64. *Deuterium Isotope Effect in Octahedral Substitutions. Part I. The Aquation of* cis- *and* trans-*Dichloro- and* cis- *and* trans-*Chloronitro-bis(ethylenediamine)cobalt*(III) *Cations.*

By S. C. CHAN.

The rate constants for the solvolytic aquation of *cis*- and *trans*-dichloro- and *cis*- and *trans*-chloronitro-bis(ethylenediamine)cobalt(III) cations have been determined in both aqueous and deuterium oxide solutions. The rates in deuterium oxide solutions are lower than those in aqueous solutions and the rate reductions are virtually independent of the nature and position of the orienting ligand. These determinations are repeated with the *N*-deuterated complexes and it is found that the rate reductions for the chloronitro-complexes are now significantly smaller than those for the dichloro-complexes, showing that the decrease in rate is greater for S_N1 than for S_N2 aquations. The observations are similar to those in the solvolysis of organic halides and the same explanations may be used. The steric courses for the aquation of the *N*-deuterated complexes have also been measured in aqueous solutions and it is found that bimolecular aquations of both the *cis*- and *trans*-complexes, as well as unimolecular aquation of the *cis*-complex proceed with complete retention of configuration, whereas unimolecular aquation of the *trans*-complex yields a mixture of isomers directly. The products of the aquation of the dichloro-complexes isomerise to equilibrium mixtures at rates comparable with those of their formation, and it is necessary to determine the rate of isomerisation and the position of equilibrium of the *N*-deuterated aquochloro-cations in aqueous solutions in order to make corrections in the steric course determinations.

DEUTERIUM isotope effects on solvolysis reactions in organic compounds have been extensively studied,[1-6] but those on the cobalt(III) complexes less so. Adamson and Basolo [7] have studied the effect of deuterium substitution, both in the complex and in the solvent, on the rates of solvolytic aquation of the chloropentamminecobalt(III) cation. They found that the deuterium systems reacted more slowly than the protium systems and suggested a detailed mechanism for the aquation process in which four water molecules are hydrogen bonded to both the Cl and an adjacent NH_3 group of the complex. Their investigations were later elaborated.[8] The bis(ethylenediamine)cobalt(III) system is, however, much more suitable for study as it provides both different isomeric species (*cis* and *trans*) and different mechanisms (S_N1 and S_N2). The work now presented deals with the unimolecular and bimolecular nucleophilic solvolytic aquations of some *cis*- and *trans*-chlorobis(ethylenediamine)cobalt(III) cations, and the isotope effects under discussion are solvent and β-secondary effects.

The solvolytic aquations of $[Co\ en_2\ A\ Cl]^{n+}$ (en = ethylenediamine) in ordinary water as solvent, where A = OH,[9] N_3,[10] Br,[11] Cl,[9] NCS,[12] NH_3,[13] CN,[14] and NO_2,[15] have been

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[1] Streitwieser, jun., *Chem. Revs.*, 1956, **56**, 571.

[2] (*a*) Cohen and Westheimer, *J. Amer. Chem. Soc.*, 1952, **74**, 4387; (*b*) Shiner, jun., *ibid.*, 1952, **74**, 5285; (*c*) Wynne-Jones, *J. Chem. Phys.*, 1934, **2**, 381.

[3] Llewellyn, Robertson, and Scott, *Canad. J. Chem.*, 1960, **38**, 222.

[4] (*a*) Shiner, jun., *J. Amer. Chem. Soc.*, 1953, **75**, 2925; 1956, **78**, 2653; (*b*) Lewis and Boozer, *ibid.*, 1954, **76**, 791, 794; (*c*) Streitwieser, jun., *ibid.*, 1956, **56**, 571; (*d*) Streitwieser, jun., Jagow, Fahey, and Suzuki, *ibid.*, 1958, **80**, 2326.

[5] Leffek, Llewellyn, and Robertson, *J. Amer. Chem. Soc.*, 1960, **82**, 6315.

[6] Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, (*a*) 3207, (*b*) 3214.

[7] Adamson and Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.

[8] Basolo, Pearson, and Stellwagen, *J. Amer. Chem. Soc.*, 1960, **82**, 1077.

[9] Baldwin, Chan, and Tobe, *J.*, 1961, 4637.

[10] Staples and Tobe, *J.*, 1960, 4803.

[11] Chan and Tobe, *J.*, 1963, 5700.

[12] (*a*) Ingold, Nyholm, and Tobe, *J.*, 1956, 1691; (*b*) Baldwin and Tobe, *J.*, 1960, 4275.

[13] (*a*) Nyholm and Tobe, *J.*, 1956, 1707; (*b*) Tobe, *J.*, 1959, 3776.

[14] Chan and Tobe, *J.*, 1963, 514.

[15] Asperger and Ingold, *J.*, 1956, 2862.

thoroughly investigated in the past, leading to the postulation of two mechanisms for the process.[15,16] When A = OH, N_3, Br, Cl, and NCS, the reaction is unimolecular, whereas a bimolecular mechanism is involved when A = NH_3, CN, and NO_2. Steric course determinations have shown that *cis*-isomers are aquated with retention of configuration, irrespective of mechanism. *trans*-Isomers also react with retention of configuration in bimolecular aquations, but unimolecular aquations lead to considerable steric change. Ingold, Nyholm, and Tobe[17] have explained this on the basis of the stereochemistry of the electromeric effect which promotes S_N1 aquations. The deuterium isotope effects on a typical unimolecular aquation (A = Cl) and a typical bimolecular aquation (A = NO_2) are now investigated.

(1) *Basic Chemistry.*—In alkaline solutions, cobalt(III) ammine complexes undergo rapid deuterium exchange with the solvent.[18] For ethylenediaminecobalt(III) complexes, the exchange of the hydrogen atoms attached to the donor nitrogen atoms with deuterium in the solvent has also been shown to be rapid.[19] *trans*-Dichlorobis(ethylenedi[$^2H_4$]-amine) cobalt(III) chloride was used as the starting material for the preparation of the other *N*-deuterated complexes and was obtained from the ordinary *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride by the following scheme:

$$trans\text{-}[Co(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2Cl_2]^+ + 2OD^- \xrightarrow{D_2O + OD^-} cis\text{-}[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2(OD)_2]^+ + 2Cl^-$$

$$cis\text{-}[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2(OD)_2]^+ + 2HCl \longrightarrow trans\text{-}[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2Cl_2]^+ + 2HDO$$

The action of excess of OD^- in D_2O on *trans*-dichlorobis(ethylenediamine)cobalt(III) cation first gives *cis*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2(OD)_2]^+$. Evaporation with concentrated hydrochloric acid to dryness gives *trans*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2Cl_2]Cl,HCl,2H_2O$, which when dried at 110° evolves HCl and water to give the acid-free anhydrous complex. The deuterium exchange in concentrated acid solutions is negligibly slow. When the *trans*-dichloro-complex is heated with deuterium oxide, it forms mainly *cis*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2D_2O\ Cl]^{2+}$, which can be isolated from the solution as the sulphate. Evaporation of the solution to dryness, however, yields the compounds, *cis*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2Cl_2]Cl$. When the *trans*-dichloro-complex is suspended in dilute sulphuric acid and then treated with mercury(II) acetate, the main product is the *trans*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2H_2O\ Cl]^{2+}$ complex. Such mercury(II) ion-induced aquations of a number of chlorobis(ethylenediamine)cobalt(III) complexes have been shown to take place with retention of configuration.[14,20] With a solution of sodium nitrite in deuterium oxide, the *trans*-dichloro complex yields a mixture of *cis*- and *trans*-chloronitro-complex, the *cis* cation being isolated as the chloride and the *trans* cation as the nitrate. The entry of the nitro-ligand involves a redox process, catalysed by Co^{II} species. Mercury(II) ion-induced aquation of the chloronitro-complexes gives the aquonitro-cations with retention of configuration.[20c] The spectra of all these *N*-deuterated complexes in aqueous solutions do not differ significantly from those of the corresponding cations containing ordinary hydrogen. Because of the slow exchange between complex and solvent in acid media, it is possible to observe the four aquation rates corresponding to (*a*) protium complexes in protium oxide, (*b*) protium complexes in deuterium oxide, (*c*) deuterium complexes in protium oxide, and (*d*) deuterium complexes in deuterium oxide.

(2) *Solvolytic Aquation of* cis- *and* trans-*Dichlorobis(ethylenediamine)cobalt*(III) *Cations.*—

$$[Co\ en_2Cl_2]^+ + H_2O \xrightarrow{k} [Co\ en_2Cl\ H_2O]^{2+} + Cl^-$$

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

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

[18] (*a*) Anderson, Briscoe, and Spoor, *J.*, 1943, 361; (*b*) Block and Gold, *J.*, 1959, 966; (*c*) Basolo, Palmer, and Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 1073.

[19] Baldwin, *J.*, 1960, 4369.

[20] (*a*) Staples and Tobe, *J.*, 1960, 4812; (*b*) Sargeson, *Austral. J. Chem.*, 1963, **16**, 352; (*c*) Tobe, personal communications.

The kinetics for the protium complexes in protium oxide as solvent have been thoroughly examined.[21–23] Discrepancies exist among results, and it is desirable to repeat the determinations so that comparisons with the deuterated systems can be made with results obtained under exactly identical conditions. We followed the progress of the reactions at 25·0° by titrating the chloride ion liberated; the anionic chloride was separated from the complex cation by means of a cation-exchange resin column and was determined by the Volhard method. The replacement of the second co-ordinated chlorine is retarded by hydrogen ions,[21a, 24] and in 0·01N-nitric acid the two steps could be separated from one another. The first-order rate constants were determined from the plots of $\log_{10} (V_\infty - V_t)$ against time, where V_t is the titre of silver nitrate at time t, and V_∞ is the corresponding value calculated from the weight of complex taken, complete replacement of one co-ordinated chlorine only being assumed. The results are in Table 1.

The steric course of the solvolysis of the protium *cis*-dichloro complex in protium oxide has been determined by Mathieu [25] 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$_2$ H$_2$O Cl]$^{2+}$ cations. This retention of configuration was later confirmed spectrophotometrically on the racemic complex by Baldwin, Chan, and Tobe [9] who also determined the steric course of solvolysis of the light *trans*-dichloro-complex in aqueous solution. The steric course determinations are now carried out on the deuterated complexes in aqueous solutions, but since the products of the reactions, *i.e.*, the aquochloro-cations, isomerise to equilibrium mixtures at rates comparable with those of their formation it is necessary to determine the rate of isomerization and the position of equilibrium of the deuterated aquochloro-cations in aqueous solutions first so that appropriate corrections may be made.

TABLE 1.

First-order rate constants for the solvolysis of *cis*- and *trans*-dichlorobis(ethylenediamine)cobalt(III) cations at 25·0°.

Complex	Solvent	10^5k (sec.$^{-1}$)
cis-[Co(H$_2$N·CH$_2$·CH$_2$·NH$_2$)$_2$Cl$_2$]$^+$	H$_2$O	24·4
,, ,, ...	D$_2$O	17·4
cis-[Co(D$_2$N·CH$_2$·CH$_2$ND$_2$)$_2$Cl$_2$]$^+$	H$_2$O	18·5
,, ,, ...	D$_2$O	15·1
trans-[Co(H$_2$N·CH$_2$·CH$_2$·NH$_2$)$_2$Cl$_2$]$^+$	H$_2$O	3·48
,, ,, ...	D$_2$O	2·44
trans-[Co(D$_2$N·CH$_2$·CH$_2$ND$_2$)$_2$Cl$_2$]$^+$	H$_2$O	2·48
,, ,, ...	D$_2$O	2·07

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

The isomerization was followed at 25·0° spectrophotomerically and was found to obey a first-order rate law. The rate constants were obtained from 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 isomerizations of the protium system have been studied by two groups,[9, 20b] both of whom were in good agreement. Their data are in Table 2 for comparison. The individual rate constants, k_1 and k_{-1} are calculated from the overall rates $(k_1 + k_{-1})$ using the known equilibrium composition.

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

[22] Basolo, Boston, and Pearson, (*a*) *J. Amer. Chem. Soc.*, 1953, **75**, 3089; (*b*) *J. Phys. Chem.*, 1955, **59**, 304.

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

[24] Chan, *J.*, 1963, 5137.

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

TABLE 2.

Isomerization of aquochlorobis(ethylenediamine)cobalt(III) cations in aqueous nitric acid (0·01N) at 25·0°.

Aquochloro-complex	$10^5(k_1 + k_{-1})$ (sec.$^{-1}$)	*cis*-Isomer (%) at equil.	10^5k_1	10^5k_{-1}
Protiated	9·5	73	2·56	6·9
N-Deuterated	6·9	71	1·97	4·9

The isomerization data showed that the steric course cannot be determined by analysing the solution when the aquation is complete, since the composition will be controlled by the isomerization equilibrium. Corrections for this isomerization can be made by measuring the composition of the product at various stages of reaction and extrapolating back to zero reaction. A combined spectrophotometric and titrimetric technique was used and the extrapolations are guided by functions of the correct form,[12] by use of the known rate constants for the aquation of the dichloro-complexes and the isomerization of the aquochloro-product, together with the measured equilibrium composition. It was found that the aquation of the *cis*-$[Co(D_2N{\cdot}CH_2CH_2{\cdot}ND_2)_2Cl_2]^+$ cation in water yields 100% *cis*-aquo-product and that of the *trans*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2Cl_2]^+$ cation in water yields 30% *cis*- and 70% *trans*-aquo-products directly. Similar data on the isomerization of the protiated aquochloro-complex in water have been reported.[9]

(3) *Solvolytic Aquation of* cis- *and* trans-*Chloronitrobis(ethylenediamine)cobalt*(III) *Cations.*—

$$[Co\,en_2NO_2Cl]^+ + H_2O \xrightarrow{k} [Co\,en_2NO_2H_2O]^{2+} + Cl^-$$

The kinetics of the protium complexes in protium oxide as solvent have been studied by two sets of workers,[15,26] but discrepancies exist among their results. Both followed the progress of the reactions by spectrophotometry but, in order that comparisons with the deuterated systems can be made under identical conditions, we have repeated the determinations using a titrimetric method. The anionic chloride in the solution was separated from the complex cation by means of a cation exchange resin column and was determined by the Volhard method. The *cis*-complex was supplied as the chloride but the *trans* complex as nitrate. Titrations showed that the aquations were virtually complete after ten half-lives. The first-order rate constants were determined from the 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 results are in Table 3.

TABLE 3.

First-order rate constants for the solvolysis of *cis*- and *trans*-chloronitrobis(ethylenediamine)cobalt(III) cations at 25·0°.

Complex	Solvent	10^4k (sec.$^{-1}$)
cis-$[Co(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2NO_2Cl]^+$	H_2O	1·20
,, ,,	D_2O	0·81
cis-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2NO_2Cl]^+$	H_2O	1·01
,, ,,	D_2O	0·80
trans-$[Co(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2NO_2Cl]^+$	H_2O	10·0
,, ,,	D_2O	6·9
trans-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2NO_2Cl]^+$	H_2O	8·5
,, ,,	D_2O	6·8

The *cis–trans* isomerization of aquonitrobis(ethylenediamine)cobalt(III) cations in water takes place extremely slowly [15] so does not affect the composition of the product of the aquation. Accordingly it was not necessary to measure the rate of isomerization and the position of equilibrium, and the steric course can be determined by analysing the solution when the aquation is complete (10 half-lives). It was found that for the aquation of the *N*-deuterated chloronitro-complexes in water, both *cis*- and *trans*-isomers react with

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[26] Kuroda, *Nippon Kagaku Zasshi*, 1960, **81**, 1528.

complete retention of configuration. The same results have been observed for the protium complexes in water.[15]

DISCUSSION

In general, the behaviour of these chlorobis(ethylenediamine)cobalt(III) complexes is identical with that of organic halides, as deuteration of the complexes and also of the solvent both reduce the rate of solvolysis. It is convenient to discuss our results under two headings: (*a*) Solvent effect, and (*b*) β-isotope effect.

(*a*) *Solvent Effect.*—Data for discussion of the solvent deuterium isotope effect on rate of solvolysis of chlorobis(ethylenediamine)cobalt(III) cations are in Table 4. The rate reductions are virtually independent of the mechanism of solvolysis, as well as of the nature and position of the orienting ligand. Furthermore these reductions are similar to those in the chloropentamminecobalt(III) system (protium complex, 1·43; deuterium complex, 1·26).[8] These observations are understandable in terms of the compactness of the solvation shell which depends on two opposing factors: (i) solvating powers of the solvents and (ii) solvation energies of the complex ions. The first factor alone determines the relative rates in protium and deuterium oxides, while the second factor may be used to account for the difference in rate-reductions between the protium and the deuterium complexes. Deuterium oxide is less effective than water in solvating ions,[27] and data on the influence of deuterium oxide on the solubility of salts [28] and on their heats of solution [29] supported this idea. Hence solvolyses will go more slowly in deuterium oxide. Provided that the substrates are not considerably different, the solvent deuterium isotope effect on reactions involving a rearrangement (whether S_N2 or S_N1) between the solvation shell and the co-ordination shell should depend largely on the solvating power of the solvent and not on the mechanism. It can thus be concluded that, as in the case of organic halides,[30] the factor by which the rate is decreased in changing from water to deuterium oxide as solvent is not diagnostic of mechanism. The greater solubility of the deuterium complex [8] than that of the protium complex indicated that it is easier to solvate the ions of the former. If, for the deuterium complexes, the reduction in the compactness of the solvation shell caused by the poorer solvating power of the deuterated solvent is more than compensated by the increase in the ease of solvation of the complex ion by deuterium oxide, then the rate reductions will be smaller.

TABLE 4.

Solvent deuterium isotope effect on the rate of solvolysis of $[\mathrm{Co\ en_2ACl}]^{n+}$ cations at 25·0°.

Orienting group A	Mechanism	k_H/k_D	Mechanism	k_H/k_D
	Protium complexes		Deuterium complexes	
cis-Cl	S_N1	1·40	S_N1	1·23
trans-Cl	S_N1	1·43	S_N1	1·20
cis-NO_2	S_N2	1·48	S_N2	1·26
trans-NO_2	S_N2	1·45	S_N2	1·25

(*b*) β-*Deuterium Isotope Effects.*—Quite contrary to the case of solvent deuterium effects, the rate reductions caused by β-isotope effects depend on the mechanism of solvolysis, being greater for S_N1 reactions than for S_N2. Data for the discussion of β-isotope effects on rate of solvolysis of chlorobis(ethylenediamine)cobalt(III) cations are in Table 5.

In organic systems there are various explanations given for the deuterium isotope effect

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[27] Pritchard and Long, *J. Amer. Chem. Soc.*, 1956, **78**, 6008.

[28] Eddy and Menzies, *J. Phys. Chem.*, 1940, **44**, 207.

[29] Lange and Martin, *Z. physik. Chem.*, 1937, *A*, **180**, 233.

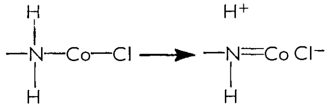
[30] Robertson and Laughton, *Canad. J. Chem.*, (*a*) 1956, **34**, 1714; (*b*) 1957, **35**, 1319.

TABLE 5.

β-Deuterium isotope effect on the rate of solvolysis of $[\mathrm{Co\ en_2ACl}]^{n+}$ cations at 25·0°.

Orienting group A	Mechanism	k_H/k_D	Mechanism	k_H/k_D
	Solvent: water		Solvent: deuterium oxide	
cis-Cl	S_N1	1·32	S_N1	1·15
trans-Cl	S_N1	1·40	S_N1	1·18
cis-NO_2	S_N2	1·19	S_N2	1·01
trans-NO_2	S_N2	1·18	S_N2	1·01

when located β to the halogen in the reacting molecule, the best one being that of hyperconjugation.[4,8]



$$-\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\mathrm{N}}}-\mathrm{Co}-\mathrm{Cl} \longrightarrow -\overset{\displaystyle \mathrm{H^+}}{\underset{\displaystyle \mathrm{H}}{\mathrm{N}}}{=}\mathrm{Co\ Cl^-}$$

In the S_N2 process ($A = NO_2$) where the rate-determining step does not involve dissociation, hyperconjugation is expected to have a smaller effect on the rate and consequently the rate reductions are smaller compared with the S_N1 process ($A = Cl$). An alternative explanation for rate reduction in S_N2 aquations would be in terms of the idea that these reactions are assisted by hydrogen bonding between the outgoing chlorine, the incoming solvent, and the β-hydrogen attached to a donor nitrogen atom.[13b,7] Such a possibility has also been suggested for organic systems.[31] Since the deuterium atom forms " hydrogen bonds " less readily than the hydrogen atom, the reaction is less assisted by the specific hydrogen bonding and hence the reduction in rate. For the bimolecular reactions, the complexes aquate with retention of configuration.

The results in Table 5 depend on the completeness of deuteration of the donating nitrogen atoms and absence of deuteration in the methylene groups of the ligands. Since all the complexes used in the investigation were obtained from *trans*-dichlorobis(ethylenedi[$^2H_4$]amine)cobalt(III) chloride under conditions which do not lead to any reduction of the deuterium content of the complex, it is necessary, but sufficient, to establish the above assumptions for this particular complex. We obtained the complex by a procedure similar to that of Baldwin [19] who had observed deuterium isotope shifts in those infrared absorption bands which have been assigned [32] to the vibrations of the NH_2 group. The bands which have been assigned [33] to the vibrations of the CH_2 group were unaffected by deuteration, indicating absence of deuteration of the methylene groups. Furthermore, there was no further reduction in rate of aquation of the product obtained by repeated deuteration of the deuterated complex with fresh deuterium oxide, indicating completeness of deuteration within limits of the purity of the deuterium oxide used ($\geqslant$99·8%).

The β-deuterium isotope effects on the *cis–trans* isomerization of aquochlorobis(ethylenediamine)cobalt(III) cations in water give a rate reduction of 1·30 for k_1 and 1·41 for k_{-1}. Comparison with data in Table 5 shows that the decreases in rate are similar to those for the aquation of the *cis*- and the *trans*-dichloro-cations in water, suggesting that both the

$$[\mathrm{Co\ en_2ACl}]^{n+} + \mathrm{H_2O^*} \longrightarrow [\mathrm{Co\ en_2AH_2O^*}]^{(n-1)+} + \mathrm{Cl^-}$$

$$[\mathrm{Co\ en_2AH_2O}]^{n+} + \mathrm{H_2O^*} \longrightarrow [\mathrm{Co\ en_2AH_2O^*}]^{n+} + \mathrm{H_2O}$$

aquation of chloro-complexes and the water exchange of aquo-complexes are mechanistically similar and that the *cis–trans* isomerization of the aquo-complex is a result of water

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[31] (*a*) Shiner, jun., and Verbanic, *J. Amer. Chem. Soc.*, 1957, **79**, 373; (*b*) Baddeley, *Ann. Reports*, 1954, **51**, 169; (*c*) Schubert and Sweeney, *J. Org. Chem.*, 1956, **21**, 119.

[32] (*a*) Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461; (*b*) Mizushima, Nakagawa, and Quagliano, *J. Chem. Phys.*, 1955, **23**, 136; (*c*) Barrow, Kreuger, and Basolo, *J. Inorg. Nucl. Chem.*, 1956, **2**, 2340; (*d*) Sheppard and Powell, *J.*, 1956, 3108, 4495.

[33] (*a*) Mizushima, Nakagawa, Ichishima, and Quagliano, *J. Phys. Chem.*, 1955, **59**, 293; (*b*) Lane, Sen, and Quagliano, *J. Chem. Phys.*, 1954, **22**, 1955.

exchange between the complex and the solvent. Similar suggestions have been made by Martin and Tobe [34] in their investigation of the isomerization and water exchange of *cis*- and *trans*-aquoamminebis(ethylenediamine)cobalt(III) salts.

Experimental

Preparations.—*cis*- and *trans*-Dichlorobis(ethylenediamine)cobalt(III) chlorides were prepared by the method of Bailar [35] and recrystallised from the minimum of water at 35° {Found: *cis*-complex; Co, 19·4; Cl^-, 11·7; co-ord. Cl, 23·4. *trans*-Complex: Co, 20·6; Cl^-, 12·4; co-ord. Cl. 24·8. Calc. for *cis*-$[Co(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2Cl_2]Cl,H_2O$: Co, 19·4; Cl^-, 11·7; co-ord. Cl, 23·4; and for *trans*-$[Co(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2Cl_2]Cl$: Co, 20·7; Cl^-, 12·4; co-ord. Cl, 24·9%}.

cis- and *trans*-Chloronitrobis(ethylenediamine)cobalt(III) salts were prepared and purified by the method of Werner.[36] The *cis* complex was isolated as the chloride and the *trans* complex as the nitrate {Found: *cis*-complex: Co, 19·8; Cl^-, 11·9; co-ord. Cl, 11·9. *trans*-Complex: Co, 18·2; co-ord. Cl, 10·9; Cl^-, 0. Calc. for *cis*-$[Co(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2NO_2Cl]\ Cl$: Co, 19·9; Cl^-, 12·0; co-ord. Cl, 12·0; and for *trans*-$[Co(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2NO_2Cl]NO_3$: Co, 18·2; co-ord. Cl, 11·0%}.

cis- *and* trans-*Dichlorobis(ethylenedi*$[^2H_4]$*amine)cobalt*(III) *Chlorides.*—*trans*-Dichlorobis(ethylenedi$[^2H_4]$amine)cobalt(III) chloride was prepared from *trans*-$[Co\ en_2Cl_2]Cl$. The protonated complex was dissolved in 99·8% deuterium oxide made alkaline (1M) by the addition of metallic sodium and the mixture was left overnight. Excess of concentrated hydrochloric acid was added and the mixture heated to dryness on a water bath. The resulting green crystals were dried at 110° and recrystallised from water at 35°. *cis*-Dichlorobis(ethylenedi$[^2H_4]$amine)cobalt(III) chloride was prepared by evaporating a neutral solution of the *trans* complex in deuterium oxide to dryness on a steam bath. The unchanged *trans* form was removed by washing with a little cold water. The crude product was recrystallised from water at 35° {Found: *cis*-complex: Co, 18·9; Cl^-, 11·5; co-ord. Cl, 22·9. *trans*-Complex: Co, 20·2; Cl^-, 12·2; co-ord. Cl, 24·4. Calc. for *cis*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2ND_2)_2Cl_2]Cl,H_2O$: Co, 18·9; Cl^-, 11·4; co-ord. Cl, 22·7; and for *trans*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2Cl_2]Cl$: Co, 20·1; Cl^-, 12·1; co-ord. Cl, 24·2%}.

cis- *and* trans-*Aquochlorobis(ethylenedi*$[^2H_4]$*amine)cobalt*(III) *sulphates* were prepared by suspending the corresponding dichloro-chlorides in dilute sulphuric acid and treating them with mercury(II) acetate. The free chloride ion is instantaneously co-ordinated to the Hg^{2+} ion and the resulting $HgCl^+$ ion rapidly removes one co-ordinated chlorine from the complexes largely with retention of configuration. The crude products were purified by fractional crystallization from cold aqueous alcohol {Found: *cis*-complex: Co, 16·0; co-ord. Cl, 9·6; Cl^-, 0. *trans*-Complex: Co, 17·5; co-ord. Cl, 10·5; Cl^-, 0. *cis*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2H_2O,Cl]SO_4,2H_2O$ requires Co, 15·8; co-ord. Cl, 9·5; and *trans*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2ND_2)_2H_2O,Cl]SO_4$ requires Co, 17·5; co-ord. Cl, 10·5%}.

cis- *and* trans-*Chloronitrobis(ethylenedi*$[^2H_4]$*amine)cobalt*(III) *Salts.*—1 mole of *trans*-dichlorobis(ethylenedi$[^2H_4]$amine)cobalt(III) chloride was dissolved in the minimum of deuterium oxide containing a trace of anhydrous cobalt(II) chloride and treated with a concentrated solution of 1 equiv. of sodium nitrite, also in deuterium oxide, stirred, and allowed to stand. The *cis*-chloride came down and was purified by addition of concentrated hydrochloric acid to a saturated solution in cold water. The filtrate was treated with solid ammonium nitrate, whereupon the crude *trans*-nitrate was obtained. This was purified by boiling with 1 equiv. of sodium nitrite in deuterium oxide, converting the salt into the *trans*-dinitro complex which could be easily purified by recrystallization. The pure *trans*-dinitro-complex was finely powdered and warmed with concentrated hydrochloric acid on a water-bath until evolution of gases had ceased. The solution was cooled and the crystals of *trans*-chloronitro-nitrate filtered off. They were purified by dissolving in concentrated hydrochloric acid and then addition of concentrated nitric acid. The acid nitrate was obtained and the acid was then removed by drying at 110° {Found: *cis*-complex: Co, 19·3; Cl^-, 11·9; co-ord. Cl, 11·8. *trans*-Complex: Co, 17·9; co-ord. Cl, 10·9; Cl^-, 0. Calc. for *cis*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2NO_2Cl]Cl$: Co, 19·3; Cl^-, 11·7; co-ord. Cl, 11·7; and for *trans*-$[Co(D_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ND_2)_2NO_2Cl]NO_3$: Co, 17·8; co-ord. Cl, 10·7%}.

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[34] Martin and Tobe, *J.*, 1962, 1388.

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

[36] (*a*) Werner, *Ber.*, 1901, **34**, 1734; (*b*) Werner and Gerb, *ibid.*, p. 1739.

cis- and *trans*-Aquonitrobis(ethylenedi[$^2H_4$]amine)cobalt(III) cations were prepared in solution from the corresponding chloronitro-complexes by the mercury(II) ion-induced aquation process. A solution of 0·1M mercury(II) perchlorate in perchloric acid was used.

Kinetics.—The reaction solutions were made up by dissolving a weighed amount of the appropriate complex in the appropriate solvent previously brought to the temperature of the reaction. For both the titrimetric and the spectrophotometric investigations, samples were withdrawn from the reaction mixture from time to time and quenched. The ionic chloride was determined by passing the sample through a cation exchange resin column (Amberlite IR 120; H^+ form) and estimating the hydrochloric acid in the effluent by the Volhard method. The resin column was surrounded by ice–water and continually flushed with water between separations. The deuterium oxide used had a purity of not less than 99·8%. Light was carefully excluded from the reaction mixture as a routine precaution.

Spectrophotometric measurements were made with silica cells and a Unicam S.P. 500 quartz spectrophotometer. Conventional thermostats kept the temperature at 25·0 ± 0·05°.

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DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HONG KONG,
HONG KONG.

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