836. *Mechanism and Steric Course of Octahedral Aquation. Part II.* Aquation of Chloro- and Bromo-isothiocyanatobisethylenediamine-cobalt*(III) *Salts.*

By M. E. BALDWIN and M. L. TOBE.

The kinetics of the aquation of *cis*-chloro- and *cis*-bromo-isothiocyanatobisethylenediaminecobalt(III) cations have been examined and the Arrhenius parameters determined. Both reactions yield only the *cis*-product. The factors causing the unusually large difference between the rates of aquation and the steric courses for the *cis*- and the *trans*-isomers are discussed. The steric course of aquation of *trans*-$[\mathrm{Co\,en_2\,NCS,Cl}]^+$ as well as of reaction between hydroxide ions and *l-cis*-$[\mathrm{Co\,en_2\,NCS,Cl}]^+$ is also reported.

MATHIEU[1] found that the change of the optical rotatory power of a solution of *l-cis*-$[\mathrm{Co\,en_2\,NCS,Cl}]\mathrm{Cl}$ could be split into two stages, first a mutarotation corresponding to the reaction

$$l\text{-}cis\text{-}[\mathrm{Co\,en_2\,NCS,Cl}]^+ + \mathrm{H_2O} \longrightarrow l\text{-}cis\text{-}[\mathrm{Co\,en_2\,NCS,OH_2}]^{2+} + \mathrm{Cl^-}$$

and, secondly, racemisation of the optically active aquo-cation. Although Mathieu did not publish rate constants for the aquation it was possible to obtain an order of magnitude for the first-order rate constant of the mutarotation and this proved to be very much greater than the rate constant for the aquation of the corresponding *trans*-cation.[2] Mathieu furthermore claimed that the product of the mutarotation was exclusively the *cis*-aquoisothiocyanatobisethylenediaminecobalt(III) cation but published an absorption spectrum virtually identical with that of the equilibrium mixture containing 85% of the *cis*-isomer.[2] The kinetics and the steric course of the aquation have been re-investigated, in an attempt to reveal why the *cis*-isomer is so much more reactive than the *trans*-isomer and whether, in fact, there is complete retention of configuration.

RESULTS

(1) *Aquation of the* cis-*Chloroisothiocyanatobisethylenediaminecobalt*(III) *Cation*.—(a) *Kinetics*. The aquation of the *cis*-chloroisothiocyanatobisethylenediaminecobalt(III) perchlorate was followed by a number of complementary methods. It was not possible to use the most direct method, namely, titration of the released chloride ions, because silver ions combine strongly with the co-ordinated thiocyanato-group.[1] Further, mercuric ions catalyse replacement of both chloride and thiocyanate groups by water.[3] Although we have since developed a method using ion-exchange resins whereby the complex cations can be instantly and cleanly removed from the solution, leaving the anions as either the free acid or the sodium salt, this technique was not available for this investigation. Aquoisothiocyanatobisethylenediaminecobalt(III) cations, however, act as weak acids and can be titrated with sodium hydroxide: the rate constants determined thus will be designated " titrimetric."

The aquation leads to an increase in the number of conducting species in solution, so the rate constants can be determined from the change in conductivity of a solution containing initially only *cis*-chloroisothiocyanatobisethylenediaminecobalt(III) perchlorate and perchloric acid. The rate, as well as the kinetic form, of the aquation depends on the nature of the electrodes used. Platinum black electrodes catalysed the early part of the aquation although the final conductivity and absorption spectrum of a solution, after ten half-lives had elapsed, were the same whether or not the electrodes were present throughout the reaction. The change in conductivity, when measured with shiny platinum electrodes, followed a first-order rate law and the rate constants were identical with those determined titrimetrically. These rate constants will be designated " conductimetric."

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* Part I, *J.*, 1959, 3776.

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

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

[3] Tobe, unpublished work.

The different absorption spectra of the products and the starting compound made it possible to determine the rate constants for aquation from the change in the optical densities of a solution originally containing only *cis*-chloroisothiocyanatobisethylenediaminecobalt(III) perchlorate. This method is, however, affected by subsequent rearrangement of the products, and determination of the optical densities for full reaction is not possible. Since other methods were available to determine the rate constants the spectrophotometric measurements were used mainly in conjunction with polarimetric and titrimetric measurements in order to determine the steric course of the reaction.

Table 1 contains the rate data for a number of temperatures. k_1 is obtained from the slope of the linear part of the plot of $\log_{10}(V_\infty - V_t)$ against time (V_t = volume of standard sodium hydroxide required to neutralise the aquo-complex) for the titrimetric runs, or $\log_{10}(C_\infty - C_t)$ against time (C_t = conductivity of the reacting solution). V_∞ and C_∞ were experimental values determined after ten half-lives and corresponded to the values expected if the reaction, went to completion. The spectrophotometric rate constants were obtained from the slope of $\log_{10}(\varepsilon_\infty - \varepsilon_t)$ against time, where ε_t was the apparent extinction coefficient of the solution at 4900 Å at time t and ε_∞ was the extrapolated extinction coefficient for 100% reaction (=218) obtained by the method described in section 1b.

TABLE 1. *First-order rate constants for aquation of* cis-*chloroisothiocyanatobisethylenediaminecobalt*(III) *perchlorate.*

Temp.	Initial [Complex] (10^{-3}M)	$10^4 k_1$ (sec.$^{-1}$)	Method	Temp.	Initial [Complex] (10^{-3}M)	$10^4 k_1$ (sec.$^{-1}$)	Method
75·1°	2·67	17·0	C	55·0°	6·40	3·08	C
,,	5·15	17·1	C	,,	9·75	3·08	C
				,,	2·72	3·08	S
70·0	2·29	10·8	C				
,,	4·85	10·6	C	50·0	3·78	1·68	T
65·0	3·45	7·00	C	45·0	3·16	0·98	T
,,	3·52	6·92	C	,,	3·43	1·11	T
,,	4·86	6·52	T	,,	3·56	1·11	S
,,	2·14	7·03	S				
,,	3·67	6·80	S	25·0	3·84	0·114	C

Although a solution of either *cis*- or *trans*-[Co en_2 NCS,Cl]$^+$, when heated until there is no further change, yields an equilibrium mixture containing both the aquo- and the chloro-isothiocyanato-species such that

$$[\text{Co en}_2\ \text{NCS,OH}_2{}^{2+}][\text{Cl}^-]/[\text{Co en}_2\ \text{NCS,Cl}^+] = 0{\cdot}15\ \text{mole l.}^{-1}\ \text{at}\ 70°,$$

where [Co en NCS,$\text{OH}_2{}^{2+}$] represents the total concentration of all the aquoisothiocyanato-complex ions and [Co en_2 NCS,Cl^+] represents the total concentration of all the chloroisothiocyanato-species, it has been found that the chloroisothiocyanato-species is exclusively in the *trans*-form. The back-reaction is much slower than aquation of the *cis*-isomer, and the assumption that it goes to completion is justified. Subsequent re-entry of some of the chloride ions can be observed if the reaction is studied for sufficient time.

(b) *Steric course.* Because of the similarity of the spectra of the *cis*-chloroisothiocyanatobisethylenediaminecobalt(III) and *cis*- and *trans*-aquoisothiocyanatobisethylenediaminecobalt(III) cations, a full spectrophotometric analysis is not possible. Since, however, the rate of isomerisation of the products is considerably less than that of the initial aquation such an analysis is not necessary and the steric course was determined in the following way.

A kinetic run was followed simultaneously by a titrimetric and a spectrophotometric technique. The quenched samples were first examined spectrophotometrically and the optical density was determined at 4900 Å, the wavelength of the absorption maximum of the *cis*-[Co en_2 NCS,OH_2]$^{2+}$ cation. A 10·0 ml. portion of the same sample was then titrated with standard sodium hydroxide and the extent of aquation determined. The apparent molar extinction coefficient (D/Cl, where D = optical density, C = total concentration of complex ion, and l = length of the light path) was plotted against % reaction. The curve, shown in Fig. 1, is initially a straight line; later, isomerisation of the product becomes important and the slope decreases as a result of the presence of the *trans*-aquoisothiocyanato-cation which absorbs less light than the *cis*-isomer at the wavelength used. Extrapolating the first linear portion to 100% reaction gives the molar extinction coefficient of the initial product. The value (218) obtained compares well with that (216) obtained for pure *cis*-[Co en$_2$ NCS,OH$_2$]S$_2$O$_6$. The *trans*-isomer has an extinction coefficient of 100 at this wavelength.

As the *cis*-aquoisothiocyanatobisethylenediaminecobalt(III) cation has not yet been resolved into a solid crystalline optically active salt it is not possible to find its specific molar rotation. Mathieu, however, measured the rotatory dispersion and circular dichroism of a solution of *l-cis*-[Co en$_2$ NCS,Cl]Cl that had fully aquated and concluded from his observations that the aquo-product, *d-cis*-[Co en$_2$ NCS,H$_2$O]$^{2+}$, has the same configuration as the starting complex. The specific molar rotation of the product of the aquation was determined at 5400 Å by plotting the apparent specific molar rotation of a solution originally *l-cis*-chloroisothiocyanatobisethylenediaminecobalt(III) perchlorate as a function of time. A rough value of $[M]_{5400} = +2700°$ was obtained by extrapolating the racemisation part of the curve to zero time. This approximate value is sufficiently large to indicate that there has been little, if any, change in configuration as a result of the aquation reaction.

FIG. 1. *The change of apparent molar extinction coefficient at* 4900 Å *of a solution originally containing cis*-[Co en$_2$ NCS,Cl]ClO$_4$, *as aquation proceeds.*

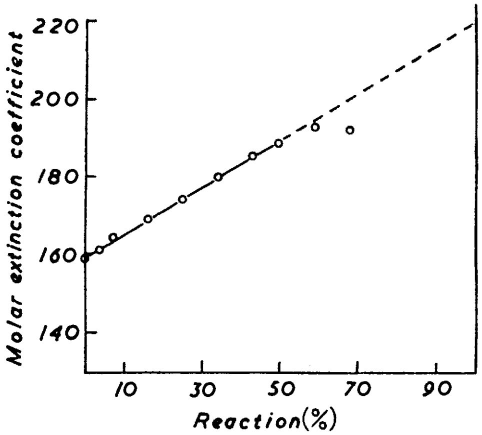
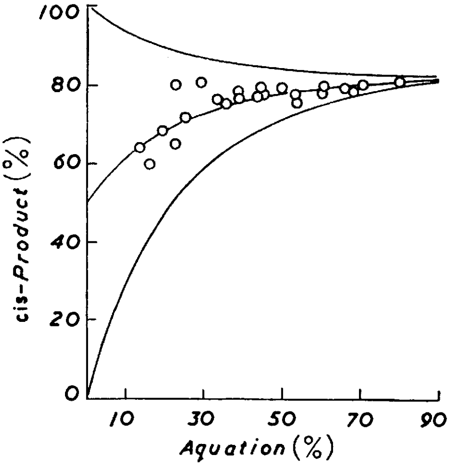


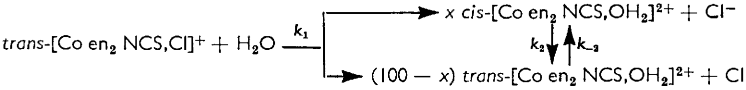
FIG. 2. *Isomeric composition of the* [Co en$_2$ NCS,OH$_2$]$^{2+}$ *produced at different stages of the aquation of trans*-[Co en$_2$ NCS,Cl]$^+$ *at* 70·6°.



The circles represent experimental results. The curves are calculated for trans ⟶ 0% cis, 50% cis, *and* 100% cis *in the initial act of aquation.*

(2) *The Steric Course of the Aquation of* trans-*Chloroisothiocyanatobisethylenediaminecobalt*(III) *Perchlorate.*—In the first study [2] it was found that the rate constant for the approach of the products to isomerisation equilibrium was about ten times faster than that for aquation of the *trans*-chloroisothiocyanato-complex. Product analyses gave a roughly constant value of about 80% of *cis*-product throughout the reaction and at the time it was thought that this value was due to the equilibration of the product. However, the steric course of such aquations has become an important factor in the understanding of the mechanism of aquation and for this reason these results have been re-examined in detail.

Owing to the relatively fast rearrangement of the aquo-products the ratio of *cis* : *trans*-isomers in the product depends on the steric course of the reaction only during the early stages. Later the ratio is controlled by the isomerisation equilibrium. It is not possible to obtain significant experimental results at the very early stages of the reaction because, there, expression of the product composition in terms of a *cis* : *trans*-ratio greatly magnifies the experimental error. In order to see whether it was at all possible to determine the steric course of this aquation, a family of curves of % reaction against % of *cis*-product (x) varying from 0 to 100% in intervals of 10%, was plotted for a reaction sequence of the type:



$$\begin{tikzcd} & x\ cis\text{-}[\mathrm{Co\ en_2\ NCS,OH_2}]^{2+} + \mathrm{Cl}^- \arrow[d, shift left, "k_2"] \\ trans\text{-}[\mathrm{Co\ en_2\ NCS,Cl}]^{+} + \mathrm{H_2O} \arrow[ur, "k_1"] \arrow[dr] & \\ & (100 - x)\ trans\text{-}[\mathrm{Co\ en_2\ NCS,OH_2}]^{2+} + \mathrm{Cl}^- \arrow[uu, shift left, "k_{-2}"] \end{tikzcd}$$

the known values of k_1, k_2, and k_{-2} being used. Fig. 2 shows some of these curves together with experimental values obtained at 70·6°. It is seen that at less than 20% reaction, the experimental error in determining the amount of *cis*-product is too great for the data to be of significance. When the reaction is more than 40% complete the product composition is controlled almost entirely by the thermodynamic equilibrium of the two aquoisothiocyanato-isomers. However, in the region between 20% and 40% reaction, the analysis is sufficiently accurate and the method sufficiently sensitive for a rough estimation of the steric course to be possible.

The product analyses were carried out spectrophotometrically. Optical densities were measured at 5800, 5300, and 4900 Å and the concentrations of *trans*-$[\mathrm{Co\ en_2\ NCS,Cl}]^+$, *trans*-$[\mathrm{Co\ en_2\ NCS,OH_2}]^{2+}$, and *cis*-$[\mathrm{Co\ en_2\ NCS,OH_2}]^{2+}$ calculated as previously described.[2]

The theoretical curves of Fig. 2 were calculated by means of formulæ derived for the study of the aquation of *trans*-bromoisothiocyanatobisethylenediaminecobalt(III) perchlorate,[2] with the values $k_1 = 4{\cdot}00 \times 10^{-5}$ sec.$^{-1}$, $k_2 = 0{\cdot}64 \times 10^{-4}$ sec.$^{-1}$, and $k_{-2} = 2{\cdot}93 \times 10^{-4}$ sec.$^{-1}$ (temp. 70·6°).

Fig. 2 shows that the initial product of the aquation of *trans*-$[\mathrm{Co\ en_2\ NCS,Cl}]^+$ contains at least 50% of the *cis*-aquoisothiocyanato-isomer. There is probably even more steric change but the method is far less sensitive for the fixing of the upper limit.

(3) *The Steric Course of the Reaction between Hydroxide ions and* l-cis-*Chloroisothiocyanatobisethylenediaminecobalt*(III) *Perchlorate in Water.*—This reaction was studied by Ingold *et al.*[2] who used the racemic *cis*-complex ion. It is now possible to extend the study to the optically active form of the cation. The reaction between the *cis*-$[\mathrm{Co\ en_2\ NCS,Cl}]^+$ cation and hydroxide ions is sufficiently fast for the steric course to be determined by analysing a solution acidified after the reaction had run to completion. The acidification, which converts the hydroxo-complex into the aquo-complex, takes place with complete retention of configuration, and analysis of the aquo-complex can be directly related to the composition of the original hydroxo-complex mixture. For a full analysis of the product it is necessary to know the specific molar rotatory power of a pure *cis*-aquoisothiocyanatobisethylenediaminecobalt(III) enantiomorph. As this is not available the values used in calculation are those obtained from a study of the aquation of a fully resolved specimen of *l-cis*-$[\mathrm{Co\ en_2\ NCS,Cl}]^+$, the method outlined in section (1b) being used. Although there is no direct proof that aquation is accompanied by full retention of configuration these calculations give a minimum value for the amount of *cis*-product with inverted configuration. The results are given in Table 2.

TABLE 2. *Proportions in which* d-cis-, l-cis,- *and* trans-*hydroxoisothiocyanatobisethylenediaminecobalt*(III) *cations are formed in the reaction of hydroxide ions with* l-cis-*chloroisothiocyanatobisethylenediaminecobalt*(III) *perchlorate in water at* 0°.

	ε_{4900}		$[M]_{5400}$
cis-Aquo-cation	216	*d-cis*-Aquo-cation	+2700°
trans-Aquo-cation	100	Aquo-cation mixture	+875
Aquo-cation mixture	193		

Formed hydroxo-isomers = Final aquo-isomers =		
	d-cis (Configuration retained)	56%
	l-cis (Configuration inverted)	24%
	trans	20%

(4) *The Aquation of* cis-*Bromoisothiocyanatobisethylenediaminecobalt*(III) *Bromide.*—(a) *Steric course.* Preliminary observations of the aquation of the *cis*-$[\mathrm{Co\ en_2\ NCS,Br}]^+$ cation indicated that aquation was considerably faster than isomerisation of the aquo-products, thus facilitating direct spectrophotometric analysis of the products at the completion of the reaction. Fig. 3 shows how the absorption spectrum of a solution originally containing *cis*-bromo-bromide changes as aquation proceeds. The isosbestic points observed are common to the spectrum of pure *cis*-aquoisothiocyanatobisethylenediaminecobalt(III) dithionate measured under similar conditions. It follows that aquation of *cis*-bromoisothiocyanatobisethylenediaminecobalt(III)

ions yields 100% of *cis*-product which then slowly isomerises. In the absence of data for optically active *cis*-[Co en_2 NCS,Br]$^+$ cation it is not possible to say whether there is complete retention of configuration in the aquation.

(b) *Kinetics.* Aquation of the *cis*-bromoisothiocyanatobisethylenediaminecobalt(III) cation was followed spectrophotometrically. The isomerisation of the products, that made the spectrophotometric method applicable only to the first stages of aquation of the *cis*-chloroisothiocyanato-complex, did not cause any difficulty in this case because the faster aquation, the high activation energy of the isomerisation [4] (28 kcal. mole^{-1}), and the lower temperatures of the investigation combined to separate the rates of the two processes.

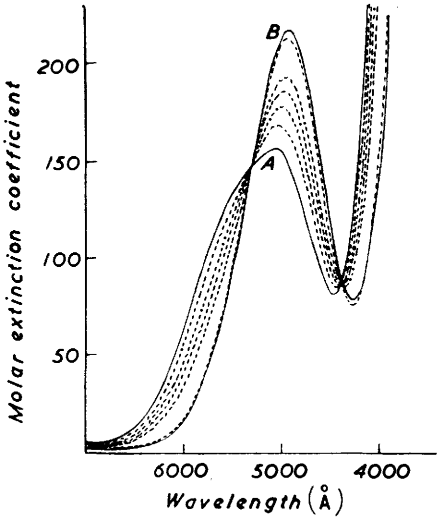


FIG. 3. *The change in the spectrum of an acidified solution of* cis-[Co en_2 NCS,Br]ClO_4.

A = pure cis-[Co en_2 NCS,Br]ClO_4. *B = pure cis*-[Co en_2 NCS,OH_2]S_2O_6,$3H_2O$. *Intermediate curves, read upwards from A, are for* 90, 150, 270, 360, *and* 1440 *min., respectively, at* 30°.

The method used to compute the rate constants differed in practice, but not in principle, from that used in section (1a). Measurements were made at 4800, 5700, 4100, 4000, 5280, and 4380 Å. At the first of these the absorption increases as the reaction proceeds (see Fig. 3), and at the next three it decreases. The last two wavelengths are those of the two isosbestic points and the constancy of the absorption at these wavelengths was used as a check on the method. The solution was assumed to contain only two absorbing species, the *cis*-bromo- and the *cis*-aquo-isothiocyanatobisethylenediaminecobalt(III) cations. The fraction (x) of reaction completed was determined at each of the first four wavelengths by using the expression, $x = (\varepsilon - \varepsilon_1)/(\varepsilon_2 - \varepsilon_1)$, where ε is the apparent molar extinction coefficient of the solution at time t, ε_1 is the extinction coefficient of the starting compound, and ε_2 the extinction coefficient of the product. The values of x determined at each of these wavelengths were averaged and the mean was used in calculating the rate constants (Table 3). The temperature-dependence of the rate constants can be summarised by the expression, $k_1 = 2{\cdot}1 \times 10^{12} \exp -23{,}100/\boldsymbol{RT}$.

TABLE 3. *First-order rate constants* (k_1) *for the aquation of* cis-*bromoisothiocyanatobisethylenediaminecobalt*(III) *bromide.*

[k_1 is determined from the slope of the plot of $\log_{10}(1 - x)$ against time. Solvent: 4×10^{-3}N-perchloric acid.]

Temp.	Initial [Complex] (10^{-3}M)	10^4k_1 (sec.$^{-1}$)	Temp.	Initial [Complex] (10^{-3}M)	10^4k_1 (sec.$^{-1}$)	Temp.	Initial [Complex] (10^{-3}M)	10^4k_1 (sec.$^{-1}$)
59·95°	0·598	13·4	43·30°	0·480	2·37	29·95°	0·520	0·469
,,	1·04	13·9	,,	0·989	2·36	,,	0·914	0·451
,,	3·03	13·6	,,	2·89	2·36	,,	3·13	0·455

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[4] Baldwin and Tobe, unpublished work.

DISCUSSION

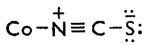
Ašperger and Ingold [5] showed the effect of a non-participating group A on the rate of replacement of a chlorine ligand by water in complex ions $[Co\ en_2\ A,Cl]^{n+}$ to depend on the electron-displacing properties of group A, and Basolo [6] extended the data. No attempt was made to distinguish between the behaviour of *cis*- and *trans*-isomers, since, from the results available, the configuration seemed to have only a small effect on the rate of aquation of the complex ion, the maximum difference being only a factor of 10. Ingold [7] later showed that, although the rate of aquation was slightly more sensitive to the influence of a *trans*- than of a *cis*-group A, the electron-displacing properties of A had a similar effect for the two isomers.

The chloro- and bromo-isothiocyanatobisethylenediaminecobalt(III) isomers do not fit into such an arrangement. Table 4 contains the relevant Arrhenius parameters, the rate constants either measured or extrapolated for the reaction at 25°, and the product analysis.

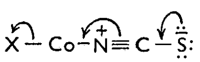
TABLE 4. *First-order rate constants $k_1 = B \exp(-E/\mathbf{R}T)$, Arrhenius parameters, and products of the aquation of* cis- *and* trans-$[Co\ en_2\ NCS,X]^+$ *cations.*

Group replaced	k_1 at 25° (sec.$^{-1}$)	E (kcal./mole^{-1})	$\log_{10} B$	*cis*-Product (%)
cis-Cl	$1{\cdot}1 \times 10^{-5}$	20·8	10·3	100
trans-Cl	5×10^{-8}	30·4	14·9	50—70
cis-Br	$2{\cdot}3 \times 10^{-5}$	23·1	12·3	100
trans-Br	5×10^{-7}	30·1	15·3	45

The two chloro-isomers differ in reactivity by a factor of 200 at 25° and there is an unusually large difference in their activation energies (~10 kcal. mole^{-1}), which is only partially compensated by a more favourable entropy term for the *trans*-isomer. These differences are also found between *cis*- and *trans*-bromoisothiocyanato-complexes but they are less marked. It is interesting that the rate constants for the exchange of the co-ordinated water in the $[Co\ en_2\ NCS,OH_2]^{2+}$ cation with isotopically labelled solvent do not show this great difference and are of the same order of magnitude for the *cis*- and the *trans*-isomer.[4] These results can be understood on the following bases. The co-ordinated thiocyanate group in these complexes can be satisfactorily represented by the structure (I).[5] The formal positive charge on the nitrogen would be expected to produce an inductive withdrawal of electrons from the cobalt, a (—*I*) effect, but there is a ready path (see II) whereby one of the lone pairs on the sulphur can conjugate with the breaking of the Co–X bond.

(I) 

$Co-\overset{+}{N}\equiv C-\ddot{\underset{..}{S}}:$

 (II)

This electromeric (+*T*) effect will be far more important than the inductive effect in determining the mechanism of aquation. All four isomers reported in Table 4 are expected to aquate by means of an S_N1 mechanism. This assignment is clear in the case of the *cis*-isomers,[7] but since the *trans*-isomers are border-line cases the assignment is based on the steric course of the reactions. Preliminary experiments have shown that *trans*-$[Co\ en_2\ Cl_2]^+$ and *trans*-$[Co\ en_2\ OH,Cl]^+$ will be aquated with considerable change of configuration whereas for *trans*-$[Co\ en_2\ NH_3,Cl]^{2+}$ [11] and *trans*-$[Co\ en_2\ NO_2,Cl]^+$ [5] there will be full retention of configuration. Since the assignment of an S_N1 mechanism to the first pair of cations and an S_N2 mechanism to the second pair of cations is more reliable there is a reasonable basis for the assumption that *trans*-$[Co\ en_2\ NCS,Cl]^+$ and *trans*-$[Co\ en_2\ NCS,Br]^+$ will be aquated unimolecularly.

The considerable difference in the reactivity of the halogenoisothiocyanato-isomers

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

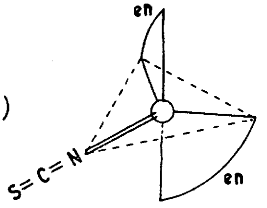
[6] Basolo, *Record Chem. Progr.*, 1957, **18**, 1.

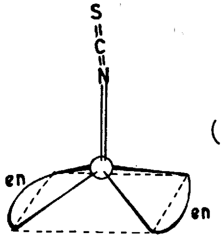
[7] Ingold, " Theoretical Organic Chemistry," Kekulé Symposium, Butterworths, London, 1959, p. 98.

can be explained in terms of the transmission of the (+*T*) effect to the reaction centre. This can be visualised as the feeding in of another lone pair of electrons from the thiocyanate ligand into the orbital being vacated by the outgoing group.

When the group is *cis* to the outgoing group there is adequate overlap without any change in the relative positions of the five ligands. This results in a square pyramidal transition state and should lead to complete retention of configuration, which is borne out by experiment. When the thiocyanate ligand is in the *trans*-position it will be unable to provide this (+*T*) effect until there is a change in configuration. For this change, two, or even all four, of the ligands *cis* to the outgoing group could move round towards it as it starts to leave, forming a trigonal bipyramidal (III) or distorted square pyramidal (IV) transition state. Since there is no other initial driving force both of these transition states will require a high activation energy. This distortion may lead to " release " of some of the solvating water on the side of the complex *trans* to the outgoing group, facilitating the reaction by the gain in entropy. Both these transition states would lead to a considerable amount of change in configuration as a result of the reaction and this is in fact found. It may be possible that these isothiocyanato-complexes behave normally and the other ligands that labilise through a (+*T*) effect, *e.g.*, Cl and HO, are abnormal. In both these cases, and for chlorine especially, the initially non-bonding lone pairs on the donor atom may provide a type of inductive filled-shell repulsion through the d_{xy} filled orbital of the cobalt to initiate the departure of an outgoing *trans*-group and so enable the (+*T*) effect to operate. Work now in progress on these complexes seems to support this idea. An additional effect, contributing to the lability of the *cis*-[Co en$_2$ NCS,Cl]$^+$ cation alone, is the possibility that the *cis*-isothiocyanate group helps to orient a solvating water molecule, which may form a hydrogen bond with the chlorine and assist its dissociation. This may be the reason for the extraordinarily low activation energy and also for the loss of entropy as a result of ordering this molecule. The effect is not found with the corresponding bromo-complex.

(III)





(IV)

EXPERIMENTAL

Preparations.—*cis*-Chloroisothiocyanatobisethylenediaminecobalt(III) perchlorate was prepared as described by Werner,[8] by the action of potassium thiocyanate on *trans*-dichlorobisethylenediaminecobalt(III) chloride. The crude *cis*-chloroisothiocyanatobisethylenediaminecobalt(III) chloride was triturated with 60% perchloric acid, whereby it first dissolved evolving hydrogen chloride and the perchlorate was then precipitated. The precipitation was made more complete by addition of methanol. The compound was recrystallised by pouring warm dilute perchloric acid on to the crystals and filtering the resultant solution by suction as rapidly as possible into a Buchner flask surrounded by ice. The perchlorate monohydrate was obtained (Found: C, 15·5; H, 4·6. Calc. for $C_5H_{18}Cl_2CoN_5O_5S$: C, 15·4; H, 4·7%). The anhydrous salt was obtained by drying the monohydrate over calcium chloride in a vacuum (Found: C, 16·3; H, 4·7; N, 19·1. Calc. for $C_5H_{16}Cl_2CoN_5O_4S$: C, 16·1; H, 4·4; N, 18·9%).

l-*cis*-Chloroisothiocyanatobisethylenediaminecobalt(III) perchlorate was prepared from the

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[8] Werner, *Annalen*, 1912, **386**, 139.

racemate by Tupizina's method.[9] A concentrated aqueous solution of the racemic *cis*-chloroisothiocyanatobisethylenediaminecobalt(III) chloride was treated with the calculated amount of ammonium (+)-α-bromocamphor-π-sulphonate and left for 1 hr. The pink precipitate was filtered off and triturated with 60% perchloric acid in which it dissolved. Very soon the perchlorate crystallised. It was filtered off and dissolved in the minimum amount of water, and the complex was once again precipitated as the (+)-α-bromocamphor-π-sulphonate and then converted into the perchlorate. This sequence of operations was carried out four times and the perchlorate obtained was recrystallised from warm dilute perchloric acid. The pure crystals were dried with calcium chloride under vacuum (Found: C, 16·3; H, 4·7. Calc. for $C_5H_{16}Cl_2CoN_5O_4S$: C, 16·1; H, 4·4%). The rotatory dispersion curve of this compound agreed very well with that reported by Tupizina.[9] The designation of this enantiomorph as the *lævo*-form arises from the negative rotatory power at wavelengths greater than 5800 Å. At the wavelengths used for measurement in this investigation the rotations were positive.

cis-Bromoisothiocyanatobisethylenediaminecobalt(III) bromide was prepared by the action of hydrobromic acid on *cis*-aquoisothiocyanatobisethylenediaminecobalt(III) dithionate according to Werner's method.[10] This compound (10 g.) was dissolved in water (30 ml.), and concentrated, bromine-free hydrobromic acid (5 ml.) was added. The mixture was heated in an evaporating basin until the colour had changed from orange to purple and then set aside to cool and crystallise. The crystals were filtered off, washed with alcohol and ether and dried by a stream of air. The yield (3·0 g.) could be improved by adding a little more concentrated hydrobromic acid to the mother-liquor and evaporating it further on a steam-bath. The product, however, is sometimes contaminated with the *trans*-bromoisothiocyanato-complex.

The crystals, which are a mixture of *cis*-bromoisothiocyanatobisethylenediaminecobalt(III) bromide and dithionate, were dissolved in 72% perchloric acid (5 ml.), and the perchlorate was precipitated by adding water (1 ml.), alcohol (100 ml.), and ether (100 ml.). The solid was filtered off, dried, and dissolved in the minimum amount of water at 40°. The filtered solution was cooled and bromine-free 50% hydrobromic acid was added drop by drop. The bromide separated as purplish-red crystals (1·4 g.) which were filtered off, washed with alcohol, and ether and dried over concentrated sulphuric acid in a vacuum (Found: Co, 14·4, 14·6; Br, 39·0; SCN, 14·0. Calc. for $[Co\,en_2\,NCS,Br]Br,\frac{1}{2}H_2O$: Co, 14·5; Br, 39·4; SCN, 14·3%).

Methods of Measurement.—Spectra were measured with a Unicam Quartz spectrophotometer S.P. 500 and silica cells. Polarimetric measurements were made with a Schmidt and Haensch polarimeter. The wavelength of the light passed through the instrument could be varied between 4000 and 6000 Å by means of a prism mounted on a micrometer screw. The original light source of this instrument was too weak to be used satisfactorily with the strongly absorbing solutions encountered and was replaced by a more intense arc lamp. Electrical conductivities were measured with a Phillips A.C. Bridge. The solutions were contained in a 25 ml. vessel equipped with shiny platinum-foil electrodes, 0·5 cm. apart.

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[9] Tupizina, Diss., Zurich, 1915.

[10] Werner, *Annalen*, 1912, **386**, 150.

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