763. *Mechanism and Steric Course of Octahedral Aquation. Part I. Aquation of some Halogeno- and Nitrato-amminebis(ethylenediamine)-cobalt(III) Ions.*

By M. L. Tobe.

Rates of aquation of *trans*-$[Co\ en_2(NH_3)NO_3]^{2+}$, *trans*-$[Co\ en_2(NH_3)Br]^{2+}$, and *trans*-$[Co\ en_2(NH_3)Cl]^{2+}$ have been measured over a range of temperature, and the Arrhenius parameters determined. In each case the initial product is *trans*-$[Co\ en_2(NH_3)H_2O]^{3+}$, which slowly isomerises to the *cis*-isomer. In no case was any *cis*-isomer formed directly. A mechanism is discussed in which hydrogen bonding between the incoming and the outgoing ligand is believed to play some part in lowering the activation energy.

Ašperger and Ingold [1] have studied the way in which the electron-displacing properties of the ligand A in complex ions of the type $[Co\ en_2ACl]^+$ (en = ethylenediamine) affect the rate of replacement of the chloride ion by water, and have suggested that the results may be explained by assuming a duality of mechanism. A conjugatively electron-donating group, such as HO or Cl, assists heterolysis of the Co–Cl bond, and promotes a unimolecular mechanism, designated as S_N1. Electron-withdrawing groups, such as H_3N^+ or O_2N, promote a bimolecular process (S_N2). The results indicate, furthermore, that bond-making is now much more important than bond-breaking, so that the transition state can be pictured as one in which both the incoming and the outgoing ligands are almost fully bound to the cobalt atom.

This paper is the first of a series in which these aquations will be examined in detail, in order to gain more insight into the factors controlling their mechanism and steric course. The complexes examined, namely, *trans*-$[Co\ en_2(NH_3)X]^{2+}$, where X = Cl, Br, or NO_3, are

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

expected, according to Ašperger and Ingold's suggestion, to undergo bimolecular aquation. This accords with Adamson and Basolo's suggested mechanism of aquation of chloro- and bromo-pentamminecobalt(III) cations;[2] for the replacement of four ammonia molecules by two molecules of ethylenediamine would not be expected to change the mechanism of the reaction. In the present work, *trans*-isomers were used, in order that the steric course of the reaction could be interpreted unambiguously.[3]

The aquation of *trans*-chloroamminebis(ethylenediamine)cobalt(III) salts has been examined before.[4,5] However, in the first investigation, the kinetics were not studied, and the analysis of the products did not take into account the rearrangement of the products; in the second, the kinetics were studied but no information on steric course was given.

The rate of isomerisation of the aquo-ammine product is dependent upon the pH of the solution, and by studying the aquation in 0·1N-perchloric acid it is possible to reduce the velocity sufficiently for the overall reaction to be treated as two consecutive first-order reactions with similar rate constants. It is then possible to distinguish between any appearance of the *cis*-aquoamminebis(ethylenediamine)cobalt(III) cation as a result of aquation and that formed by the rearrangement of the *trans*-isomer. Such an analysis of the overall reaction into its components, with determination of the steric course of the initial substitution by water, has been completed for the aquations of the *trans*-chloro-, -bromo-, and -nitrato-ammine cations mentioned above.

(1) *Isomerisation of the* trans-*Aquoamminebis*(*ethylenediamine*)*cobalt*(III) *Cation in Aqueous Solution*.—*trans*-Aquoamminobis(ethylenediamine)cobalt(III) nitrate, when heated in aqueous solution, rearranges to the *cis*-form. The solution, at equilibrium, contains no spectrophotometrically detectable amount of the *trans*-isomer. Further, an optically active sample of the *cis*-isomer racemises when heated in acidified aqueous solution very much more slowly than the *trans*- is converted into the *cis*-isomer.

The rate at which the *trans*-isomer rearranges in aqueous solution depends upon the concentration of the hydrogen ions. Table 1 gives the rate constants k_2 for the reaction *trans*-$[\text{Co en}_2(\text{NH}_3)\text{H}_2\text{O}]^{3+} \longrightarrow$ *cis*-$[\text{Co en}_2(\text{NH}_3)\text{H}_2\text{O}]^{3+}$ at different hydrogen-ion concentrations. The rate of isomerisation obeys the kinetic expression

$$-\text{d}[trans]/\text{d}t = 5{\cdot}5 \times 10^{-5}[trans] + 3{\cdot}4 \times 10^{-7}[trans]/[\text{H}^+]$$

for the range $0{\cdot}2\text{N} > [\text{H}^+] > 0{\cdot}002\text{N}$.

This acid-dependence is now being studied in more detail by Dr. D. F. Martin, and it seems that the kinetic form can be attributed to a very easy reaction path *via* the *trans*-hydroxoamminebis(ethylenediamine)cobalt(III) cation. If the pK of the *trans*-aquoamminebis(ethylenediamine)cobalt(III) cation is assumed to be about 6, it would follow that the first-order rate constant for the isomerisation of the *trans*-hydroxoammine complex ion is of the order of 10^{-1} sec.$^{-1}$ at 72·8°.

TABLE 1. *Rate constants for the rearrangement of trans*-$[\text{Co en}_2(\text{NH}_3)\text{H}_2\text{O})]^{3+}$ *at* 72·8°.

[The constant k_2 is obtained from the slope of the plot of log $(D_\infty - D_t)$ against time (t), where D_∞ is the optical density of the solution at 4800 Å, the subscripts referring to the time. The optical density of the solution after 10 half-lives was taken as D_∞ and corresponded very well with that expected for the pure *cis*-isomer.]

$[\text{H}^+]$ (N)	0·201	0·193	0·0426	0·0123	0·0026	no added acid
10^5k_2 (sec.$^{-1}$)	5·3 *	5·6	5·9	7·4	17·2	131 *

* Data refer to the perchlorate except that nitrate was used for this run.

(2) *Aquation of the* trans-*Chloroamminebis*(*ethylenediamine*)*cobalt*(III) *Cation*.—(2a) *Kinetics*. Nyholm and Tobe[5] reported rates of aquation of *trans*-$[\text{Co en}_2(\text{NH}_3)\text{Cl}]\text{Cl},\text{ClO}_4$

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[2] Adamson and Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.
[3] Brown, Ingold, and Nyholm, *J.*, 1953, 2674.
[4] Basolo, Stone, and Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 819.
[5] Nyholm and Tobe, *J.*, 1956, 1707.

at two temperatures. Since the reaction does not go to completion, the system was treated as if the reverse reaction was also of first order, and the first-order constant for the rate of approach to equilibrium was determined. This is equal to the sum of the constants for the forward and the back reaction. A knowledge of the position of equilibrium then gave the forward and the backward rate constants. This treatment is open to criticism, since the components present at equilibrium are the *cis*-isomers, and the back reaction has a second-order kinetic form. The results have been recalculated by using, for the value for the optical density at 3000 Å after " infinite time," that calculated for a similar solution containing only the aquoammine isomers, which have very similar extinction coefficients at this wavelength. The semilogarithmic plot then departs from linearity after about 40—50% reaction, but it is easy to measure the initial slope, and from it to calculate the true first-order rate constant for the aquation. These recalculations are reported in Table 2, together with the value obtained in this investigation at 72·8°.

TABLE 2. *Spectrophotometric first-order rate constants for the aquation of trans-*$[Co\ en_2(NH_3)Cl]^{2+}$ *in* 0·1—0·17N-$HClO_4$.

Temperature	89·9°	72·8°	62·6°	62·6°
$10^3 \times$ Initial [Complex] (M)	3·82	2·55	2·42	3·92
$10^5 k_1$ (sec.$^{-1}$)	41·7	8·12	2·88	2·90

(2b) *Steric course.* When this reaction was first studied by Nyholm and Tobe it was thought that the reversibility of the aquation, leading to an accumulation of some *cis*-chloroammine complex, would make impossible an accurate spectrophotometric determination of the isomeric distribution of the aquoammine species. It has since been shown, however, that such pessimism is unjustified, and that, provided the reaction is carried out in the presence of sufficient acid, a full spectrophotometric analysis is possible.

The absorption spectra of *trans*-chloroamminebis(ethylenediamine)cobalt(III) chloride perchlorate and *cis*- and *trans*-aquoamminebis(ethylenediamine)cobalt(III) bromides have already been published.[5] The full spectrophotometric analysis was carried out by determining the changes in the optical density of an aqueous solution of *trans*-chloroamminebis(ethylenediamine)cobalt(III) chloride perchlorate, 0·10N with respect to perchloric acid, at three wavelengths, 5220, 5070, and 3000 Å.

TABLE 3. *Molar extinction coefficients.*

Wave-length (Å)	*trans*-Chloroammine	*cis*-Aquoammine	*trans*-Aquoammine
5220	47·7	47·7	36·3
5070	43·2	58·6	43·2
3000	312	19	19·7

The relevant molar extinction coefficients are given in Table 3. The way in which these data were used can be illustrated in the following formula:

$$\%trans\text{-}[Co\ en_2(NH_3)H_2O]^{3+} = 100[(D_{5220}/cl) - 47{\cdot}7]/(36{\cdot}3 - 47{\cdot}7)$$

where D_{5220} is the optical density of the solution at 5220 Å, c is the initial concentration of the chloroammine complex, and l is the length of the light path. The percentage of *trans*-$[Co\ en_2(NH_3)Cl]^{2+}$ and of *cis*-$[Co\ en_2(NH_3)H_2O]^{3+}$ can be obtained from analogous formulæ using data at 3000 Å and 5070 Å, respectively.

TABLE 4. *Spectrophotometric analysis of trans*-$[Co\ en_2(NH_3)Cl]Cl.ClO_4$ *during its aquation at* 72·8°.

Initial concn. of *trans*-$[Co\ en_2\ (NH_3)Cl]^{2+}$ = 0·00255M. Hydrogen-ion concn. = 0·100N.

Time (min.)		0	21·2	40·5	60·0	90·5	124·5	165·0	210·0	268·0
% *trans*-$[(NH_3)Cl]$	calc.	100	90	82	75	64	54	45	36	27
	found	100	92	82	75	65	55	47	39	32
% *trans*-$[(NH_3)H_2O]$	calc.	0	9	16	23	30	37	41	43	43
	found	0	6	15	22	30	38	41	42	38
% (*cis*-$[(NH_3)H_2O]$	calc.	0	0	1	3	5	9	14	21	30
	found	0	0	0	0	4	8	15	20	31

Table 4 gives the result of the application of these formulæ to an actual run. The composition is given in terms of percentage of total amount of complex ion present. For the first 25% of the reaction, no *cis*-product has been detected. This is a very good indication that no *cis*-product is produced in the actual act of aquation, *i.e.*, that *trans*-$[Co\ en_2(NH_3)Cl]^{2+}$ gives 100% *trans*-$[Co\ en_2(NH_3)H_2O]^{3+}$ on reacting with water.

That the *cis*-product is formed only as a result of the rearrangement of the *trans*-aquoamminebis(ethylenediamine)cobalt(III) cation can be seen by comparing the experimental results with those calculated for a reaction of the form

$$\textit{trans}\text{-}[Co\ en_2(NH_3)Cl]^{2+} + H_2O \xrightarrow{k_1} \textit{trans}\text{-}[Co\ en_2(NH_3)H_2O]^{3+} + 8Cl^-$$

$$\textit{trans}\text{-}[Co\ en_2(NH_3)H_2O]^{3+} \xrightarrow{k_2} \textit{cis}\text{-}[Co\ en_2(NH_3)H_2O]^{3+}$$

where $k_1 = 8{\cdot}12 \times 10^{-5}$ sec.$^{-1}$ and $k_2 = 5{\cdot}70 \times 10^{-5}$ sec.$^{-1}$. These values were obtained experimentally by the methods outlined in sections (2*a*) and (1) respectively.

The agreement is good for the first half-life and then deviations appear. These can be directly related to the appearance of *cis*-chloroamminebis(ethylenediamine)cobalt(III) cations, produced by the back reaction. The spectrum of the solution after ten half-lives corresponds very closely to that of a mixture of 87% of *cis*-aquoammine complex and 13% of *cis*-chloroammine complex.

(3) *Aquation of the* trans-*Bromoamminebis(ethylenediamine)cobalt*(III) *Cation.*—(3*a*) *Kinetics.* The rate has been determined spectrophotometrically by following the changes in the optical density at 3000 Å. At this wavelength, the molar extinction coefficient of *trans*-$[Co\ en_2(NH_3)Br]S_2O_6$ is 960, much greater than the value of about 19 for both of the aquoammine products. It was therefore possible to determine the rate constants of the aquation accurately.

Since the aquation is reversible, it is not possible to follow it to completion. The values used for the optical density of a solution after "infinite time" (D_∞) were those calculated for a solution containing only the aquoammine isomers in the same concentration. The semilogarithmic plots do not depart significantly from linearity during the first two half-lives, so that it is a simple matter to determine the initial slopes.

The rate constants for the reaction, measured at three different temperatures, are given in Table 5.

TABLE 5. *First-order rate constants for the aquation of* *trans*-$[Co\ en_2(NH_3)Br]^{2+}$ *in* 0·1N-$HClO_4$.

10^4 × Initial [Complex] (M)	10^5k (sec.$^{-1}$)	10^4 × Initial [Complex] (M)	10^5k (sec.$^{-1}$)	10^4 × Initial [Complex] (M)	10^5k (sec.$^{-1}$)
At 72·8°		At 60·0°		At 45·0°	
1·36	37·4	1·36	9·6	1·04	1·57
2·69	38·7	2·69	9·5	2·08	1·63
5·38	37·9	5·38	9·4	5·21	1·64
29·5	38·5	26·9	9·2		

(3*b*) *Steric course.* The increase in the rate of aquation on going from the chloro- to the bromo-complex makes it easier to isolate the aquation from the subsequent rearrangement of the products. However, a consideration of the rate constants of the two reactions will show that the rearrangement will have made considerable progress before the initial aquation is complete.

The absorption spectrum of *trans*-$[Co\ en_2(NH_3)Br]S_2O_6$ is given in Fig. 1. When this was considered in conjunction with the spectra of the *cis*- and *trans*-products, it was found that an accurate full analysis, like that described in section (2*b*), was not possible. However, the *trans*-bromoammine- and the *trans*-aquoammine-bis(ethylenediamine)-cobalt(III) cations have the same molar extinction coefficients at 5170 Å ($\varepsilon = 38{\cdot}6$), whereas the *cis*-aquoammine complex ion absorbs more strongly ($\varepsilon = 50{\cdot}3$). It was therefore possible to calculate the amount of *cis*-aquoammine cation present at any stage.

Table 6 shows how ε_{5170} varies with time for a typical run. The amount of *cis*-aquoammine complex ion that is present is also calculated, and it is apparent that no *cis*-product is detected until after the first half-life of the reaction. This result is quite consistent with the assumption that the actual act of aquation produces only *trans*-aquoammine cations, and that the *cis*-aquoammine cations appear only as a result of subsequent rearrangement.

TABLE 6. *Appearance of* cis-*aquoamminebis(ethylenediamine)cobalt*(III) *cations in an aqueous solution originally containing* trans-*bromoamminebis(ethylenediamine)cobalt*(III) *dithionate.*

Temperature = 72·8°. Initial concn. of *trans*-[Co en$_2$(NH$_3$)Br]S$_2$O$_6$ = 0·00295M. Solvent = 0·10N-HClO$_4$.

Time (sec.)	0	300	600	900	1380	1980	2765	3600	4530
ε_{5170}	38·4	38·6	38·6	38·4	38·6	38·8	39·0	39·2	40·0
cis-Product (%)	0	0	0	0	0	2	3	5	12

(The half-life of the aquation under these conditions is 1800 sec., whereas the half-life of the rearrangement is 12,000 sec.)

(4) *Aquation of* trans-*nitratoamminebis(ethylenediamine)cobalt*(III) *Dithionate.*—(4a) *Kinetics.* The rates of aquation of this complex ion were determined spectrophotometrically at 3000 Å, by the method described previously. At this wavelength the molar extinction coefficient of the complex is 211. The change in the optical density of a solution in the course of the reaction is therefore much less than that found in the aquation of the corresponding *trans*-bromoammine complex, and thus the kinetics had to be studied at higher complex concentrations, where Beer's law was not strictly obeyed.

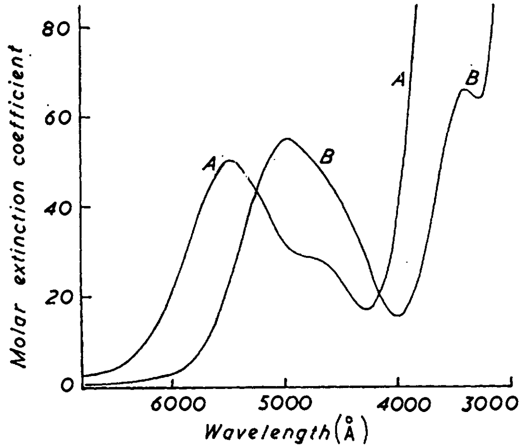


FIG. 1. *Absorption spectra of* (*A*) trans-[Co en$_2$(NH$_3$)Br]S$_2$O$_6$, *and* (*B*) trans-[Co en$_2$(NH$_3$)NO$_3$]S$_2$O$_6$ *in* 0·1N-*perchloric acid.*

The molar extinction coefficient at 3000 Å of a solution of the complex in 0·1N-perchloric acid was found to decrease according to a first-order rate law from 211 for the pure *trans*-nitratoammine complex to 35 after ten half-lives. Thereafter it decreased very slowly to a final value of 20 at a rate corresponding roughly to that of the isomeric rearrangement. The extra absorption (35 rather than 20), first observed in the solution which had reacted substantially to completion, may be due to the presence of small traces of the *trans*-nitroamminebis(ethylenediamine)cobalt(III) complex (ε ~800), which then decompose, in the presence of acid, at the rate of the observed slow optical change. These observations, however, are also consistent with the idea that there is some form of interaction between nitrate ions and the *trans*-aquoammine cation, resulting in an increase in the absorption of light in the near-ultraviolet region. Thus pure *trans*-[Co en$_2$(NH$_3$)H$_2$O](NO$_3$)$_3$ in the millimolar region of concentration has a molar extinction coefficient of 34 at 3000 Å, whereas that of the bromide and the perchlorate is 19. This effect was not observed with the *cis*-isomer.

Because of these observations, the first-order rate constants for the aquation were calculated by using the experimentally determined optical density of the solution after ten half-lives had passed, as "D_∞." The first-order rate constants are in Table 7.

TABLE 7. *First-order rate constants for the aquation of trans*-[Co $en_2(NH_3)NO_3]^{2+}$ *in* 0·1N-$HClO_4$.

10^4 × Initial [Complex] (M)	10^4k (sec.$^{-1}$)	10^4 × Initial [Complex] (M)	10^4k (sec.$^{-1}$)	10^4 × Initial [Complex] (M)	10^4k (sec.$^{-1}$)
At 60·0°		At 45·0°		At 30·0°	
3·40	6·5	3·83	1·05	9·43	0·142
8·51	6·6	9·43	1·04	13·2	0·141
11·93	6·7	13·4	1·05	19·2	0·141

(4b) *Steric course.* A full spectrophotometric analysis of the reaction mixture was not possible because of the spectra of the three species. {See Fig. 1 for the absorption spectrum of *trans*-[Co $en_2(NH_3)NO_3]S_2O_6$.} However, since the aquation is about fifty times faster than the rearrangement, such a treatment is not really necessary.

The absorption spectrum of an aqueous solution of *trans*-[Co $en_2(NH_3)NO_3]S_2O_6$ in 0·1N-perchloric acid, which had been kept at 60° for 3 hr (roughly ten half-lives), was found to correspond exactly to that expected for a solution containing aquoamminebis(ethylenediamine)cobalt(III) nitrate in the proportions of 95% of *trans*- to 5% of *cis*-isomer. The amount of *cis*-isomer found corresponded almost exactly to that which would have been formed by the rearrangement in this time.

DISCUSSION

Adamson and Basolo [2] studied the deuterium isotope effect upon the rate of the aquation of the chloro- and bromo-pentamminecobalt(III) cations, and concluded that the transition state corresponds to that expected for a bimolecular reaction with attack from that side of the octahedron which bears the outgoing group. The isotope effect was said to indicate that the reaction process is assisted by hydrogen-bonding between the outgoing ligand, the incoming water, and a *cis*-ammonia ligand (Fig. 2).

Ašperger and Ingold [1] have also discussed the nature of the transition state for bimolecular aquation with special reference to the isomeric [Co $en_2(NO_2)Cl]^+$ ions, and have also deduced attack adjacent to the outgoing group. In this case the evidence is very strong, being based on a study of the products of the reaction. The detailed mechanism, however, is quite different from that put forward by Adamson and Basolo. It is suggested that water, by virtue of the electronegativity of the oxygen, can make use of one of the empty 4*d* orbitals of the cobalt atom in order to establish its attack. In the transition state the water and the chlorine are each bound by a 3*d*4*d* hybrid orbital, so that the cobalt atom is making nearly seven full bonds. It is suggested that this process can be achieved most satisfactorily when the water and the chlorine are adjacent in the transition state, thus explaining the retention of configuration.

Our study of the aquation of the complex ions, *trans*-[Co $en_2(NH_3)X]^{2+}$, where X = Cl, Br, or NO_3, has shown conclusively that in all three cases aquation is accompanied by complete retention of configuration. This observation is very much in agreement with the mechanism but forward by Ašperger and Ingold, since the nature of the outgoing group would not be expected to influence the steric course of the reaction. If, on the other hand, it were hydrogen-bonding only that brought the incoming group into a position adjacent to the outgoing group, we might expect to find that, when ligands that do not readily form hydrogen bonds are replaced by water, non-adjacent attack is possible.

Examination of the Arrhenius parameters of the three reactions (Table 8) leads us to believe that Ašperger and Ingold's mechanism is responsible for the attack of water adjacent to the outgoing group, but that when hydrogen-bonding is possible it will lower the activation energy of the process. This is suggested by the circumstance that, along the series Cl, Br, NO_3, the activation energy increases, although the rate increases, and the free-energy decrement of the aquation, ΔG, as estimated from equilibrium composition, increases. This indicates that breakage of the Co–X bond has not proceeded far in the transition state, but that a stereospecific interaction between the incoming water and the outgoing group, in the order Cl > Br > NO_3 lowers the activation energy, and even more markedly lowers the entropy of activation. This can be understood in terms of hydrogen-bonding, provided that a reasonable suggestion can be made to account for the relative weakness with which the nitrato-group must be assumed to form a hydrogen bond. One possible suggestion is that the two terminal oxygen atoms of the nitrato-group have already taken advantage of their favourable position for hydrogen-bonding with adjacent ammino- or amino-ligands (Fig. 3).

TABLE 8. *Parameters of the equation,* $k = B \exp(-E^{\ddagger}/\boldsymbol{R}T)$ *for the reactions* *trans*-$[Co\ en_2(NH_3)X]^{2+} + H_2O = $ *trans*-$[Co\ en_2(NH_3)H_2O]^{3+} + X^-$

X	Cl	Br	NO_3
$E^{\ddagger}$ (kcal./mole)	23·6	24·6	25·5
$\log_{10} B$	10·9	12·0	13·5

FIG. 2.

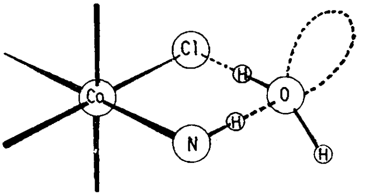
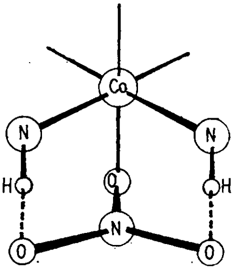


FIG. 3.



Whether one should assume that incoming water is hydrogen-bonded, not only through its hydrogen to the departing ligand, but also through its oxygen to a hydrogen atom, seems much more doubtful. There seems to be no specific evidence for this process, which retracts the unshared water electrons (Fig. 2) and turns their orbital away from the cobalt nucleus with which they have to combine.

The analogous system, $[Co(NH_3)_5X]^3$, where X = Cl, Br, or NO_3, has been investigated by a number of workers,[6] and the activation energies of the aquation are very similar to those of the acidoamminebis(ethylenediamine)cobalt(III) system. In general, the acidopentamminecobalt(III) cations aquate at rates that are higher than those of the corresponding ethylenediamine complexes. This increased rate has been attributed to the more compact solvent shell about the pentammine complex.[7]

EXPERIMENTAL

Preparations.—*trans*-Chloroamminebis(ethylenediamine)cobalt(III) chloride perchlorate was prepared by the method of Nyholm and Tobe [5] (Found: Co, 16·6%; equiv., 120. Calc. for $C_4H_{19}O_4N_5Cl_3Co$: Co, 16·1%; equiv., 122).

trans-Aquoamminebis(ethylenediamine)cobalt(III) nitrate was prepared by Nyholm and Tobe's method [5] (Found: Co, 14·6. Calc. for $C_4H_{21}O_{10}N_8Co$: Co, 14·7%).

trans-Nitroamminebis(ethylenediamine)cobalt(III) nitrate and bromide, the starting materials

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[6] References from Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley and Sons, Inc., New York, 1958, p. 122.

[7] Ašperger and Ingold, *J.*, 1956, 2872.

for the following preparations, were prepared by the action of liquid ammonia on *trans*-chloronitrobis(ethylenediamine)cobalt(III) nitrate as described by Werner.[8]

trans-Bromoamminebis(ethylenediamine)cobalt(III) dithionate was prepared by digesting *trans*-nitroamminebis(ethylenediamine)cobalt(III) bromide with bromine-free, hydrobromic acid (40%) on a steam-bath until no more NO_2 was evolved. On evaporation of the mixture to dryness, a mixture of the *cis*- and the *trans*-bromoamminebis(ethylenediamine)cobalt(III) bromide was obtained. It was possible to obtain the *trans*-isomer in a pure form by fractional crystallisation, but this is tedious and results in very small yields. It was found that, if a solution of the mixed bromides was treated with sodium dithionate, the insoluble *trans*-bromoamminebis(ethylenediamine)cobalt(III) dithionate was precipitated first. The dithionate was recrystallised from hot water and obtained as fine pale purple needles (Found: Br, 18·5; Co, 14·0%; equiv., 148. Calc. for $C_4H_{19}O_6N_5S_2BrCo$: Br, 18·3; Co, 14·5%; equiv., 145).

trans-Nitratoamminebis(ethylenediamine)cobalt(III) dithionate was prepared in an analogous way. *trans*-Nitroamminebis(ethylenediamine)cobalt(III) nitrate (24 g.) was added slowly to a hot (85°) 6N-solution of nitric acid (80 ml.), and the mixture was kept at this temperature until the evolution of NO_2 slackened. The solution was then decanted into an evaporating basin, and heated upon a steam-bath until the evolution of NO_2 had almost ceased. It is essential to steer between insufficient reaction, on one hand, when the product will be seriously contaminated with unchanged nitro-complex, and too much reaction, on the other, when low yields are obtained, because the product rearranges to the *cis*-form, and also because dinitrato-complexes are formed.

The very thick syrup was allowed to cool, and was then dissolved in water (60 ml.) at 30°. The solution was filtered, and the filtrate treated with solid sodium dithionate (6 g.). An orange-pink precipitate consisting almost entirely of *cis*-nitratoamminebis(ethylenediamine)-cobalt(III) dithionate came down. The mixture was left for 24 hr., and the product filtered off (11·5 g.). Sufficient solid sodium acetate was added to the filtrate to raise the pH to 5, and then sodium dithionate was added to saturate the solution. Needle-shaped crystals of *trans*-nitratoamminebis(ethylenediamine)cobalt(III) dithionate started to separate. The mixture was left at 0° for 24 hr., and the *trans*-isomer, together with some sodium dithionate, was filtered off, washed with water to remove the sodium dithionate, and recrystallised as quickly as possible from water at 60° (yield 1·5 g). The salt, dried over calcium chloride, is anhydrous (Found: equiv., 140. Calc. for $C_4H_{19}O_9N_6S_2Co$: equiv., 139).

Analytical Procedures.—(a) *Equivalent weight.* About 0·1 g. of the complex was weighed out accurately and suspended, or dissolved, in 10 ml. of water and treated with excess of alkali. The solution containing $[Co\ en_2(NH_3)OH]^{2+}$ was passed through a column of Amberlite IR-120 resin in the acid form. The cationic species were replaced by hydrogen ions, and the effluent was titrated with standard sodium hydroxide. Since the complex ion is retained on the resin in the aquo-form, one mole of the complex will liberate 3 equiv. of acid.

(b) *Halogen determination.* The effluent from the above treatment was also analysed argentometrically for the halogen originally present in the complex.

(c) *Cobalt determination.* About 0·1 g. of the complex was weighed out and dissolved in 20 ml. of N-ammonia solution. The solution was heated to 60° and hydrogen sulphide was passed through it until all the cobalt had been precipitated as its sulphide, which was filtered off and roasted. The cobalt was then estimated iodometrically by Laitinen and Burdett's method.[9]

Methods of Measurement.—Spectrophotometric measurements were made by using a 4 cm. silica cell and a Unicam SP.500 spectrophotometer.

The methods used to make up the solutions for kinetic measurements require mention. *trans*-$[Co\ en_2(NH_3)Cl]Cl.ClO_4$ is quite soluble in water: the reaction solution could thus be made up by adding the appropriate amount of water and perchloric acid to a weighed out amount of complex. *trans*-$[Co\ en_2(NH_3)Br]S_2O_6$ is nearly insoluble in water, and was therefore handled as follows. The appropriate amount of complex (0·1 g.) was weighed into a standard flask, and 1·0 ml. of 72% perchloric acid was added. This caused the salt to dissolve, the dithionate group being destroyed and sulphur dioxide evolved. The flask was evacuated with a water pump in order to remove as much as possible of the sulphur dioxide, and the volume was made up to 100 ml. with distilled water. This solution was then used as a stock solution, and diluted

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[8] Werner, *Annalen*, 1912, **386**, 227.

[9] Laitinen and Burdett, *Analyt. Chem.*, 1952, **23**, 1268.

as required. The appropriate amount of 1·00N-perchloric acid was added at this stage, so as to maintain the pH at 1. There was no difference in the absorption spectrum of a solution so prepared and that of a solution of the bromide prepared and purified by another method, less convenient than that here described. The treatment, therefore, had no effect upon the complex ion. *trans*-[Co $en_2(NH_3)NO_3]S_2O_6$, although insoluble in water, will dissolve in 0·1N-perchloric acid. The appropriate amount of complex was weighed out, and suspended in 10. ml. of water; then 1 ml. of 72% perchloric acid was added to dissolve the complex. (This is quite a good way of distinguishing the *trans*-isomer from the *cis*-, which remains undissolved after this treatment.)

After the appropriate solution had been made up to volume, aliquot parts of about 11 ml. were sealed into clean, dry, Pyrex test-tubes. These were placed in a thermostat, and individual tubes were withdrawn at intervals and cooled as quickly as possible in ice. The contents were then allowed to warm to room temperature and poured into the spectrophotometer cell for measurement.

Thermostats held the temperatures constant to ±0·05°. Light was excluded, either by using Ucepal baths or, at the lower temperatures, by adding Nigrosine Black to the water in the bath.

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