

263. *Mechanism and Steric Course of Octahedral Aquation. Part V.\*  
The Isomerisation, Racemisation, and Water Exchange of cis- and  
trans-Aquoamminebis(ethylenediamine)cobalt(III) Salts.*

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*trans*-[Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O]<sup>3+</sup> salts rearrange to the *cis*-isomer in aqueous solution at a rate that first increases with pH and then becomes independent of it. The acid dependence is due to an alternative isomerisation path involving the *trans*-[Co en<sub>2</sub> NH<sub>3</sub> OH]<sup>2+</sup> cation which isomerises 400 times faster than the aquo-complex. The rate of racemisation of (+)-*cis*-[Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O]<sup>3+</sup> has a similar acid dependence. Both aquoammine isomers exchange their co-ordinated water about 80 times faster than they rearrange but isomerisation of *trans*-[Co en<sub>2</sub> NH<sub>3</sub> OH]<sup>2+</sup> takes place with no detectable exchange of co-ordinated oxygen with the solvent. The mechanism of water exchange and isomerisation of the aquoammine complexes is discussed. An intramolecular mechanism is suggested for the isomerisation of the hydroxoammine complexes, involving a unimolecular dissociation of one end of an ethylenediamine chelate ring under the labilising influence of the hydroxyl group.

AQUO-COMPLEXES of the type [Co en<sub>2</sub> A H<sub>2</sub>O]<sup>n+</sup> isomerise in aqueous solution at rates that depend upon the nature of ligand A. Often the rate of isomerisation is similar to that

\* Part IV, *J.*, 1961, 4637.

of the aquation of the corresponding chloro-complex  $[\text{Co en}_2 \text{A Cl}]^{(n-1)+}$ , suggesting that isomerisation is the result of a reaction that is mechanistically similar to aquation. In order to verify the hypothesis that the isomerisation is the result of steric change that accompanies the exchange of co-ordinated water with the solvent, it was necessary to compare the rates of isomerisation of aquo-complexes with the rates of water exchange. There are few published data on water exchange in this type of complex.

$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  has been studied in detail<sup>1</sup> but is unsuitable for work on the steric course. Kruse and Taube<sup>2</sup> have compared the rates of isomerisation with those of water exchange in the complexes  $[\text{Co en}_2 (\text{H}_2\text{O})_2]^{3+}$ ,  $[\text{Co en}_2 \text{OH H}_2\text{O}]^{2+}$ , and  $[\text{Co en}_2 (\text{OH})_2]^+$  and conclude that the isomerisation of the aquo-complexes is due to the water exchange leading to steric change. The  $[\text{Co en}_2 \text{NH}_3 \text{H}_2\text{O}]^{3+}$  isomers afford a system that does not differ greatly from the  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  cation and is a suitable starting point for the study of the mechanism and steric course of water exchange.

(1) *Isomerisation of trans-Aquoamminebis(ethylenediamine)cobalt(III) Salts.*—When heated in aqueous solution, *trans*- $[\text{Co en}_2 \text{NH}_3 \text{H}_2\text{O}]^{3+}$  rearranges to the *cis*-isomer at a rate that increases as the acidity of the solution decreases. A preliminary report<sup>3</sup> gave data for acid concentrations,  $0.2N > [\text{H}^+] > 0.002N$  at  $72.8^\circ$  and these have now been extended over a wider range of temperature and acidity.

Buffers could not be used to control and maintain the pH of the solution as those that were tried reacted with the complex but it is noteworthy that there is reasonable agreement between the rate constants for the unknown reaction in buffer solution and those for the isomerisation at the same pH. Solutions in the pH range 1–3 were prepared by adding known amounts of perchloric acid to a solution of *trans*- $[\text{Co en}_2 \text{NH}_3 \text{H}_2\text{O}](\text{NO}_3)_3$  in water, and those in the range 5.8–9 by adding known amounts of alkali, but it was not possible, in the absence of buffers, to cover the range 3–5.5 satisfactorily. A solution of the *trans*-aquoammine nitrate in water has a pH of about 4.5 at  $20^\circ$  but the rate is very sensitive to small changes of pH in this region. The hydrogen-ion concentration of solutions of  $\text{pH} < 3$ , where the acidity comes mainly from a strong acid, should not change much with temperature, but at higher pH, where the acidity is controlled by the self-buffering of the aquo-complex, the pH of the solution at the reaction temperature will be quite different from that at room temperature. At the higher pH, the best rate correlation was obtained by assuming that the alkali added completely converted an equivalent amount of the aquo-complex into the hydroxo-complex. The isomerisation rate constants are reported in Table 1 and the dependence of the first-order rate constant upon the hydrogen-ion concentration is best given by the formula:

$$k_{\text{obs}} = \frac{k_1 + k_2 K / [\text{H}^+]}{1 + K / [\text{H}^+]}$$

The values of  $k_1$ ,  $k_2$ , and  $K$  were determined in the following way. When  $[\text{H}^+] > 10^{-4}M$ ,  $K / [\text{H}^+] \ll 1$  and the expression simplifies to

$$k_{\text{obs}} = k_1 + k_2 K / [\text{H}^+]$$

When  $k_{\text{obs}}$  is plotted against  $1 / [\text{H}^+]$  a straight line is obtained with slope  $k_2 K$  and intercept  $= k_1$ . When  $[\text{H}^+] < 10^{-8}M$ ,  $K / [\text{H}^+] \gg 1$  and  $k_{\text{obs}}$  becomes independent of the hydrogen-ion concentration and equal to  $k_2$ . Values for all three constants were calculated at  $50.2^\circ$  and  $60.0^\circ$ , but only  $k_1$  was determined at higher temperatures and only  $k_2$  at lower ones. The values for these derived constants are given in Table 2.

<sup>1</sup> (a) Rutenburg and Taube, *J. Chem. Phys.*, 1952, **20**, 825; (b) Taube and Posey, *J. Amer. Chem. Soc.*, 1953, **75**, 1463; (c) Hunt and Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 2642.

<sup>2</sup> Kruse and Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 2642.

<sup>3</sup> Tobe, *J.*, 1959, 3776.

TABLE 1.

First-order rate constants for the rearrangement of *trans*-aquoamminebis(ethylenediamine)cobalt(III) nitrate to the *cis*-isomer.

Rate constants,  $k_{\text{obs}}$ , were determined spectrophotometrically from the slope of the semi-logarithmic plot of  $\log_{10}(D_{\infty} - D_t)$  against time, where  $D_t$  and  $D_{\infty}$  are the optical densities of the acidified solution at time,  $t$ , and after ten half-lives. ( $D_{\infty}$  corresponds to  $\epsilon_{\infty} = 65.4$ .) The ionic strength of the solution was adjusted to 0.1 with sodium perchlorate solution.

Temp.	[Complex] (mmole/l.)	pH	Added NaOH *	$10^5 k_{\text{obs}}$ (sec. <sup>-1</sup> )	Temp.	[Complex] (mmole/l.)	pH	Added NaOH *	$10^5 k_{\text{obs}}$ (sec. <sup>-1</sup> )
74.2°	2.56	1.22	—	6.4	50.2°	10.00	1.22	—	0.179
68.5	2.53	1.10	—	2.9	"	2.50	2.88	—	0.39
"	2.53	1.44	—	2.8	"	5.33	2.84	—	0.41
60.0	1.77	1.20	—	0.77	"	2.57	3.40	—	1.41
"	2.45	1.40	—	0.76	"	2.55	4.50	—	4.15 <sup>a</sup>
"	2.51	1.94	—	0.80	"	2.55	5.54	0.25	18.7
"	2.66	3.03	—	2.6	"	5.05	6.37	0.50	25.4
"	2.61	3.43	—	5.3	"	5.08	6.38	0.50	23.1
"	2.50	4.55	—	15.4 <sup>a</sup>	"	2.55	6.43	0.60	24.8
"	2.49	4.73	—	16.7 <sup>a</sup>	"	2.58	9.60	3.00	59 <sup>b</sup>
"	2.53	6.37	0.5	164	"	2.52	10.2	3.00	67 <sup>b</sup>
"	2.50	6.31	0.6	129	44.6	2.54	—	1.00	12.7
"	2.47	7.38	1.0	243	35.0	2.54	—	0.97	4.3
50.2	2.54	1.10	—	0.187	30.0	36.0	—	1.00	2.2
"	5.06	1.22	—	0.164					

<sup>a</sup> Solution of complex nitrate in water. <sup>b</sup> Some decomposition was observed at the later Stages of the reaction.

\* Moles per mole of complex.

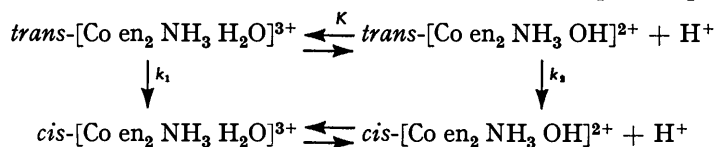
TABLE 2.

Rate constants derived from the data in Table 1.

Temp.	$10^5 k_1$ (sec. <sup>-1</sup> )	$Kk_2$ (mole l. <sup>-1</sup> sec. <sup>-1</sup> )	$10^4 k_2$ (sec. <sup>-1</sup> )	$10^5 K$ (moles/l.)
74.2°	6.4	—	—	—
72.8 *	5.5	$3.4 \times 10^{-7}$	—	—
68.5	2.9	—	—	—
60.0	0.75	$1.7 \times 10^{-8}$	30	6
50.2	0.16	$3.5 \times 10^{-9}$	4.6	8
44.6	—	—	1.27	—
35.0	—	—	0.43	—
30.0	—	—	0.22	—

\* Data from ref. 3.

The dependence of the rate of isomerisation on pH is consistent with the idea that the hydroxoammine complex rearranges very much faster than the aquo-complex, *i.e.*,



The constant,  $K$ , obtained from the kinetic experiments should therefore be equal to the acid dissociation constant of the aquo-complex. It was not possible to determine these values directly at the higher temperatures but  $K$  was found to be  $1.6 \times 10^{-6}$  mole/l. for *trans*-[Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O](NO<sub>3</sub>)<sub>3</sub> at 20° and ionic strength = 0.1. Although there is little information on the change in the acid dissociation constant of aquo-complexes with temperature, a fourfold increase for a rise in temperature of 40° is not unreasonable.<sup>4</sup>

(2) *Racemisation of cis-Aquoamminebis(ethylenediamine)cobalt(III) Salts.*—Mathieu<sup>5</sup>

<sup>4</sup> Cf. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

<sup>5</sup> Mathieu, *Bull. Soc. chim. France*, 1937, **4**, 687.

showed that a  $10^{-2}$ M-solution of (+)-*cis*-[Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O]<sup>3+</sup> lost 12% of its optical activity during 5 months at 20°, indicating a rate constant for racemisation of about  $10^{-8}$  sec.<sup>-1</sup>. This racemisation has now been studied in greater detail and the pH dependence examined. As it was not possible to resolve the racemic *cis*-[Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O]<sup>3+</sup> cation, the optically active complex was prepared from (+)-*cis*-[Co en<sub>2</sub> NH<sub>3</sub> Br]Br<sub>2</sub> which was allowed to aquate in acid solution.<sup>6</sup> The bromide ions were then removed by an anion exchange resin and replaced by perchlorate ions. The solution of partially resolved (+)-*cis*-[Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O](ClO<sub>4</sub>)<sub>3</sub> was then used for the racemisation studies. The loss of optical activity, measured at the sodium-D line, followed a first-order rate law but, owing to the low transmittance of the solution, it was necessary to use dilute solutions and so the total changes of rotation were never much more than 0.1°. The rate constants, therefore, cannot be very accurate. The rates of racemisation were determined in solutions sufficiently acidic for the reaction to go entirely through the aquoammine complex or in solutions containing only the hydroxoammine complex. Despite the absence of data for the regions of intermediate pH, it will be clear from the data in Table 3, that the racemisation follows

TABLE 3.

First-order rate constants for the racemisation of (+)-*cis*-aquoamminebis(ethylenediamine)cobalt(III) perchlorate ( $k_1$ ) and of (+)-*cis*-hydroxoamminebis(ethylenediamine)cobalt(III) perchlorate ( $k_2$ ).

Temp.	[Complex] mmole/l.	pH	$k_1$ (sec. <sup>-1</sup> )	$k_2$ (sec. <sup>-1</sup> )
100.3°	11.5	1.0	$3.3 \times 10^{-4}$	—
75.0	5.05	1.0	$2.3 \times 10^{-5}$	—
50.2	6.94	1.45	$9.0 \times 10^{-7}$	—
„	7.50	9.0	—	$2.7 \times 10^{-4}$

the same rate law as the isomerisation of the *trans*-complex and that the hydroxoammine is much more labile than the aquoammine complex. All measurements were made on acidified solutions and the spectra of these solutions corresponded exactly to that of a freshly prepared solution of the *cis*-aquoammine complex, indicating that, in every case, a racemisation and not a decomposition was being observed.

(3) *Exchange of Co-ordinated Water with Solvent.*—The salts of the *cis*- and the *trans*-[Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O]<sup>3+</sup> cation are, with the exception of the *trans*-nitrate, very soluble in water, and a preliminary search for a precipitant that would act in dilute solution was unsuccessful. It was necessary to resort to freeze-drying to separate the complex from the solvent. In order to decide which salt would be most suitable for the oxygen-isotope analysis, the bromides, chlorides, iodides, and nitrates were examined. The *cis*-chloride and -bromide lose co-ordinated water quite readily to give the corresponding *cis*-chloroammine and -bromoammine complexes. The rate of loss of water depends upon the state of subdivision of the sample: a very finely divided specimen loses all its water when stored in a vacuum over concentrated sulphuric acid for 2 days. The *cis*-bromide is obtained as a well-defined hydrate, [Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O]Br<sub>3</sub>·H<sub>2</sub>O and as long as the water of crystallisation is present the complex is indefinitely stable, but it is not possible to remove this water without, at the same time, removing the water of co-ordination. A sample of the *cis*-bromide monohydrate was kept over concentrated sulphuric acid at 20 mm. pressure until the loss of weight corresponded to the removal of half of the water present. The aqueous solution of the product had a spectrum that was identical to that of a 1 : 1 mixture of *cis*-[Co en<sub>2</sub> NH<sub>3</sub> Br]Br<sub>2</sub> and *cis*-[Co en<sub>2</sub> NH<sub>3</sub> H<sub>2</sub>O]Br<sub>3</sub>·H<sub>2</sub>O. The *trans*-aquoammine chloride and bromide have a similar composition and behave similarly, yielding the *trans*-chloroammine and -bromoammine complexes, respectively. This interdependence of co-ordinated water and crystal water might account for the observation that there is exchange between the co-ordinated water and crystal water of solid

<sup>6</sup> Cf. Baldwin and Tobe, *J.*, 1960, 4275.

$[\text{Co en}_2 (\text{H}_2\text{O})_2] (\text{BiBr}_6) \cdot n\text{H}_2\text{O}$ .<sup>2</sup> The *cis*- and *trans*-aquoammine nitrates were the most suitable salts for the exchange studies since they are both obtained without water of crystallisation (although the *cis*-salt tends to be hygroscopic), and lose their water smoothly when heated above 80° at 5 mm. pressure to yield the nitrateammine complex. It is noteworthy that both isomers give the *cis*-product on dehydration.

The rate of exchange of the co-ordinated water in *trans*- $[\text{Co en}_2 \text{NH}_3 \text{H}_2\text{O}]^{3+}$  with the solvent was measured by dissolving the nitrate in water that was enriched with  $^{18}\text{O}$  water (1.4% excess abundance) and brought to pH 1.3 with 72% perchloric acid. Samples were withdrawn from time to time and the solvent removed by freeze-drying. Adsorbed water was then removed by leaving the complex over concentrated sulphuric acid at 25 mm. pressure for 15 hr., and the co-ordinated water was then driven off by heating the complex at 5 mm. pressure, collected, and equilibrated with carbon dioxide. The oxygen isotope abundance in the carbon dioxide was then measured mass spectrometrically. The experiment, carried out at 30°,  $[\text{complex}] = 2.5 \times 10^{-2}\text{M}$ ,  $[\text{H}^+] = 0.05\text{M}$ , gave a rate constant,  $k_{\text{exchange}} = 4.5 \times 10^{-6} \text{ sec.}^{-1}$ . The spectrum of the reaction mixture, measured from time to time during the reaction, showed that very little isomerisation had taken place. When 67% of the co-ordinated water had been exchanged, less than 10% of the complex was in the *cis*-form.

The method used to follow the exchange of the *cis*-aquoammine complex was less reliable. The complex, supplied as the bromide, was dissolved in water and shaken with excess of silver oxide. The filtered solution, which contained the hydroxoammine hydroxide, was acidified to pH 3 with perchloric acid and freeze-dried. The deliquescent perchlorate was dissolved in the isotopically labelled solvent, the solution was acidified, and samples were removed at appropriate times and freeze-dried. The perchlorate residue was dissolved in acetone and a few drops of nitric acid (6M) were added to the solution, whereby the *cis*-aquoammine nitrate was precipitated. This was washed with acetone and ether and dried over concentrated sulphuric acid. The solid was then heated in a sealed tube with a known amount of carbon dioxide at 120° for 12 hr. In most cases the complex dissolved in the liberated water and the tube was then left for some days at room temperature to ensure complete equilibration before the isotopic composition of the carbon dioxide was measured. The experiment, carried out at 25°,  $[\text{complex}] = 3.5 \times 10^{-2}\text{M}$ ,  $[\text{H}^+] = 0.01\text{M}$ , gave a rate constant,  $k_{\text{exchange}} = 1.1 \times 10^{-6} \text{ sec.}^{-1}$ .

The exchange of the oxygen in the *trans*- $[\text{Co en}_2 \text{NH}_3 \text{OH}]^{2+}$  cation was studied by measuring the oxygen-18 abundance in a previously enriched sample of the *trans*-complex during, and after, its rearrangement to the *cis*-isomer. *trans*- $[\text{Co en}_2 \text{NH}_3 \text{H}_2\text{O}] (\text{NO}_3)_3$  was dissolved in enriched water, and the solution was acidified to pH 1 with 72% perchloric acid and heated at 60° for 4 hr. The solvent was removed by freeze-drying and the residue dissolved in water of normal isotopic abundance. The aquo-complex was converted into the hydroxo-complex by adding the appropriate amount of 0.1N-sodium hydroxide, the equivalence point being determined by a glass electrode. The solution, at pH 9.5, was diluted to 100 ml. and a sample taken immediately for isotopic analysis. The spectrum of a diluted and acidified portion of the reaction mixture was also measured to determine the amount of isomerisation. The reaction mixture was then kept at 30° and sampled periodically for isotopic and isomeric analysis. The samples for isotope analysis were first acidified to pH 3 with nitric acid and freeze-dried, and the co-ordinated water examined by the method already described for the *trans*-aquoammine complex. The results are given in Table 4.

TABLE 4.

Isomerisation and oxygen exchange of *trans*-hydroxoamminebis(ethylenediamine)-cobalt(III) salts at 30.0°.

Time (min.) .....	0	1325	2751	4135
Isomeric composition of solution (% <i>cis</i> ) .....	32	87	98.5	100
Excess abundance of $^{18}\text{O}$ in complex (%) .....	0.41	0.39	0.38	0.39

## DISCUSSION

The relevant data from the foregoing have been collected in Table 5, where the relationship between the isomerisation and ligand exchange rates can be clearly seen.

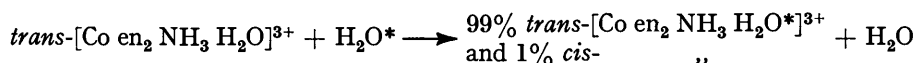
TABLE 5.  
Comparison of exchange, isomerisation, and racemisation rates for *cis*- and *trans*-aquo- and -hydroxo-amminebis(ethylenediamine)cobalt(III) salts.

Complex	Temp.	$k_{\text{isom.}}$ (sec. <sup>-1</sup> )	$k_{\text{rac.}}$ (sec. <sup>-1</sup> )	$k_{\text{exch.}}$ (sec. <sup>-1</sup> )
<i>trans</i> -[Co en <sub>2</sub> NH <sub>3</sub> H <sub>2</sub> O] <sup>3+</sup> .....	30.0°	5 × 10 <sup>-8</sup> *	—	4.5 × 10 <sup>-8</sup>
<i>trans</i> -[Co en <sub>2</sub> NH <sub>3</sub> OH] <sup>2+</sup> .....	„	2 × 10 <sup>-5</sup>	—	no exchange after seven half-lives
<i>cis</i> -[Co en <sub>2</sub> NH <sub>3</sub> H <sub>2</sub> O] <sup>3+</sup> .....	25.0	—	3 × 10 <sup>-8</sup> *	1.1 × 10 <sup>-8</sup>

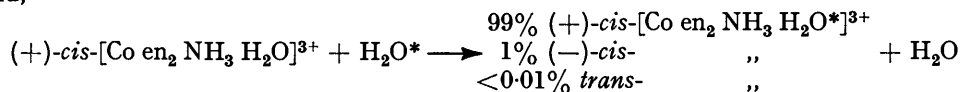
\* Extrapolated values.

These data show that the mechanism of the rearrangement of the aquoammine complexes is quite different from that of the rearrangement of the hydroxoammine complexes, and the two mechanisms are therefore discussed separately.

Although there is much known about the isomerisation and racemisation of complexes of the type [Co en<sub>2</sub> A H<sub>2</sub>O]<sup>n+</sup> little is known about the rates at which the co-ordinated water exchanges with the solvent. When A = H<sub>2</sub>O and OH, water exchange and rearrangement have similar rates,<sup>2</sup> whereas, it has now been shown that when A = NH<sub>3</sub>, exchange is much faster than rearrangement. All these observations can be reconciled if water exchange is visualised as an aquation process in which the replaced ligand is also water. Isomerisation and racemisation, therefore, represent those exchanges that result in steric change. When A = H<sub>2</sub>O and OH most of the acts of exchange must result in steric change, whereas, when A = NH<sub>3</sub>, the data indicate that



and,



Each time the *(-)-cis*-enantiomorph is formed two optically active ions cancel out so that  $k_{\text{rac.}} = 2k_{\text{(+)→(-)}}$ .

It is instructive to compare the aquation of the aquo-complexes, [Co en<sub>2</sub> A H<sub>2</sub>O]<sup>n+</sup> (exchange), with that of the corresponding chloro-complex [Co en<sub>2</sub> A Cl]<sup>(n-1)+</sup>; when A = NH<sub>3</sub> the rate constants of the two reactions are similar, 2 × 10<sup>-6</sup> and 4 × 10<sup>-7</sup> sec.<sup>-1</sup>, respectively at 25°, and both react almost exclusively with retention of configuration, (1% steric change would not be detectable by the methods used in the study of the aquation of the chloro-complexes<sup>3</sup>). When A = *trans*-OH,  $k$  (chloro-complex) = 1.6 × 10<sup>-3</sup> sec.<sup>-1</sup>,<sup>7</sup> and  $k$  (aquo-complex) = 4 × 10<sup>-3</sup> sec.<sup>-1</sup>.<sup>2</sup> The chloro-complex is aquated with 75% change of configuration,<sup>7</sup> and the aquo-complex exchanges water only slightly faster than it isomerises.<sup>2</sup> For A = *trans*-H<sub>2</sub>O the exchange and isomerisation data are known but nothing is known about the rate and steric course of the *trans*-chloro-aquo-complex. It is unlikely that these data will ever be available since the *trans*-isomer rearranges to the *cis*-form before it can be aquated.<sup>7</sup> Work is now in progress on the compounds with A = NCS and NO<sub>2</sub>, and, although it is premature to discuss the results, nothing has been found to contradict the idea that the aquation of the aquo-complexes is mechanistically very similar to the aquation of the corresponding chloro-complex.

The temperature-dependence of the rearrangement of the *trans*-aquoammine complex

<sup>7</sup> Baldwin, Chan, and Tobe, *J.*, 1961, 4637.

is given by  $k = 10^{17} \exp(-33,900/RT)$  sec.<sup>-1</sup>. The temperature dependence of the water-exchange rate constant was not measured, but the water exchange of the very similar  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  has a heat of activation ( $\Delta H^\ddagger$ ) of 26.6 kcal./mole.<sup>1c</sup> Even after allowance for the difference between four ammonia molecules and two ethylenediamine molecules it is very unlikely that the activation energy of water exchange in *trans*- $[\text{Co en}_2 \text{NH}_3 \text{H}_2\text{O}]^{3+}$  exceeds 29 kcal./mole. There remains, therefore, a difference of at least 5 kcal./mole in the activation energies of the path involving steric change and that leading to retention of configuration.

Two distinct mechanisms can account for the experimental observations. A bimolecular ( $S_N2$ ) attack by water on the complex has two reaction paths available. The first, in which attack is adjacent to the outgoing group, would lead to exchange with complete retention of configuration, whereas, the second, involving attack from the opposite side of the octahedron, would lead to an edge displacement, so that the exchange would be accompanied by steric change. As the water molecule is a relatively weak nucleophile, bond making will make a large contribution to the activation energy. Since this energy will be less when the incoming and outgoing groups are adjacent,<sup>8</sup> the difference in the activation energies of the two bimolecular paths is easily explained.

An alternative point of view favours a unimolecular ( $S_N1$ ) mechanism for the exchange. In order to explain the experimental results it is necessary to visualise the formation of a "cobaltium ion" that retains a "memory" of the octahedron from which it was formed; a square pyramid, formed by infinitely extending the Co-OH<sub>2</sub> bond would do this. This "cobaltium ion" can either take up a water molecule and form an aquo-complex with the same configuration as before, or rearrange, with an activation energy >5 kcal./mole, to a new configuration, probably trigonal bipyramidal, which would lead, on re-entry of water, to both *cis*- and *trans*-products. This mechanism has been suggested by Kruse and Taube<sup>2</sup> to explain the water exchange of the diaquo-complex. It is very hard to believe that, surrounded as it is by an environment of water molecules, the "cobaltium ion" has time to rearrange before it captures a water molecule. This reasoning, and the desire to argue by analogy with the corresponding chloroammine complexes,<sup>3</sup> makes the bimolecular mechanism seem preferable, but, at the moment, insufficient experimental evidence is available for a conclusive assignment of mechanism.

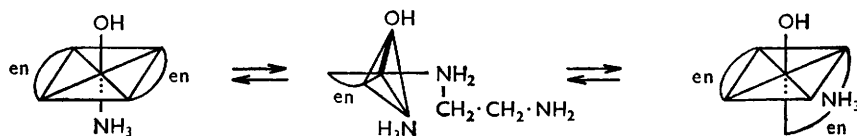
Taube *et al.* have shown that the volume change of activation ( $\Delta V^\ddagger$ ) for the exchange of water with the  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  cation is small and independent of pressure and has interpreted this by what may be described as an  $S_N1$  process in which the "cobaltium ion" is not fully formed when the transition state is reached.<sup>1c</sup> The calculation of the volume changes expected for the limiting cases of  $S_N1$  and  $S_N2$  mechanisms, however, ignores any contraction, or expansion, of the co-ordination sphere due to the other five ligands responding to the decrease, or increase, in the co-ordination number of the cobalt atom. This could be sufficient to counterbalance the changes due to the loss or gain of a water molecule.

The rearrangement of the  $[\text{Co en}_2 \text{NH}_3 \text{OH}]^{2+}$  cations takes place without any exchange of the attached ligands. This has been demonstrated conclusively for the hydroxyl group by the isotopic-labelling experiment, and permissively for ammonia and ethylenediamine, since at pH 3, where half of the isomerisation is through the hydroxo-complex, the system is thermodynamically unstable so that complete dissociation of ammonia or ethylenediamine would result in decomposition and not isomerisation. A truly intramolecular mechanism, in which none of the metal-ligand bonds breaks, cannot be ruled out but appears to be energetically unlikely. The most plausible mechanism involves the dissociation of one end of an ethylenediamine group under the +*E* effect of the hydroxyl group. Reattachment, which is much more likely than the breaking of the second bond, may lead to steric change.

A mechanism involving one-ended displacement of a chelate has been suggested to

<sup>8</sup> Ašperger and Ingold, *J.*, 1956, 262.

explain the exchange of all twelve oxygen atoms in  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  with the solvent under conditions where there is no exchange between the co-ordinated and ionic oxalate.<sup>9</sup> The mechanism also conforms to the accepted labilising power of the hydroxyl group. Complexes of the type  $[\text{Co en}_2 \text{A OH}]^{2+}$  can undergo one of two reactions in aqueous solution depending upon the nature of the Co-A bond. When A is bound less strongly than



ethylenediamine, *e.g.*, A = Cl, Br, or NCS, aquation occurs and A is lost. When A is bound more strongly, *e.g.*, A = NH<sub>3</sub> or OH, isomerisation takes place by the mechanism discussed above. The rearrangement of  $[\text{Co en}_2 (\text{OH})_2]^+$  takes place with partial exchange of the co-ordinated oxygen<sup>2</sup> and it is probable that, in addition to the chelate-opening mechanism, there is direct bimolecular attack by the hydroxide ions in solution leading to exchange. This cannot be avoided by studying the reaction in less alkaline solutions as the isomerisation and exchange then go *via* the aquohydroxo<sub>3</sub>-complex where the aquo-group is labilised by the hydroxo-group.

#### EXPERIMENTAL

**Preparations.**—*trans*-Aquoamminebis(ethylenediamine)cobalt(III) nitrate was prepared from *cis*- $[\text{Co en}_2 \text{NH}_3 \text{Br}] \text{Br}_2$ .<sup>10</sup> As the main product of this reaction is the *cis*-aquoammine bromide, an alternative method was adopted when a sufficient stock of the *cis*-isomer had been accumulated. Purified *trans*- $[\text{Co en}_2 \text{NCS Cl}] \text{ClO}_4$  (10 g.) was mixed with 10*N*-sulphuric acid (20 ml.) and the slurry was cooled to 0°. Hydrogen peroxide solution (30%; 60 ml.) was added in portions, the mixture being cooled and stirred whenever the temperature rose above 30°. The mixture was left for 3 hr. at room temperature and then treated with a saturated solution of sodium dithionate. A red precipitate of *trans*- $[\text{Co en}_2 \text{NH}_3 \text{Cl}] \text{S}_2\text{O}_8$  was filtered off, washed with water, alcohol, and ether, and air dried. The yield was 7.8 g. Mercuric oxide (4.5 g.) was dissolved in a mixture of water (5 ml.) and 60% perchloric acid (6 ml.) and to this solution was added *trans*- $[\text{Co en}_2 \text{NH}_3 \text{Cl}] \text{S}_2\text{O}_8$  (7.5 g.). The pink complex started to dissolve but almost immediately an orange solid was precipitated. After 2 hr. at room temperature, the mixture was filtered and the precipitate treated with more water and mercuric perchlorate solution; it soon dissolved. The combined filtrates were then passed through an anion-exchange resin (Amberlite IR-A 400) in the hydroxide form, whereby all the anions were replaced by hydroxide and the mercuric species precipitated and retained as the hydroxide. The effluent and washings were acidified to pH 3 and freeze-dried. The residue was dissolved in water (15 ml.), and concentrated nitric acid (10 ml.) was added slowly to the cooled solution. The *trans*-aquoammine nitrate crystallised, and was washed with alcohol and ether and recrystallised from the minimum amount of water at 40° (yield, 4.5 g.) (Found: Co, 14.7; N, 28.2; H<sub>2</sub>O, 4.4. C<sub>4</sub>H<sub>21</sub>CoN<sub>5</sub>O<sub>10</sub> requires, Co, 14.7; N, 27.7; H<sub>2</sub>O, 4.5%). *cis*-Aquoamminebis(ethylenediamine)cobalt(III) bromide was prepared from *cis*- $[\text{Co en}_2 \text{NH}_3 \text{Br}] \text{Br}_2$ <sup>10</sup> and recrystallised from ethanol-water at 40° [Found: Br, 51.0; H<sub>2</sub>O, 7.2. C<sub>4</sub>H<sub>23</sub>Br<sub>3</sub>CoN<sub>5</sub>O<sub>3</sub> requires Br, 50.8; H<sub>2</sub>O, 7.6%].

**Kinetics.**—Solutions were prepared by dissolving a weighed amount of the appropriate complex in water to which the appropriate amount of perchloric acid or sodium hydroxide had been added. The ionic strength was then adjusted with standardised sodium perchlorate solution. For reactions studied above 40°, aliquot portions were sealed in Pyrex tubes, placed in a thermostat, and withdrawn and frozen individually at the appropriate times. Reactions were studied at the lower temperatures by dissolving a weighed amount of the complex in a known volume of prepared solvent previously brought to the required temperature. The solution was replaced in the thermostat and samples were withdrawn for analysis when required. Spectrophotometric measurements were made by using silica cells and a Unicam SP 500 Quartz

<sup>9</sup> Cf. Krishnamurty and Harris, *Chem. Revs.*, 1961, **61**, 213, for references.

<sup>10</sup> Nyholm and Tobe, *J.*, 1956, 1707.



spectrophotometer. Polarimetric measurements were made with a Hilger and Watts Mark III polarimeter, a sodium lamp being used as light source.

The isotopic exchange experiments were carried out in the ways described above. Where the co-ordinated water was removed from the complex before analysis, about 0.2—0.3 g. of the complex was weighed into a Pyrex tube which was then connected to a collecting tube. Transfer of the solid was always carried out in a dry box since the finely divided material was hygroscopic. The assembly was evacuated and the walls of the connecting tube were flamed to remove adsorbed moisture. When evacuation was complete, the apparatus was isolated from the vacuum system and the collecting tube immersed in liquid air. The tube containing the complex was immersed in an oil bath which was then slowly heated to 80°. When most of the water had been driven over, the temperature was allowed to rise to 140° before heating was discontinued. If the heating is too strong some solid complex may be carried over in the water-vapour stream. When heating was complete, the tube containing the complex was reweighed and the loss of weight determined. This loss of weight always agreed with the loss of one mole of water per mole of complex. The specimen of water was then equilibrated with a small, known amount of carbon dioxide whose isotopic composition was then determined. As the mole ratio of water to carbon dioxide was >100:1 no correction for dilution was made.

All reactions were carried out in the absence of light.

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