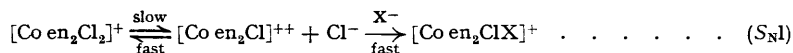**548.** *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part III.* Steric Course of Some Unimolecular Substitutions in the* cis-*Dichlorobisethylenediaminecobalt*(III) *Ion.*

By D. D. BROWN and R. S. NYHOLM.

This is the first of a series of reports on the steric course of octahedral substitutions of *cis*- and *trans*-complexes of transition metals by mechanisms kinetically characterised. The present report is on unimolecular substitutions by chloride ion and by thiocyanate ion in the *cis*-cobalt(III) cation discussed in Part II.* It is shown that the optically inactive, quinquecovalent, heterolysis product, slowly formed in the common first stage of these unimolecular substitutions, takes up the substituting anion at comparable rapid rates in all the distinguishable positions among its retained ligands. Two possible stereochemical pictures are offered, and some attempt is made to assess their relative likelihood.

IN Part II it is shown that the nucleophilic replacement of one chlorine atom in the *cis*-dichlorobisethylenediaminecobalt(III) ion by any of the four substituting agents, nitrate, chloride, bromide, and thiocyanate ion, in solvent methyl alcohol, is rate-controlled by one common process, which is of first order with respect to the cation, but is independent of the substituting anion, and results in a complete loss of optical activity from the cation. The explanation offered is that these are all unimolecular substitutions, rate-governed by a heterolysis of the cation, which eliminates the displaced group, and leaves an optically inactive quinquecovalent cobaltium ion :

$$[\text{Co en}_2\text{Cl}_2]^+ \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} [\text{Co en}_2\text{Cl}]^{++} + \text{Cl}^- \xrightarrow[\text{fast}]{\text{X}^-} [\text{Co en}_2\text{ClX}]^+ \quad . \quad . \quad . \quad . \quad . \quad (S_N1)$$

With this cobaltium ion (as, for temporary convenience, we may informally call it †) the substituting anion combines in the final and rapid step of the unimolecular mechanism.

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* Part II, preceding paper.

† The analogy is with " carbonium," the name applied to what is left when a maximally covalent form of carbon, CR₄, loses one ligand R with its bonding electrons.

The stereochemical problem which this mechanism presents is that of where, among the ligands remaining in the cobaltium ion, does the substituting agent enter. In order to answer this, it is necessary to find out what stereoisomeric products are formed, and, if there is more than one, how fast each is formed. We have studied this question in two examples taken from the field opened by the work of Part II.

(1) *Steric Course of Substitution by Chloride Ion in the* cis-*Dichloro-cation.*

(1a) *Spectrophotometric Study of Stereoisomeric Changes in the Dichloro-cation.*—We saw in Part II that the rate of loss of optical activity from the *cis*-dichloro-cation, which is identical with the radiochemically measured rate of substitution of bound chlorine by attacking chloride ion, follows accurately a first-order law. No measurable solvolysis, even of a temporary kind, occurs, for no net liberation of chloride ion can be detected at any time during or after the polarimetrically or radiochemically measured change. Thus the dissolved substance remains of the same composition from the beginning of the change to the end.

It does, however, suffer stereochemical isomerisation, apart from the loss of optical activity, because the colour changes from violet to green. Green is the colour of the *trans*-dichloro-cation, and, indeed, the absorption spectrum of the solution, if measured some time after the polarimetrically or radiochemically measured change is over, is quantitatively identical with that of a freshly prepared solution of the right amount of a salt of the *trans*-cation.

Two things follow. First, thermodynamically, the *trans*-cation is so much more stable than the *cis*- under the experimental conditions, that, in equilibrium, we have an inappreciable proportion of the *cis*-cation; in other words, the *trans*-cation is formed very nearly irreversibly. Secondly, from a kinetic viewpoint, while many routes of reversible change may be open to, and may be utilised by, the *cis*-cation, one route at least is available which leads to (and in principle from) the *trans*-cation.

The equality of rate between chlorine exchange and rotation loss is consistent with only two routes of molecular isomeric change : either alone might be pursued, or both might be pursued concurrently. They are as follows :

(A) Every original *l-cis*-cation* which suffers the occurrence destroying its optical activity directly yields as its monosubstitution product the *trans*-cation.

(B) Of any large number of original *l-cis*-cations undergoing the process which destroys their optical activity, 50% directly yield as their monosubstitution products new *l-cis*-cations, while the other 50% directly give *d-cis*-cations.

The above kinetic conclusion amounts to the statement that process (A) is involved. No matter whether it is involved exclusively, or whether it is pursued concurrently with process (B), even, perhaps, with process (B) operating to a predominating extent, thermodynamics will still determine that the final product is the pure *trans*-cation.

Thus all that remains unknown about the stereochemical course of the substitution is the proportion in which process (B) accompanies process (A). And this we can determine by comparing the rate of production of the *trans*-cation with the rate of loss of optical activity from original *cis*-cation.

The rate of production of the *trans*-cation has been determined spectrophotometrically. The absorption spectra of the *cis*- and *trans*-cations, shown together in Fig. 1, make it obvious that in order to make this measurement one has only to follow the fall in optical density at wave-length λ 5400 Å. A special series of experiments, with freshly prepared solutions of mixtures of weighed *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) chlorides in various ratios, confirmed that the optical density is a strictly linear function of percentage composition.

The formation of the *trans*-isomer, as measured photometrically, was found to follow an overall first-order rate law. In detail, the process was of first order with respect to the *cis*-cation and of zeroth order with respect to chloride ion. The latter point was clearly shown by the trivial kinetic effect of large excesses of added lithium chloride : even with

* For this use of *d*- and *l*-, see *J.*, 1953, 2674 (footnote).

50-fold excess the rate was increased only by a factor of 1·5, as illustrated in Table 1.   This small rate change is closely similar to that observed in measurements of the loss of optical rotation, and is to be similarly interpreted as an ionic strength effect.   But at any given ionic strength the rate of formation of the *trans*-cation is not as great as the rate of loss of optical activity from the *cis*-cation.   For the temperature 35·8°, the former rate is 82 ± 2%

TABLE 1.—*Rate of conversion of cis*-[Co en$_2$Cl$_2$]$^+$Cl$^-$ *into trans*-[Co en$_2$Cl$_2$]$^+$Cl$^-$ *alone and in the presence of* LiCl *in anhydrous* MeOH *at* 35·8°.

Run No.	9	10	11	12	13
[{Co en$_2$Cl}$^+$Cl$^-$] (mmole/l.)	1·75	1·92	2·12	1·79	1·76
[LiCl] (mmole/l.)	—	25·2	50·0	72·0	90·2
10^3 μ (μ = ionic strength)	1·75	27·1	52·1	73·8	92·0
[Cl$^-$]/[{Co en$_2$Cl}$^+$]	1·0	14·1	24·6	41·2	52·3
$10^4 k_1{}^{\text{phot-Cl}}$ (with k_1 in sec.$^{-1}$)	0·88	1·07	1·12	1·20	1·30
$10^4 k_1{}^{\text{pol-Cl}}$ (from Part II)	1·05	1·28	1·40	1·52	1·58
$k_1{}^{\text{phot-Cl}}/k_1{}^{\text{pol-Cl}}$	0·84	0·84	0·80	0·79	0·82

of the latter, as also appears from Table 1.   In view of the other rate and product relations of which we have to take account as explained above, the stereochemical conclusion is that, of 100 original *l-cis*-cations once substituted at 35·8°, 82 produce *trans*-cations, 9 give new *l-cis*-cations, and 9 yield *d-cis*-cations.
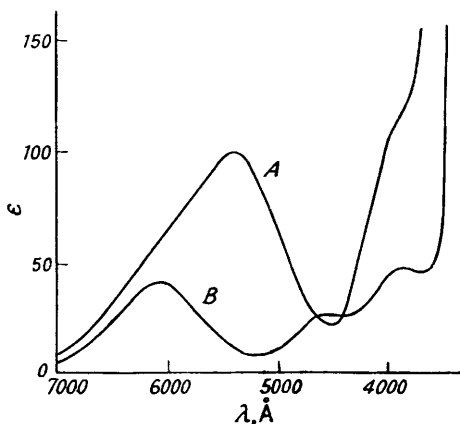

FIG. 1.

Absorption spectra :
A = *cis*-[Co en$_2$Cl$_2$]$^+$Cl$^-$.
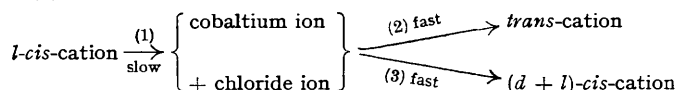B = *trans*-[Co en$_2$Cl$_2$]$^+$Cl$^-$.

The photometrically measured rate of production of the *trans*-isomer has a positive temperature coefficient, as shown by the data in Table 2.   Formally, the results can be represented by an Arrhenius equation, with 23·69 kcal./mole as the activation energy, and 5·09 × 10^{12} sec.$^{-1}$ as the frequency factor.   The temperature coefficient of the rate of formation of the *trans*-cation is thus a little larger than that of the rate of rotation loss from the *cis*-cation, with the result that, as the temperature is raised, the former rate becomes a larger fraction of the latter, as also appears in Table 2.

TABLE 2.—*Temperature dependence of the rate of conversion of cis*-[Co en$_2$Cl$_2$]$^+$Cl$^-$ *into trans*-[Co en$_2$Cl$_2$]$^+$Cl$^-$ *in* MeOH.

| Run No.	14	9	15	16
[{Co en$_2$Cl}$^+$Cl$^-$] (mmole/l.)	1·77	1·75	2·06	1·92
$T°$ − 273·16°	26·31	35·84	45·43	53·83
$10^4 k_1{}^{\text{phot-Cl}}$ (with k_1 in sec.$^{-1}$)	0·261	0·883	2·74	7·43
$10^4 k_1{}^{\text{pol-Cl}}$ (from Part II)	0·313	1·05	3·07	7·95
$k_1{}^{\text{phot-Cl}}/k_1{}^{\text{pol-Cl}}$	0·83	0·84	0·89	0·93

Of more significance than the temperature coefficient of the rate of formation of the *trans*-isomer, is the temperature coefficient of the ratio of the rates of formation, from original *cis*-cation, of *trans*-cation and of new *cis*-cation.   For this should give directly the difference between the Arrhenius energies of activation of the alternative final fast steps of the

unimolecular mechanism, the recombination of chloride ion with the cobaltium ion in the stereochemically distinguished positions. If we label the steps of the mechanism (1), (2), and (3), as is done below, then we know from the record of Part II that the Arrhenius activation energy of the slow heterolysis (1) is $E_1 = 22\cdot64$ kcal./mole; and what we can try to find out is $E_2 = E_3$, the difference between the Arrhenius energies of activation of those final processes of ionic reunion that lead to the *trans*-cation (2), and to the enantiomeric *cis*-cations (3) :

$$l\text{-}cis\text{-cation} \xrightarrow[\text{slow}]{(1)} \left\{ \begin{array}{l} \text{cobaltium ion} \\[2ex] + \text{ chloride ion} \end{array} \right\} \begin{array}{l} \xrightarrow{(2)\ \text{fast}} trans\text{-cation} \\[2ex] \xrightarrow{(3)\ \text{fast}} (d + l)\text{-}cis\text{-cation} \end{array}$$

Qualitatively, it is obvious from the trend of the rate ratios given in Table 2 that $E_2 - E_3$ is positive, *i.e.*, that a larger energy barrier resists the entry of chloride ion into the cobaltium ion to form the *trans*- than to form the *cis*-dichloro-cation. For the purpose of quantitatively evaluating $E_2 - E_3$, our results are not as precise as could be wished; but we can make something of them by using the Arrhenius equation as a smoothing device, that is, calculating back, from the equations given in Part II and here, smoothed

Fig. 2. *Schematic picture of S_N1 substitution.*
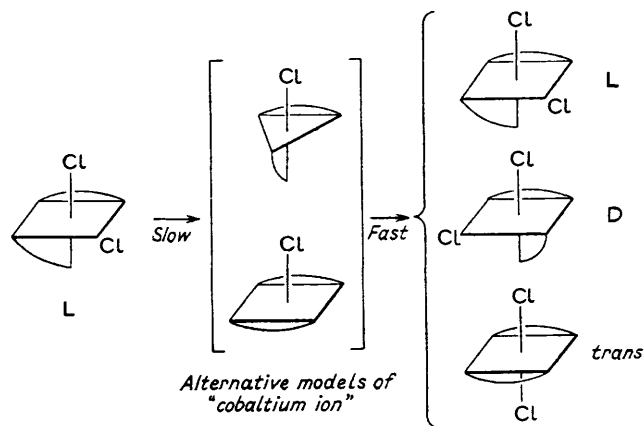
polarimetric and spectrophotometric rates, and thus smoothed ratios of the rates of production of *trans*-cation and of *dl-cis*-cation, for the four investigated temperatures. From these ratios, by an application of the Arrhenius equation, we find $E_2 - E_3 \approx 5$ kcal./mole.

(1b) *Stereochemial Picture of the Course of Unimolecular Substitution by Chloride Ion in the* cis-*Dichloro-cation.*—The relations described between the rate of chlorine exchange in this system, the rate of loss of optical activity, and the rate of appearance of the *trans*-isomer, show that the original *cis*-cation is first slowly heterolysed to give an optically inactive cobaltium ion, which then rapidly recombines with chloride ion in all the stereochemically possible ways. Two pictures can be given of this process, as is shown in Fig. 2. They differ with respect to the geometry of the quinquecovalent cobaltium ion, which can be based either on the model of the triangular bipyramid, or on that of the square pyramid : either would provide for the loss of optical activity. A final decision between these alternatives is not easy, but we offer an argument which seems to us to be a slight indication in favour of the triangular bipyramid.

In the triangular-bipyramid model of the cobaltium ion, the atoms are related nearly as they would be if the ion were formed by taking a chloride ion out of the *cis*-dichloro-cation without geometrical reorganisation. Therefore very little reorganisation is required when the bipyramidal ion combines with a chloride ion to give the *cis*-dichloro-cation. On the other hand, the bipyramidal ion can combine with chloride ion to produce the *trans*-dichloro-cation only with an accompanying displacement of one end of an ethylene-diamine residue. Hence we should expect a higher energy barrier to oppose the union

of the bipyramidal ion with chloride ion to give the *trans*- than to give the *cis*-dichloro-cation : in terms of our previous notation, $E_2 - E_3$ should be positive.

In the square-pyramidal model of the cobaltium ion, the atoms are related just as they would be if the ion had been formed by removing a chloride ion from the *trans*-dichloro-cation without further geometrical change. Therefore no reorganisation is required when the square-pyramidal ion combines with chloride ion to produce the *trans*-dichloro-cation. On the other hand, the square-pyramidal ion can combine with chloride ion to give the *cis*-dichloro-cation only with displacement of one end of an ethylenediamine residue. Hence we should expect a higher energy barrier to resist union of the square-pyramidal ion with chloride ion to form the *cis*- than to form the *trans*-dichloro-cation : in symbols, $E_2 - E_3$ should be negative.

In the preceding Section the experimental result was given that $E_2 - E_3$ is positive. This favours the triangular-bipyramidal model of the cobaltium ion.

(2) *Steric Course of Substitution by Thiocyanate Ion in the* cis-*Dichloro-cation.*

(2a) *Spectroscopic Study of the Proportions of Formed Stereoisomeric Chlorothiocyanato-cations.*—This substitution was examined more briefly than the chloride-ion substitution, because the precision of the measurements proved to be lower, in particular, too low to justify a study of temperature coefficients such as that already described.

It was shown in Part II that the *cis*-dichloro-cation undergoes both of the two possible stages of displacement of its bound chlorine by entering thiocyanate ion, but that the rates are different enough to enable about the first 40% of the first stage of substitution to be followed kinetically, without appreciable interference from the second stage. If, for convenience, we speak of the observed specific rate of reaction in this range as the " initial " rate, then it can be said that the initial rate of entry of thiocyanate ion into the dichloro-cation is of first order with respect to the cation and zero order with respect to thiocyanate ion. Provided that the thiocyanate ion is in such excess as to exclude an appreciable simultaneous displacement of bound chlorine by entering chloride ion, the initial rate of entry of thiocyanate ion is identical with the rate of loss of optical activity from the *cis*-dichloro-cation, likewise a process of first order with respect to the cation and of zero order with respect to the substituting anion, whether chloride or thiocyanate ion.

The rate relations here summarised could be produced by substitution in either or both of the following forms, namely, that every original dichloro-cation which undergoes the change destroying its optical activity gives either the *trans*-chlorothiocyanato-cation, or the *d*- or *l*-*cis*-chlorothiocyanato-cation, as its first substitution product.

We have to consider the most general possibility, which is that these two types of molecular process occur concurrently; and we can ascertain the proportions in which they do so, if, having found, as in Part II, the total rate of entry of the first thiocyanato-substituent, we determine, for the same conditions, the rate of formation of, say, the *cis*-chlorothiocyanato-cation separately. How this may be done optically can be appreciated by glancing at Fig. 4 of Part II. The absorption curves of the *cis*-dichloro-cation and the *trans*-chlorothiocyanato-cation intersect at the wave-length 5000 Å; and hence, at this wave-length, the formation of the *trans*-substitution product leaves no optical record. At the same wave-length, the *cis*-chlorothiocyanato-cation has a much larger optical absorption than the original *cis*-dichloro-cation; and therefore an observation of the change of optical density at this wave-length will measure solely the formation of the *cis*-substitution product. The results of such measurements can be expressed by stating what proportion of the total chlorothiocyanato-cation, which has been formed at any time during the followed portion of the reaction, consists of the *cis*-isomeride. Mean values of this proportion, as measured over about the first 40% of monosubstitution, are given in Table 3. To within the somewhat large experimental error, they signify that of 100 original *l*-*cis*-dichloro-cations once substituted by thiocyanate ion at 35·8°, 36 produce *trans*-chlorothiocyanato-cations, while 64 give *cis*-chlorothiocyanato-cations.

(2b) *Stereochemical Picture of the Course of Unimolecular Substitution by Thiocyanate Ion in the* cis-*Dichloro-cation.*—The relations described among the various rates measured

for this substitution show that the *cis*-dichloro-cation is first slowly heterolysed to the already discussed cobaltium ion, which then rapidly combines with the thiocyanato-ion in all the stereochemically possible ways.

As we have not investigated the temperature dependence of the rate of this ionic union in its different stereochemical forms, we cannot with certainty interpret the observation that, in the conditions used, the thiocyanate ion goes mainly into *cis*-positions,

TABLE 3.—*Proportions of cis-[Co en$_2$Cl(NCS)]$^+$ in the total [Co en$_2$Cl(NCS)]$^+$ formed from cis-[Co en$_2$Cl$_2$]$^+$ by substitution with NCS$^-$ in MeOH at 35·8°.*

Run No.	23A	25A	26A	27A
[{Co en$_2$Cl$_2$}$^+$Cl$^-$] (mmole/l.)	0·72	0·67	0·67	0·59
[LiNCS] (mmole/l.)	13·7	30·0	49·7	90·0
Percentage of *cis*-[Co en$_2$Cl(NCS)]$^+$	58	67	64	66

although chloride ion predominantly takes the *trans*-position. However, this difference seems to involve no general stereochemical principle. The small rate ratios which create the distinction could well arise from differences of interaction between the substituting agent and the bound chlorine atom in the cobaltium ion. If such effects led to a different activation-energy difference for *trans*- and *cis*-combination of the thiocyanate ion than of the chloride ion, then at other temperatures the thiocyanate ion would partition its attack qualitatively like the chloride ion.

(3) *Illustrative Experimental Data.*

Materials were prepared for this work as outlined in Part II, where the spectrophotometric technique, as here employed, is described. No more is therefore necessary than to illustrate, as is done in Tables 4 and 5, the production of the results which have been summarised above

TABLE 4.—*Change of optical density at 5400 Å during isomerisation of cis-[Co en$_2$Cl$_2$]$^+$Cl$^-$ in the presence of LiCl in MeOH at 35·8°. (Run no. 13.)*

[{Co en$_2$Cl$_2$}$^+$Cl$^-$] = 1·763 × 10^{-3}M; [LiCl] = 90·2 × 10^{-3}M; D = optical density in a 2-cm. cell for λ 5400 Å; k_1 = (2·303/t) log$_{10}$ $(D_\infty - D_0)/(D_\infty - D_t)$.

t (min.)	0	29	62·5	89	119	151·5	180	210·5	220	239·5
D_t	0·296	0·245	0·1975	0·168	0·138	0·1165	0·0975	0·0815	0·0795	0·074
% Reaction	0	20·9	38·3	49·4	60·6	68·4	75·5	81·4	82·1	84·4
10$^4k_1$ (min.$^{-1}$)	—	80	77	76	78	76	78	80	78	78

Directly observed D_∞ = 0·032. Mean k_1 = 0·0078 min.$^{-1}$.

TABLE 5.—*Change of optical density at 5000 Å during substitution of cis-[Co en$_2$Cl$_2$]$^+$Cl$^-$ with LiNCS at 35·8° in MeOH. (Run no. 25A.)*

Initially [{Co en$_2$Cl$_2$}$^+$Cl$^-$] = 0·674 × 10^{-3}M; [LiNCS] = 30·0 × 10^{-3}M. D = optical density in a 4-cm. cell for λ 5000 Å.

t (min.)	0	21·5	29·7	43·0	53·7	66·0	79·3
D_t	0·171	0·203	0·211	0·224	0·233	0·248	0·261
% Reaction giving *cis*-	0	9·4	11·7	15·6	18·2	22·6	26·4
% Total reaction *	0	13·8	17·0	23·7	27·4	34·1	40·6
% *cis*- in product	—	68·0	68·8	65·9	66·3	66·3	65·0

D_∞ if total product were *cis*-, as calculated from absorption spectrum = 0·512.

* Determined (Run 25) as described in Part II.

for each of the reactions studied with respect to the stereochemical composition of the first substitution product.

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