct form.[11]

TABLE 2.

Isomerisation of *trans*-aquohydroxobis(ethylenediamine)cobalt(III) perchlorate in aqueous solution.

Temperature = 0·0°			Temperature = 10·2°		
Initial [Complex] (mmole/l.)	$(k_1 + k_{-1})$ $\times 10^5$ (sec.$^{-1}$)	*cis* (%) at equil.	Initial [Complex] (mmole/l.)	$(k_1 + k_{-1})$ $\times 10^5$ (sec.$^{-1}$)	*cis* (%) at equil.
6·07	6·6	59	6·03	42	59
6·08 *	6·6	59	7·02	42	59
7·05	6·6	59	8·08	42	59
8·00	6·6	59	9·07	42	59
9·08	6·6	59			

* Starting with *cis*-[Co $en_2OH,H_2O]Br_2,H_2O$.

A complete spectrophotometric analysis of the three components of the reaction mixture was not possible in either case since the spectra of the *trans*-dichloro- and *trans*-aquochloro-cations are too similar, as are the spectra of the *cis*-dichloro- and *cis*-aquochloro-cations. The problem was solved by a combined spectrophotometric and titrimetric technique. Two samples were withdrawn from the reaction mixture within a short time of one another and frozen. The ionic chloride content of the first sample was determined by titration and the optical density of the second sample was determined at an appropriate wavelength. The chloride titre afforded the total amount of aquo-complex present, and the apparent molar extinction coefficient the concentration of one of the two aquochloro-isomers. When the *trans*-dichloro-isomer was studied the optical density was measured at 490 mμ where the extinction coefficients of the *trans*-dichloro- and *trans*-chloroaquo-cations are equal (14·1) and very different from that of the *cis*-chloroaquo-cation (72·2). When the *cis*-dichloro-isomer was studied optical densities were measured at 525 mμ where $\varepsilon(cis\text{-}Cl_2) = \varepsilon(cis\text{-}H_2OCl) = 89{\cdot}2$, and $\varepsilon(trans\text{-}H_2OCl) = 13{\cdot}2$. These results were used to determine the rate constants and also to calculate the quantities required for Fig. 2. The constants used to guide the extrapolations of the product composition back to zero reaction were:

$$k_c = 2{\cdot}44 \times 10^{-4}\ \text{sec.}^{-1};\ k_t = 3{\cdot}53 \times 10^{-5}\ \text{sec.}^{-1};$$
$$k_1 + k_{-1} = 9{\cdot}57 \times 10^{-5}\ \text{sec.}^{-1};\ \text{and}\ k_1/k_{-1} = 0{\cdot}36.$$

Measurements were made at 25·0°.

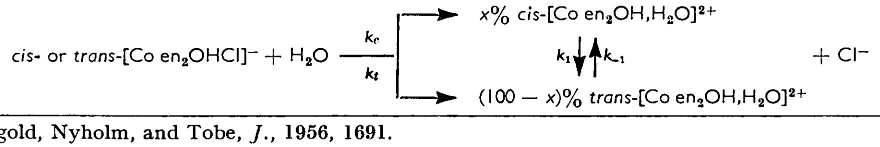
It will be seen from Fig. 2 that

$$trans\text{-}[\mathrm{Co\ en_2Cl_2}]^+ + \mathrm{H_2O} \longrightarrow \left.\begin{array}{l}35\%\ cis\\ 65\%\ trans\end{array}\right\}[\mathrm{Co\ en_2H_2OCl}]^{2+} + \mathrm{Cl}^-$$

and

$$cis\text{-}[\mathrm{Co\ en_2Cl_2}]^+ + \mathrm{H_2O} \longrightarrow 100\%\ cis\text{-}[\mathrm{Co\ en_2H_2OCl}]^{2+} + \mathrm{Cl}^-$$

(4) *The Aquation of* cis- *and* trans-*Chlorohydroxobis(ethylenediamine)cobalt*(III) *Salts.*—



$$cis\text{- or } trans\text{-}[\mathrm{Co\ en_2OHCl}]^- + \mathrm{H_2O} \begin{array}{c}\xrightarrow{k_c}\\ \xrightarrow[k_t]{}\end{array} \begin{array}{c} x\%\ cis\text{-}[\mathrm{Co\ en_2OH,H_2O}]^{2+}\\ k_1\downarrow\uparrow k_{-1}\\ (100 - x)\%\ trans\text{-}[\mathrm{Co\ en_2OH,H_2O}]^{2+}\end{array} + \mathrm{Cl}^-$$

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[11] Ingold, Nyholm, and Tobe, *J.*, 1956, 1691.

(4a) *Kinetics.* The rates of aquation of both these isomers have been determined at 25° by Basolo *et al.*[12] who studied the rate of release of co-ordinated chloride from a mixture of both isomers together with some *trans*-dichloro- and *cis*- and *trans*-dihydroxo-complex. The rate constants quoted agree well with those found in this work with pure complexes. We followed the progress of the reaction by titrating the ionic chloride released or by measuring the change in the conductivity. Both our methods gave similar rate constants and, at the higher temperatures where the reaction is too fast for accurate sampling, only the conductivity method was used. Attempts to prepare a pure sample of *cis*-[Co en$_2$OHCl]Br were unsuccessful and the product was always contaminated with up to 50% of *cis*-Co en$_2$OH,H$_2$O]Br; recrystallisation only served to increase the amount of the latter salt.

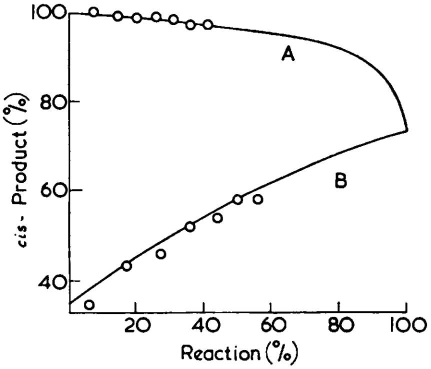

FIG. 2. Product analyses during the aquation of (A) *cis*- and (B) *trans*-[Co en$_2$Cl$_2$]Cl at 25·0°.

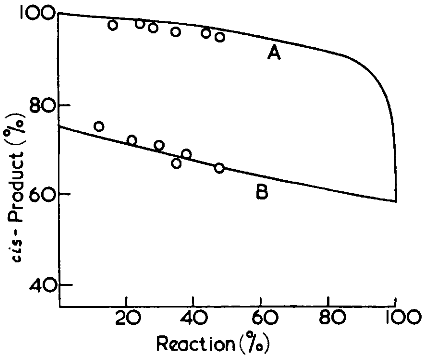

FIG. 3. Product analyses during the aquation of (A) *cis*- and (B) *trans*-[Co en$_2$OHCl]$^+$ at 0°.

Although the impure complex could be used to determine the rate of aquation it was useless for determination of the steric course and so the *cis*-chlorohydroxo-complex was prepared *in situ* by adding about 4% less than the calculated amount of alkali to a solution of *cis*-[Co en$_2$H$_2$OCl]SO$_4$. The titrimetric rate constants were determined from the semi-logarithmic plots of $\log_{10}(V_\infty - V_t)$ against time, where V_t and V_∞ are the titres of silver nitrate at time t and after ten half-lives respectively. The experimental " infinity " corresponds almost exactly to the titre expected if the remaining aquochloro-complex did not aquate under the experimental conditions. The conductimetric rate constants were computed from the conductivity data in an analogous way. The rate constants, determined over a range of temperature, are given in Table 3. Values obtained by other workers are included for comparison.

(4b) *Steric course.* Owing to the rapid isomerisation of the products, it was necessary, once again, to analyse the reaction mixture during the reaction and apply corrections for the isomerisation. The samples were acidified before measurement so that the labile hydroxo-complexes were converted into the relatively inert aquo-complexes. The relation between the spectra of the chloroaquo- and the diaquo-complex is very similar to that between the dichloro- and the chloroaquo-species, so that a complete spectrophotometric analysis was not feasible. By combining chloride analyses with optical-density measurements it was possible to calculate " % of reaction " and " % of *cis*-product." The *cis*-chloroaquo-complex was studied at **496** mμ where the molar extinction coefficients of the *cis*-chloroaquo-, the *cis*-diaquo-, and the *trans*-diaquo-complex are 77·0, 77·0, and 18·7, respectively: and the *trans*-chloroaquo-complex was studied at 470 mμ where the molar extinction coefficients of the *trans*-chloroaquo-, the *cis*-diaquo-, and the *trans*-diaquo-complex are 23·3, 65·2, and 24·1, respectively. The values derived from results obtained

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[12] Basolo, Meeker, and Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 2673.

TABLE 3.

First-order rate constants for the aquation of *cis*- and *trans*-chlorohydroxobis-(ethylenediamine)cobalt(III) salts in aqueous solution.

Temp.	Initial [Aquo-complex] (mmole/l.)	Added [Alkali] (mmole/l.)	10^4k (sec.$^{-1}$)	Method *
	cis-$[Co\ en_2OHCl]^+$			
0·0°	7·38	7·00	3·12	T
,,	8·42	8·00	3·13	T
,,	9·37	9·00	3·13	T
,,	10·41	10·00	3·14	T
,,	7·18	6·80	2·97	C
,,	8·24	8·00	3·01	C
,,	9·31	9·00	3·00	C
,,	10·38	10·00	3·02	C
10·2	7·44	7·00	15·9	T
,,	8·49	8·00	15·8	T
,,	9·39	9·00	15·7	T
,,	10·44	10·00	15·8	T
23·75	7·41	7·00	98	C
,,	8·50	8·00	100	C
,,	9·38	9·00	102	C
,,	10·43	10·00	101	C

Temp.	Initial [Complex] (mmole/l.)	10^4k (sec.$^{-1}$)	Method *
	trans-$[Co\ en_2OHCl]^+$		
0·0°	4·50	0·315	T
18·8	3·42	5·64	C
25·0	3·72	16·5	C
,,	6·20	15·9	T
31·6	12·6	43·5	C

* T = titrimetric; C = conductimetric.

Basolo, Meeker, and Pearson [12] report the values $1·3 \times 10^{-2}$ and $1·4 \times 10^{-3}$ sec.$^{-1}$ for the *cis*- and the *trans*-isomer, respectively, at 25°.

from neutral solutions at 0° are plotted in Fig. 3. The extrapolations were guided by the appropriate functions, with the following values:

$$k_c = 3·07 \times 10^{-4}\ \text{sec.}^{-1};\ k_t = 3·14 \times 10^{-5}\ \text{sec.}^{-1};$$
$$k_1 + k_{-1} = 6·59 \times 10^{-5}\ \text{sec.}^{-1};\ \text{and}\ k_1/k_{-1} = 0·698.$$

It was found that

$$trans\text{-}[Co\ en_2OHCl]^+ + H_2O \longrightarrow \left.\begin{matrix}75\%\ cis\text{-}\\25\%\ trans\text{-}\end{matrix}\right\}[Co\ en_2OH,H_2O]^{2+} + Cl^-$$

$$cis\text{-}[Co\ en_2OHCl]^+ + H_2O \longrightarrow 100\%\ cis\text{-}[Co\ en_2OH,H_2O]^{2+} + Cl^-$$

(5) *Summary and Discussion.*—The results reported above are collected in Table 4.

TABLE 4.

Rates, Arrhenius parameters and products of the aquation of dichloro- and chlorohydroxo-bis(ethylenediamine)cobalt(III) complexes in aqueous solution

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

Group A	k at 25° (sec.$^{-1}$)	E (kcal./mole)	$\log_{10} B$	*cis*-Product (%)
(*a*) *cis*- or *trans*-$[Co\ en_2ACl]^+ + H_2O \longrightarrow$ *cis*- and *trans*-$Co\ en_2AH_2O]^{2+} + Cl^-$				
cis-Cl	$2·44 \times 10^{-4}$	22·2 [8b]	12·5	100
trans-Cl	$3·53 \times 10^{-5}$	24·2 [8b]	13·0	35
cis-OH	$1·2 \times 10^{-2}$ *	23·1	15·0	100
trans-OH	$1·6 \times 10^{-3}$	26·2	16·4	75
(*b*) *cis*-$[Co\ en_2AH_2O]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ *trans*-$[Co\ en_2AH_2O]^{2+}$				
Cl	$9·5 \times 10^{-5}$	27·2	15·9	73 (equil.)
OH	$5·0 \times 10^{-3}$ *	28·1	18·2	59 ,,

* Extrapolated values.

In a previous publication,[13] the relation between the polar effects of the non-participating ligands, the mechanism of the aquation reaction, and the orientation of the substitution was discussed. In those aquations to which a unimolecular mechanism has been assigned there is always a path whereby a suitably placed lone pair of electrons on a non-participating ligand can conjugate with the metal and assist the dissociation of the leaving group. The stereochemical requirement of this electromeric effect is that the two conjugating orbitals be non-orthogonal, a situation which can only be achieved without alteration of the bond angles of the remaining ligands when the two groups are *cis*. A ligand *trans* to the dissociating group cannot develop the electromeric effect without some change in geometry, with a result that the entry of water into the " cobaltium ion " intermediate may lead to a product whose configuration differs from that of the starting compound.

These conclusions are supported by experimental fact, since all the *cis*-isomers studied are aquated with complete retention of configuration, whereas every *trans*-$[\mathrm{Co\ en_2AX}]^{n+}$ complex to which a unimolecular mechanism for aquation has been assigned on other grounds is aquated with extensive change of configuration. Although the concept of a positive electromeric ($+E$) effect assisting the unimolecular dissociation predicts steric change when a *trans*-isomer reacts, it does not allow an estimate to be made of its extent.

For the *trans*-complexes of the type $[\mathrm{Co\ en_2ACl}]^{n+}$ the labilising effect (and possibly the $+E$ effect) of ligand A decreases along the series OH $>$ N_3 $>$ Cl $>$ NCS, whereas the amounts of steric change observed are 75%, 20%,[1] 35%, and >50%,[5] respectively. There appears to be no correlation between the labilising effect and the amount of steric change, nor should this be expected since it should be realised that, once the relative positions of the five remaining ligands are changed in forming the " cobaltium ion," the product composition will be determined by the factors controlling the subsequent entry of water. With the limited amount of experimental evidence available it is premature to attempt an explanation of this aspect of the reaction and we are now studying the effects of other electron-displacing groups and of other dissociating ligands in an attempt to throw more light on the subject.

There is also a lack of correlation between the rates of aquation and the activation energies for the *trans*-isomers of the above series. The values found are 26·2, 23·1,[1] 24·2,[8b] and 30·4 [11] kcal./mole for the ligands A = OH, N_3, Cl, and NCS, respectively, arranged in order of decreasing labilising power. This does not vitiate the idea that the labilising power of ligand A arises from its electron-displacement properties. To understand this it is necessary to consider the solvation of the complex ion, especially the difference in the solvation of the complex and the transition state. Since all the reactions under comparison involve stretching of the Co–Cl bond in complex ions of the same charge and similar size, most of the contributions to the solvent effect will be constant along the series and can be neglected. Any specific solvation about ligand A that is disturbed by an increase in the A–Co–en bond angle will produce an effect—probably one of desolvation—that will depend very much upon the nature of A. In the absence of a satisfactory model it is not possible to make accurate calculations of this effect but, since the interaction is probably hydrogen-bonding in character, the desolvation on formation of the transition state may be approximated to a melting process, and the relative enthalpy and entropy changes can then be deduced from those of the melting of ice. The free-energy change for the fusion of ice is, of course, zero at 0° and can be estimated to be very small (<0·2 kcal./mole) at 25°,[14] so that the free energy of desolvation will only contribute a fraction of the rate. The entropy and enthalpy changes for the fusion of ice, however, are quite considerable, $\sim$3·6 cal. mole^{-1} deg.$^{-1}$ and $\sim$1·6 kcal./mole, respectively.[14] It can be concluded that, although the partial desolvation resulting from the change in geometry will have a marked effect on the energy and entropy of activation, the effects will work

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

[14] Cf. Dorsey, " Properties of Ordinary Water Substance," Reinhold Publ. Corp., New York, 1940, pp. 264, 480.

in opposition to one another and have little effect on the rate of aquation at temperatures not greatly removed from 0°.

EXPERIMENTAL

Preparations.—*trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared by the standard method [15] and recrystallised from the minimum amount of water at 35° {Found: Co, 20·6; Cl^-, 12·4; co-ordinated Cl, 24·8. Calc. for $[Co(C_2H_8N_2)_2Cl_2]Cl$: Co, 20·7; Cl^-, 12·4; co-ordinated Cl, 24·9%}.

cis-Dichlorobis(ethylenediamine)cobalt(III) chloride was prepared from the *trans*-isomer [15] and recrystallised from water at 35° {Found: Co, 19·4; Cl^-, 11·7; co-ord. Cl, 23·4. Calc. for $[Co(C_2H_8N_2)_2Cl_2]Cl,H_2O$: Co, 19·4; Cl^-, 11·7; co-ord. Cl, 23·4%}.

cis-Chloroaquobis(ethylenediamine)cobalt(III) sulphate was prepared from *trans*-$[Co\ en_2Cl_2]Cl$ by Werner's method.[16] It was recrystallised by dissolving it in the minimum amount of water at 40° (5 g. in 100 ml.), cooling the filtered solution in ice, and adding ethanol (50 ml.) {Found: Co, 16·7; co-ord. Cl, 10·0; Cl^- absent. Calc. for $[Co(C_2H_8N_2)_2H_2OCl]SO_4,1\frac{1}{2}H_2O$: Co, 16·6; co-ord. Cl, 10·0%}.

trans-Hydroxochlorobis(ethylenediamine)cobalt(III) chloride was made by the method of Meisenheimer and Kinderlen [17] by adding an aqueous solution of diethylamine to *trans*-$[Co\ en_2Cl_2]Cl$. The dove-grey paste that was formed was filtered off, washed successively with 7 : 3 ethanol–water, ethanol, and ether. The crude product was dissolved in ice-cold water (6·5 g. in 25 ml.), and the solution filtered as quickly as possible. Ethanol (26 ml.) was added and the mixture cooled in ice. The crystals formed were filtered off, washed with alcohol and ether, and dried in a stream of air. At least one more recrystallisation was necessary to give a pure product {Found: Co, 20·65; Cl^-, 12·60; co-ord. Cl, 12·4. Calc. for $[Co(C_2H_8N_2)_2OHCl]Cl,H_2O$: Co, 20·65; Cl^-, 12·45; co-ord. Cl, 12·45%}.

cis-Hydroxoaquobis(ethylenediamine)cobalt(III) bromide was prepared by Werner's method [18] from $[Co\ en_2CO_3]Br$ and recrystallised on addition of alcohol and ether to a concentrated aqueous solution {Found: Co, 15·0; Br, 40·8. Calc. for $[Co(C_2H_8N_2)_2OHH_2O]Br_2,H_2O$: Co, 15·0; Br, 40·8%}. In 0·1N-perchloric acid it has a spectrum identical with that published for the *cis*-diaquo-complex.[7]

trans-Hydroxoaquobis(ethylenediamine)cobalt(III) perchlorate was prepared from *trans*-$[Co\ en_2Cl_2]NO_3$. The latter complex (15 g.) was suspended in water (30 ml.), and this mixture heated. Some of the complex dissolved and was aquated but most remained undissolved. The solution was decanted and passed through a column of anion-exchange resin (Amberlite IR-A 400; OH^- form) and washed out with a further 40 ml. of water. The combined effluent, which contained only $[Co\ en_2(OH)_2]OH$ was allowed to react with the unchanged *trans*-dichloronitrate and then recycled through the resin. This process was repeated until all the solid had dissolved. The effluent was acidified to pH 3 with 72% perchloric acid and then freeze-dried to a volume of 40 ml. Pyridine (3 ml.) was then added drop by drop to the solution cooled in ice. A crystalline precipitate of the trans-*hydroxoaquo-perchlorate* separated and was filtered off, washed very carefully with alcohol and ether, and dried over concentrated sulphuric acid (yield, 3·6 g.) {Found: equiv., 210. $[Co(C_2H_8N_2)_2(OH)H_2O](ClO_4)_2,\frac{1}{2}H_2O$ requires equiv. = $\frac{1}{2}M$ = 210}. A solution of this complex in 0·1N-perchloric acid has a spectrum identical with that published for the *trans*-diaquo-complex.[7]

[The equivalent weight was determined by passing a solution of a known amount of the complex through a cation-exchange resin column (Amberlite IR 120; H^+ form) and titrating the perchloric acid in the effluent with standard alkali.]

Kinetics.—The reaction solutions were made up by dissolving a weighed amount of the complex in the solvent previously brought to the temperature of the reaction. For the titrimetric and spectrophotometric investigations samples were withdrawn from the reaction mixture from time to time by means of a pipette surrounded with an ice-filled jacket. The reaction was stopped, either by cooling the sample to −78° or by adding it to acid. The ionic chloride was determined by passing the sample through a cation-exchange resin (Amberlite IR 120; H^+ form) and estimating the hydrochloric acid in the effluent by Volhard's method. Since

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[15] Bailar, *Inorg. Synth.*, 1946, **2**, 222.

[16] Werner, *Annalen*, 1912, **386**, 122.

[17] Meisenheimer and Kinderlen, *Annalen*, 1924, **438**, 241.

[18] Werner, *Annalen*, 1912, **386**, 89.

the complex ion can still undergo aquation when absorbed in the ion-exchange resin, it was necessary to surround the resin column by ice–water and to flush the resin continually with water between each separation. Spectrophotometric measurements were made with silica cells and a Unicam S.P. 500 quartz spectrophotometer. Conductivities were measured on a Wayne–Kerr universal bridge B 221. The shiny platinum electrodes were in contact with the solution throughout the reaction.

Although no tests were made to see whether light affected the reaction it was excluded as routine.

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