547. *Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part II.* Kinetics and Molecularity of Nucleophilic Substitutions in the* cis-*Dichlorobisethylenediaminecobalt*(III) *Ion.*

By D. D. Brown and C. K. Ingold.

The kinetics of substitutions by 7 anions which displace chlorine from the *cis*-dichlorobisethylenediaminecobalt(III) ion have been studied in solvent methyl alcohol by polarimetric, spectroscopic, chemical, and radiochemical methods, as far as was in each case appropriate and convenient. For 4 of the anionic reagents, all weakly nucleophilic, substitution has S_N1 kinetics, and a common absolute rate, which is also the rate at which the original cation loses optical activity in the absence of stronger nucleophilic substituting agents. The expected ionic-strength and mass-law effects have been observed. For 3 anions, all more strongly nucleophilic, substitution has S_N2 kinetics, with rates differing widely, in order of nucleophilic power. The rate relations indicate that the nucleophilic attack is on the metal atom. These results closely parallel what was demonstrated by Gleave, Hughes, and Ingold in 1935 for nucleophilic substitution on carbon, and are considered to justify an extension of the concept of dual mechanism to substitution on cobalt, and tentatively, in view of the arguments of Part I, to octahedral substitutions generally.

(1) *Preliminary Survey.*

We describe here the kinetic course of a number of substitutions in which one chlorine atom is displaced as chloride ion from the *cis*-dichlorobisethylenediaminecobalt(III) ion by various anionic substituting agents, ranging in complexing power from the weakly

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* Part I, preceding paper.

nucleophilic nitrate and chloride ions, through bromide, thiocyanate, and nitrite ions, to the successively more nucleophilic azide ion and methoxide ion, the solvent being methyl alcohol throughout :

$$cis\text{-}[\mathrm{Co\ en_2Cl_2}]^+ + \mathrm{X}^- \longrightarrow [\mathrm{Co\ en_2ClX}]^+ + \mathrm{Cl}^-$$
$$\mathrm{X}^- = \mathrm{NO_3}^-, \mathrm{Cl}^-, \mathrm{Br}^-, \mathrm{SCN}^-, \mathrm{NO_2}^-, \mathrm{N_3}^-, \mathrm{OMe}^-$$

We shall deal with the observed kinetic orders, and the absolute and relative rates of the substitutions; and also with the conclusions which can be drawn concerning their molecularity. The results will establish duplexity of mechanism in this range of substitutions. In other papers we shall consider the steric course of some of the substitutions.

In order to be able to compare the rates of the substitutions it was necessary to employ the same solvent throughout. Water was unsuitable, since, owing to its high complexing power, it would have usurped the function of substituting agent at the weakly nucleophilic end of the anion series (Part I, Section 2). A solvent of low complexing power was required. There are many such solvents; but only a few of them are able to dissolve the salts which it was proposed to use in concentrations sufficient to permit the type of kinetic investigation planned. Methyl alcohol and ethylene glycol are among these few solvents, and methyl alcohol was selected as being generally the more convenient.

The choice of a *cis*- rather than a *trans*-form of halogeno-cobalt complex for this first experimental study of the mechanism of substitutions displacing halogen from cobalt complexes, followed from our decision to use an optically active complex. This plan arose in part from a desire to have the polarimetric method, in addition to other methods, available for following the kinetics of the substitutions. It also looked ahead to subsequent studies on the steric direction of substitutions; for a comparison of the rate of an isotopic substitution of halogen with the rate of concomitant loss of optical activity must evidently throw light on the stereochemistry of the substitution.

The selection of the particular *cis*-complex used in this work was determined by a preliminary survey of the optical rotatory and absorption spectra of a number of *cis*-cations. Salts of each of the *cis*-series, $[\mathrm{Co\,en_2Cl_2}]^+\mathrm{X}^-$, $[\mathrm{Co\,en_2(NCS)Cl}]^+\mathrm{X}^-$, $[\mathrm{Co\,en_2(NCS)Br}]^+\mathrm{X}^-$, $[\mathrm{Co\,en_2(NH_3)Cl}]^{++}\mathrm{X_2}^-$, and $[\mathrm{Co\,en_2(NH_3)Br}]^{++}\mathrm{X_2}^-$ were prepared and resolved by way of their (+)-α-bromocamphor-π-sulphonates. They were examined with respect to their rotation and absorption in methyl alcohol. Of the above cations, only the first gave rotations which, in the dilute solutions to be employed in the kinetic studies, were large enough to permit accurate kinetic observations at wave-lengths which were convenient for the light source and to the detecting eye, and were not too strongly absorbed by the solutions. We knew that the use of a dichloro-cation involved the consequence that displacement of the first chlorine atom might be kinetically overlapped by displacement of the second; we expected to be able to avoid this complication, where necessary, by studying initial rates of reaction.

For the unsymmetrical substitutions, that is, displacements of a chlorine atom from the dichloro-cation by reaction with any of the listed anions except chloride ion, we had available three kinetic methods, namely, the polarimetric method, the spectrophotometric method, and the method of chemical analysis, usually a matter of following the liberation of chloride ion by potentiometric titration. For the symmetrical substitution, that is, displacement of the bound chlorine by reaction with chloride ion, we used the radio-isotope ^{36}Cl, of half-life about 10^5 years, for isotopic label; and thus we again had available three kinetic methods, namely, the polarimetric and spectrophotometric methods, and measurement of the transfer of radioactivity. But because of the special nature of this reaction, only the radioactivity method allows a direct deduction of the rate of substitution, though we have been able to find relations between this rate and the polarimetric and spectrophotometric rates. The polarimetric rate proved to be important for the present discussion of the molecularity of substitution. The spectrophotometric rate is relevant to the investigation of the spatial direction of substitution, as described in the next paper.

In the Sections 2—8, we consider results concerning the kinetics and molecularity of substitution, first for the symmetrical case of substitution by chloride ions, and then for unsymmetrical substitutions, notably by thiocyanate ion, for which the kinetic form of reaction is similar, and by azide ion, for which it is different. These three examples mark out the pattern of the results, which we shall then fill in by reference to the reactions of the other anions already listed. In Section 9 (p. 2692) the results will be collectively discussed.

(2) *Action of Chloride Ion on the* cis-*Dichloro-cation.*

(2*a*) *Loss of Optical Activity from the Dichlorocobalt*(III) *Chloride.*—That enantiomer of the *cis*-dichlorobisethylenediaminecobalt(III) ion which gives the less water-soluble (+)-α-bromocamphor-π-sulphonate was designated by Werner as the *l*-form. Werner's label doubtless derives from the circumstance that he measured rotations using cadmium red light, for which the cation is lævorotatory. We retain Werner's label, although for our polarimetric kinetics we used sodium yellow light, for which the cation is strongly dextrorotatory. The rotation and absorption spectra of the cation in methyl alcohol are shown in Fig. 3 and 4 respectively (p. 2686). For sodium light we find $[M_D]$ +2520°. Mathieu reports $[M_D]$ +2000° (*Bull. Soc. chim.*, 1936, **3**, 463, 476), while Bailar, Haslam, and Jones give $[M_D]$ +1850° (*J. Amer. Chem. Soc.*, 1936, **58**, 2226) for aqueous solutions.

In solution in anhydrous methyl alcohol, the *l*-dichlorocobalt(III) chloride loses its optical activity gradually, but completely, according to a first-order law. This, then, is not a mutarotation, such as was found by Mathieu to accompany conversion of the dichloro-salt into the chloroaquo-salt in aqueous solution (*Bull. Soc. chim.*, 1937, **4**, 687). In methyl alcohol the optically inactive product still has the composition of the dichloro-salt. The rate law shows that no optically active intermediate of appreciable concentration intervenes between the active factor and inactive product. This isomeric conversion in methyl alcohol is about 9 times slower than the aquation studied by Mathieu in solvent water.

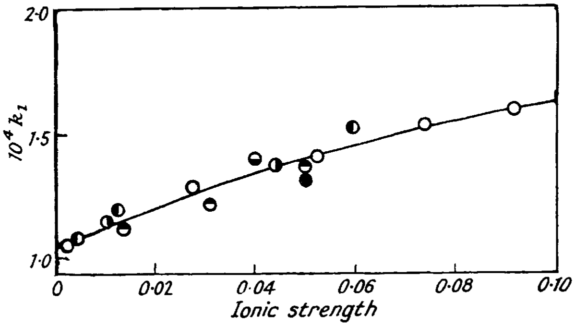


FIG. 1. *First-order rate constants for substitution in* cis-$[Co\ en_2Cl_2]^+$ *in* MeOH *at* 35·8°.

○ Substitution by Cl^-, polarimetric.
◒ ,, ,, ,, radioactivity.
◓ ,, ,, NCS^-, polarimetric.
● ,, ,, ,, spectrophotometric.
◐ ,, ,, Br^-, polarimetric.
◑ ,, ,, NO_3^-, polarimetric.

The first-order reaction in methyl alcohol is of zero order with respect to chloride ion. This was shown, in the first place, by adding excess of chloride ion in the form of lithium chloride. Even when a 50-fold excess was thus supplied, the first-order rate-constant, $k_1^{\text{pol-Cl}}$, was increased only by a factor of 1·5, as is shown in Table 1. A graph is given in Fig. 1, partly for comparison with rates obtained by other methods and reported below. Obviously this small rate-change is a salt effect. Account being taken of differences of solvent, it is of the same order of magnitude as some of the ionic-strength effects associated with the unimolecular substitutions of alkyl halides in hydroxylic solvents (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979).

TABLE 1.—*Rate of loss of optical activity from* $[Co\ en_2Cl_2]^+Cl^-$ *alone and in the presence of* LiCl *in* MeOH *at* 35·8°.

Run No.	1	2	3	4	5
$[\{Co\ en_2Cl_2\}^+Cl^-]$ (mmole/l.)	1·75	1·92	2·12	1·79	1·76
[LiCl] (mmole/l.)	—	25·2	50·0	72·0	90·2
$10^3\mu$ (μ = ionic strength)	1·75	27·1	52·1	73·8	92·0
$[Cl^-]/[\{Co\ en_2Cl_2\}^+]$	1·0	14·1	24·6	41·2	52·3
$10^4 k_1^{\text{pol-Cl}}$ (with k_1 in sec.$^{-1}$)	1·05	1·28	1·40	1·52	1·58

The conclusion that the reaction rate is not specifically dependent on chloride ion would not be remarkable if the chloride ion did not stoicheiometrically intervene; but we shall show that it does. The kinetic conclusion itself will be amplified in later Sections, where we show that chloride ion can be replaced by other anions, which likewise act as substituting agents, but do so without affecting the rate of the loss of optical activity which accompanies their substitution.

The process leading to loss of optical activity from the dichlorocobalt(III) chloride in methyl alcohol is formally shown to be activated by measurement of the temperature coefficient of the reaction rate. The data in Table 2 give a good Arrhenius plot, leading to the value 22·64 kcal./mole for the activation energy, and $1{\cdot}07 \times 10^{12}$ sec.$^{-1}$ for the frequency factor.

TABLE 2. *Temperature dependence of the rate of loss of optical activity from* $[\mathrm{Co\,en_2Cl_2}]^+\mathrm{Cl}^-$ *in* MeOH.

Run No.	6	1	7	8
$[\{\mathrm{Co\,en_2Cl_2}\}^+\mathrm{Cl}^-]$ (mmole/l.)	1·77	1·75	2·06	1·92
$T° - 273{\cdot}16°$	26·31	35·84	45·43	53·83
$10^4 k_1^{\mathrm{pol\text{-}Cl}}$ (with k_1 in sec.$^{-1}$)	0·313	1·05	3·07	7·95

(2*b*) *Constancy of Chloride-ion Concentration during and after Rotation Loss.*—Chemical analysis can show whether or not chloride ion is liberated permanently or temporarily from the complex cation under the conditions of the rotation loss. It can also determine whether the product formed by rotation loss subsequently proceeds to liberate chloride ion.

Previous workers have reported difficulty in titrating chloride ion by silver ion in aqueous solutions of the dichlorocobalt(III) chloride. This is due in part to the rapidity of aquation (Mathieu, *Bull. Soc. chim.*, 1936, **3**, 2121, 2152). It is due in part also to a specific interaction between silver salts and the dichloro-cation (Werner, *Annalen*, 1912, **386**, 93). Mathieu obtained some success by potentiometric titration at 0°. In our experience, potentiometric titration in methyl alcohol at 0° works fairly well. We found that the end-points are sharpened if the methyl-alcoholic solution is diluted with 4 vols. of acetone. Table 3 records some estimations of chloride ion made at different times during the rotation loss, and also after it was substantially complete.

TABLE 3. *Estimated percentage of* Cl^- *in cis*-$[\mathrm{Co\,en_2Cl_2}]^+\mathrm{Cl}^-$ *at various times after dissolution in* MeOH *at* 35·8°.

(Time of half-change for rotation loss = 1·8 hours.)

Time (hours)	0·25	0·75	4·5	13·0
% Cl^- (by titration in MeOH alone)	102	101	—	101
„ („ „ MeOH–$\mathrm{Me_2CO}$)	101	—	101	100

The slight over-estimation of chloride ion is just outside the error of the analytical method. It is due to a slow attack by silver salts on the complex cation, as was established by over-titrating, and then noting the slow disappearance of silver ion as indicated by the falling electromotive force. The over-estimation is smaller at later times than at earlier, because a product of the isomerisation which accompanies the rotation loss, the *trans*-dichlorocobalt(III) cation (see Part III, following paper) reacts with silver ion more slowly than does the original *cis*-isomer. The over-estimation is also reduced by titrating in acetone, because the responsible reaction is retarded by acetone, as we should expect from the theory of kinetic solvent effects for a reaction between two ions of like charge (Hughes and Ingold, *J.*, 1935, 252; Cooper, Dhar, Hughes, Ingold, MacNulty, and Woolf, *J.*, 1948, 2043).

The conclusion to be drawn from the analyses illustrated is therefore that appreciable chloride is not liberated from the complex cation either during or after the rotation loss.

(2*c*) *Chlorine Exchange between Chloride Ion and the Dichlorocobalt*(III) *Cation.*—No kinetically followed halogen exchange in co-ordination compounds seems to have been reported in the literature, though Grinberg observed very rapid exchange of bromine with a platinum complex, while Ettle and Johnson found no measurable exchange of chlorine with a cobalt complex in solution in water (cf. Section 2*b* of Part I).

The method of the present work was to add lithium radio-chloride to ordinary *cis*-dichlorobisethylenediaminecobalt(III) chloride in methyl alcohol, and, after various times at 35·8°, to chill samples to 0°, precipitate the chloride ion by the addition of a small excess of methyl-alcoholic silver nitrate at 0°, filter, and wash the precipitate quickly with a standard amount of ice-cold water, and measure the radioactivity of the combined filtrate made up to a standard volume.

The errors of the separation are (1) that a little covalently bound chlorine is pulled out of the complex cation by the silver salts, which are present in slight excess in order to ensure removal of all the anionic radioactivity, and (2) that a little of the complex cation remains adsorbed in the silver chloride. These errors were compensated when computing percentages of exchange at any finite time, by taking as the percentage for infinite time an experimental value determined by the same procedure. As two chlorine atoms are available to be exchanged, one-half of the value thus determined is the figure appropriate to represent equilibrium exchange with respect to one chlorine atom. This figure could be raised to 98% of the theoretical by using no excess of silver, but otherwise following our standard procedure for washing the silver chloride precipitate; but in fact it was kept slightly below the value stated by the employment of a definite small excess of silver.

We dealt with the complications that exchange of the second chlorine atom will overlap that of the first, and that the isomeric product of exchange, the *trans*-dichloro-cation (see Part III) also contains exchangeable chlorine, by extrapolating mean specific rates, as measured at various stages of the exchange, back to yield the initial specific rate. This extrapolation also eliminated the need to correct for the gradual dilution, as exchange proceeded, of the supplied radio-chloride ion by produced ordinary chloride ion, though actually the degree of radioactive dilution was rendered nearly negligible by the use of lithium radio-chloride in large excess.

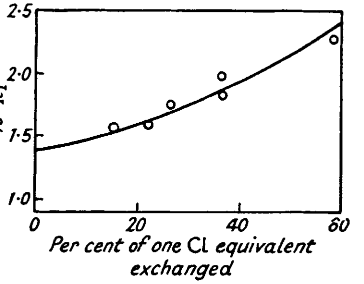


FIG. 2. *Mean specific rate of chlorine exchange between radio*-Cl^- *and* [Co en_2Cl_2]$^+$ *as a function of the percentage progress of exchange ; in* MeOH *at* 35·8°. (*Runs* 18 *and* 19.)

The extrapolation for runs (nos. 18 and 19) conducted at 35·8° and an ionic strength $\mu = 0{\cdot}040$ is shown in Fig. 2. The resulting value for the first-order rate-constant of exchange of the first chlorine atom, as measured by the radioactivity method, together with the estimated error, is entered as $k_1^{\text{rad-Cl}}$ below. The value of the polarimetric rate-constant under corresponding conditions, $k_1^{\text{pol-Cl}}$, along with the estimated error, is given for comparison (cf. Fig. 1) :

$10^4k_1^{\text{rad-Cl}}$, with $k_1^{\text{rad-Cl}}$ in sec.$^{-1}$ (35·8°, $\mu = 0{\cdot}040$, MeOH) $= 1{\cdot}4 \pm 0{\cdot}1$
$10^4k_1^{\text{pol-Cl}}$, ,, $k_1^{\text{pol-Cl}}$,, ,, ,, $= 1{\cdot}35 \pm 0{\cdot}03$

We conclude that in principle the rates are identical.

(3) *Action of Thiocyanate Ion on the* cis-*Dichloro-cation.*

(3*a*) *Polarimetric Study of Rate of Displacement of Chlorine by the Thiocyanate Ion.*— When a solution of lithium thiocyanate is added to one of the dichlorocobalt(III) chloride in methyl alcohol, substitution takes place, as is evident from the gradual colour change, and from analysis of the final product. Actually the substitution goes through two stages, though the second is considerably slower than the first :

$$[\text{Co en}_2\text{Cl}_2]^+ \xrightarrow{\text{NCS}^-} [\text{Co en}_2\text{Cl(NCS)}]^+ + \text{Cl}^- \xrightarrow{\text{NCS}^-} [\text{Co en}_2(\text{NCS})_2]^+ + 2\text{Cl}^-$$

If the displacement of chlorine from the cation by thiocyanate ion in the first of these substitutions took place any faster than chlorine is displaced by chloride ion, or than optical activity is lost by the cation in the absence of thiocyanate ion, then we should be able to observe the increased rate through the rotation change, and also in other ways to be mentioned later.

The method of examining this question through the rotation change will be clear from the curves, shown in Fig. 3, for the optical rotation spectra in methyl alcohol of the *cis*-dichlorocobalt(III) ion and the *cis*-chlorothiocyanatocobalt(III) ion. In each case the isomer represented is that which Werner called *l*-; it is also the isomer which gives the less water-soluble (+)-α-bromocamphor-π-sulphonate. It will be seen that at λ 5893 Å, the mean wave-length of the sodium yellow doublet, the rotation of the optically active chlorothiocyanato-ion is not significantly different from zero. It follows that, when one thiocyanato-group replaces one chlorine atom in the original dichloro-cation, then the product, no matter which isomers are formed, whether *d-cis-*, *l-cis-*, *dl-cis*, or *trans-*, will, at this wave-length, have the rotation zero. At the same wave-length, the rotation of the original *l-cis*-dichloro-cation is large. Therefore any substitution by thiocyanate ion, at a rate exceeding that at which optical activity is lost from the dichloro-cation in the absence of thiocyanate ion, should show itself as an increased rate of loss of rotation at the stated wave-length.

The measurements made on these principles were not of high accuracy, because the small solubility of *l-cis*-dichlorobisethylenediaminecobalt(III) thiocyanate limited the available concentration of the dichloro-cation, and because the high absorptive power for Na-*D* light of the formed chlorothiocyanato-ion reduced the intensity of the transmitted light. However, over the first 60% of reaction, which is as much as could be followed owing to the increasing light absorption, and to within the error of the observations, the reaction followed a first-order rate-law; and the rate constants, given in Table 4, were almost the same, for the same temperature and ionic strength, as the rate constants for rotation loss by the dichloro-cation when the only anion present was chloride ion (see Fig. 1). As Table 4 shows, the reaction with thiocyanate ion, though of first order overall, is of zeroth order with respect to thiocyanate ion: the thiocyanate ion was always held in large excess, but an increase by 3½ times in its concentration only slightly increased the rate. This slow increase of rate with ionic strength is quite similar to that observed for the rotation loss of the cation when chloride ion was the only anion (Section 2*a*).

TABLE 4. *Rates of loss of optical activity from solutions of* $[\mathrm{Co\,en_2Cl_2}]^+\mathrm{Cl}^-$ *and* LiNCS *in* MeOH *at* 35·8°.

Run No.	20	21	22
$[\{\mathrm{Co\,en_2Cl_2}\}^+\mathrm{Cl}^-]$ (mmole/l.)	0·72	0·67	0·67
[LiNCS] (mmole/l.)	13·7	30·0	49·7
$10^3\mu$ (μ = ionic strength)	14	31	50
$[\mathrm{NCS}^-]/[\{\mathrm{Co\,en_2Cl_2}\}^+]$	19	45	76
$10^4 k_1^{\mathrm{pol \cdot NCS}}$ (with k_1 in sec.$^{-1}$)	1·10	1·20	1·35

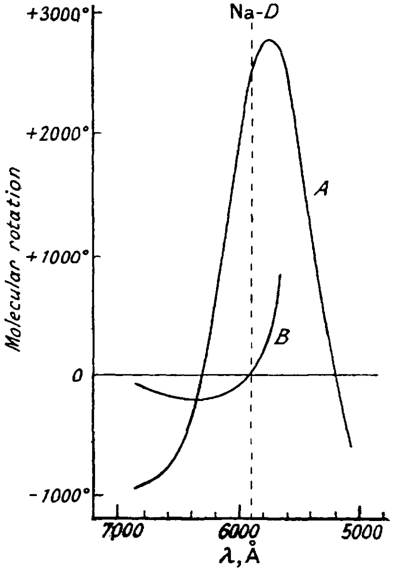
In order to simplify the foregoing account, we have anticipated the conclusion, for which we must now give the evidence, that the chemical process accompanying the loss of optical activity from the dichloro-cation in the presence of thiocyanate ion is essentially a substitution of bound chlorine by the thiocyanato-group.

(3*b*) *Spectrophotometric Study of the Displacement of Chlorine by the Thiocyanate Ion.*—For the above-described polarimetric experiments, solutions of the dichloro-cation were prepared with the aid of its chloride, rather than its thiocyanate, because of the readier solubility of the former salt, and because chloride ion was in any case going to be produced. However, thiocyanate ion was supplied in large excess over chloride ion, in order to ensure that nearly all the substitution would be effected by the thiocyanate ion. The colour change made it obvious that such substitution was concerned with the rotation loss. But in order to determine whether this was substantially the sole chemical process, it was necessary to examine the rate of change of some variable which would distinguish thiocyanate substitution from chloride exchange.

It was not found possible chemically to follow the liberation of chloride ion, because, as in aqueous solution (Werner, *Annalen*, 1912, **386**, 53), so in methyl-alcoholic solution, silver ion combines with complex cobalt ions containing a bound thiocyanato-group. Therefore we employed a spectrophotometric method, a chemical check being made on the end-product of substitution.

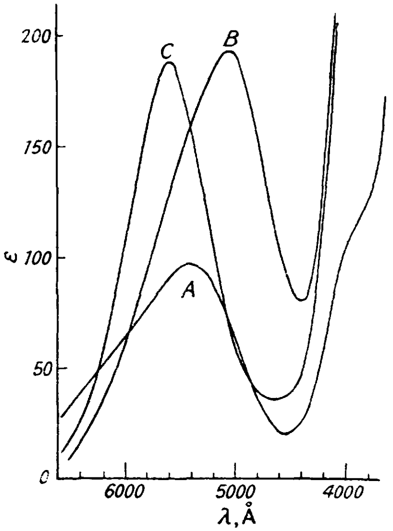
The principle of the method can be followed from Fig. 4, which records the absorption spectra, in methyl-alcoholic solution, of the *cis*-dichloro-cation, and of prepared samples of the *cis*- and *trans*-forms of its monosubstitution product, the chlorothiocyanato-cation. At λ 5400 Å the two chlorothiocyanato-isomers have the same extinction coefficient, which is considerably larger than that of the dichloro-compound. Therefore, by following the increase in absorption at this wave-length, we can observe the rate of introduction of the thiocyanato-group, independently of where it enters the complex.

FIG. 3.



Rotatory dispersion of:
A = [Co en_2Cl_2]$^+Cl^-$,
B = [Co $en_2Cl(NCS)$]$^+ClO_4^-$,
in methyl alcohol at 0°.

FIG. 4.



Absorption spectra in methyl alcohol:
A = *cis*-[Co en_2Cl_2]$^+Cl^-$,
B = *cis*-[Co $en_2Cl(NCS)$]$^+$ *bromocamphorsulphonate*$^-$,
C = *trans*-[Co $en_2Cl(NCS)$]$^+NCS^-$.

Actually the optical density, starting from the value for *cis*-[Co en_2Cl_2]$^+$, did not stop increasing when the value appropriate to [Co $en_2Cl(NCS)$]$^+$ was reached, because a second stage of substitution supervened with the production of still more strongly absorbing ions [Co $en_2(NCS)_2$]$^+$; and when, finally, a steady optical density was attained, a red salt whose analysis agreed with the formula [Co $en_2(NCS)_2$]$^+NCS^-$, could be isolated by precipitation with ether. However, at 35·8°, the time of half-conversion in the first substitution was about 2 hours, and in the second about 12 hours. Therefore we could obtain the specific rate of the first substitution from measured mean specific rates of change of optical density, from that of [Co en_2Cl_2]$^+$ towards that of [Co $en_2Cl(NCS)$]$^+$ at small degrees of conversion, the final step being to extrapolate to the limit of low conversions.

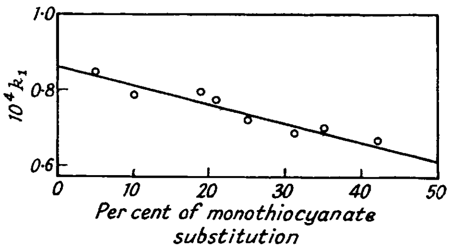
The extrapolations reveal what we interpret as a mass-law retardation, quite similar to that found (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979) for the unimolecular hydrolysis of benzhydryl (diphenylmethyl) halides: owing to the reversibility of the initial heterolysis, the developed chloride ion returns to the cation from which it separated to an increasing degree as reaction progresses, thereby retarding the thiocyanate substitution, even though this eventually proceeds to completion. The retardation is illustrated in Fig. 5. It is found, consistently with this interpretation, that as the initial excess of thiocyanate ion is increased, the progressive retardation is lessened, until it becomes inappreciable at the largest excesses employed.

The extrapolated initial specific rates of substitution by the thiocyanate ion in the dichloro-cation, as determined by this method, are given in Table 5. As in these experiments some chloride ion is present initially, the mass-law effect should reduce the spectrometrically measured initial rates, below the polarimetric rates reported in the preceding Section, which refer strictly to total rates of substitution by thiocyanate ion plus chloride ion. However, as the excess of thiocyanate is increased, the spectrophotometric rate should converge on the polarimetric rate, even though both rates are being increased by the increasing ionic strengths of the solutions. All this happens, as is illustrated in Fig. 6. Evidently the polarimetric rate is equal to the rate of substitution by thiocyanate ion, when this is the only substitution taking place, just as the same polarimetric rate is equal to the rate of substitution by chloride ion when that is the sole form of substitution.*

TABLE 5. *Spectrophotometrically measured rate of substitution by* NCS^- *in cis*-$[Co\ en_2Cl_2]^+$ *to give* $[Co\ en_2Cl(NCS)]^+$ *in* MeOH *at* 35·8°.

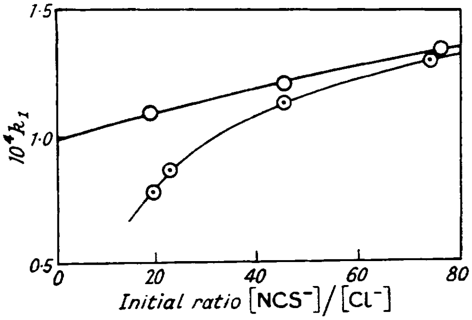
Run No.	23	24	25	26
$[\{Co\ en_2Cl_2\}^+Cl^-]$ (mmole/l.)	0·72	0·71	0·67	0·67
[LiNCS] (mmole/l.)	13·7	15·6	30·0	49·7
$10^3\mu$ (μ = ionic strength)	14	16	31	50
$[NCS^-]/[Cl^-]$	19	22	45	74
$10^4k_1^{phot\cdot NCS}$ (with k_1 in sec.$^{-1}$)	0·78	0·87	1·13	1·30

FIG. 5.



Spectrophotometric rate of substitution in cis-$[Co\ en_2Cl_2]^+$ *by* NCS^- *in* MeOH *at* 35·8°, *showing progressive retardation by mass-law effect of developing chloride ion.* (*Run* 24.)

FIG. 6.



Rates of substitution in cis-$[Co\ en_2Cl_2]^+$ *by* NCS^- *in* MeOH *at* 35·8°.

○ Polarimetric rates (substitution by NCS^- plus Cl^-)

○ Initial spectrophotometric rates (substitution by NCS^- only).

(4) *Action of Azide Ion on the* cis-*Dichloro-cation.*

(4*a*) *Study by Potentiometric Titration of the Rate of Displacement of Chlorine by the Azide Ion.*—The reaction between azide ion and the dichlorocobalt(III) cation proceeds through two stages of substitution :

$$[Co\ en_2Cl_2]^+ \xrightarrow{N_3^-} [Co\ en_2ClN_3]^+ + Cl^- \xrightarrow{N_3^-} [Co\ en_2(N_3)_2]^+ + 2Cl^-$$

When slightly more than one molecular proportion of azide ion is supplied, the first stage of substitution goes practically to completion, giving no indication of appreciable rever-

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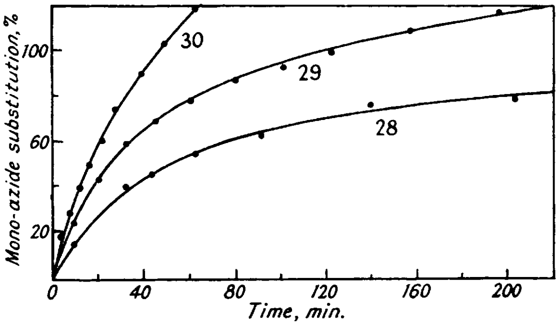
* It should be noted that the mass-law effect on rate of substitution by thiocyanate would be overestimated if we should compute it directly from the proportional separation of the two curves in Fig. 6. This is because substitution in the dichloro-cation by chloride ion does not leave the optical density unchanged, but reduces it. For, as will be noted in Part III, this substitution in the *cis*-cation is associated with partial conversion into the *trans*-isomer, which is less light-absorbing at the wave-length here employed. However, the comparison in the text is still correct, because, as the mass-law retardation tends to zero with increasing excess of thiocyanate ion, so the expected over-estimation tends to zero; and thus the curves of Fig. 6 should still coalesce at high excesses of thiocyanate.

sibility. With excess of azide ion the successive stages of substitution occur, overlapping in time, though the second stage is sufficiently slower than the first to enable approximate rate constants to be calculated for the first stage, with neglect of the second, from measurements made over the first 70% of the first stage.

The kinetics of the substitution have been followed by potentiometric titration of the liberated chloride ion. That they are different from the kinetics of the substitutions already discussed will be clear from the curves in Fig. 7, which show the course of azide substitutions in the initial presence of slightly more than one, slightly more than two, and a little less than three azide ions to one complex cobalt ion. Evidently the rate of substitution depends on the concentration of the entering azide ion.

The results of a closer analysis of the data are given in Table 6. When we try to compute first-order rate constants the values drift; but if, nevertheless, we calculate mean first-order constants for the first 70% of reaction, these values, instead of being the same in the various runs, rise approximately in proportion to the initial concentrations of azide ion (line 4). If, guided by this result, we compute mean second-order constants for the first 70% of reaction, the values are nearly the same for the different runs (line 5).

FIG. 7.



Rates of substitution in cis-[Co en$_2$Cl$_2$]$^+$ *by* N$_3^-$ *in* MeOH *at* 35·8°.
(28) *Initially* [Co en$_2$Cl$_2$]$^+$ 0·94, N$_3^-$ 1·04 *millimolar.*
(29) " " 0·82, " 1·72 "
(30) " " 0·80, " 2·21 "

However, there are still appreciable drifts, indicating roughly compensatory disturbances, some of which, including the incursion of a second stage of substitution, we can eliminate by an extrapolation to give initial second-order rates. The resulting values (line 6) are not quite the same in the different runs. But we can calculate that they represent rates only 3—6 times greater than the rate of the uniform first-order reaction of the dichloro-cation, which we measured by its rotation loss, and also by its substitution with chloride ion, and with thiocyanate ion, and must expect to find as a constituent of the reaction with azide ion. It is easy to make an upper-limiting correction for this first-order process, by assuming that every one of the molecular acts composing it introduces an azido-group, and that none exchanges chlorine, or, in other words, that the mass-law retardation by chloride ion of unimolecular azide substitution is negligible. Thus corrected, the second-

TABLE 6. *Titrimetrically measured rates of substitutions by* N$_3^-$ *in cis*-[Co en$_2$Cl$_2$]$^+$ *to give* [Co en$_2$ClN$_3$]$^+$ *in* MeOH *at* 35·8°.

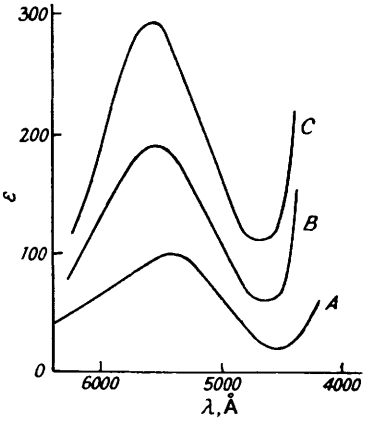
(1) Run No.	28	29	30
(2) [{Co en$_2$Cl$_2$}$^+$Cl$^-$] (mmole/l.)	0·94	0·82	0·80
(3) [NaN$_3$] (mmole/l.)	1·04	1·72	2·21
(4) 10^4k_1 (k_1 in sec.$^{-1}$; first 70% reaction)	3·22	5·33	7·07
(5) k_2 (sec.$^{-1}$ mole^{-1} l.; first 70% reaction)	0·31	0·31	0·32
(6) k_2 (sec.$^{-1}$ mole^{-1} l.; initial rate)	0·34	0·31	0·29
(7) k_2 (initial; corr. for unimolecular process)	0·24	0·25	0·25
(8) $k_2^{\text{anal}\cdot\text{N}_3}$ (sec.$^{-1}$ mole^{-1} l.) (best value)	0·26—0·27		

order rate constants become constant among the runs (line 7). The over-correction will, of course, become less as larger initial concentrations of azide ion diminish the mass-law retardation of the unimolecular part of the reaction. It follows that the true second-order rate constant can be estimated by extrapolation to high azide concentrations: an estimate on this basis is given (line 8). In practice we were prevented from employing very large excesses of azide ion by the low solubility of the azides of the complex cations.

Examination of the kinetics at 25·9° led to an uncorrected initial k_2 of 0·112 sec.^{-1} mole^{-1} l., and a maximally corrected value 0·096 sec.^{-1} mole^{-1} l. If we take, as the best estimate for this temperature, the value 0·100 sec.^{-1} mole^{-1} l., then this, along with the figure for 35·8° given in Table 6, leads to an Arrhenius energy of activation of 18 kcal./mole for the second-order substitution by azide ion. An approximate knowledge of the temperature coefficient of this reaction is useful in connexion with a comparison of rates made later.

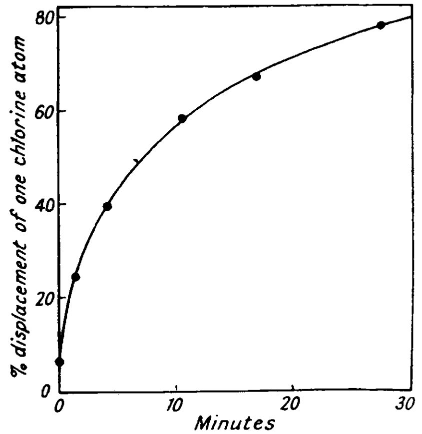
(4*b*) *Changes in Absorption during the Displacement of Chlorine by Azide Ion.*—The curves of Fig. 8 show the changes in light absorption which accompany substitution of the chlorine in the *cis*-dichlorobisethylenediaminecobalt(III) ion by azido-groups. The lowest curve applies to the original cation $[\text{Co en}_2\text{Cl}_2]^+$, and the uppermost curve to its final substitution product $[\text{Co en}_2(\text{N}_3)_2]^+$, the stereochemical form of which is not yet known, though one salt of this composition has been described (Strecker and Oxenius, *Z. anorg. Chem.*, 1934, **218**, 151). We have not yet studied the intermediates $[\text{Co en}_2\text{ClN}_3]^+$ in isolation.

FIG. 8. *Absorption spectra during azide substitution.*



Run 30 (*see Fig.* 7):
A, at time zero. B, at time 100 *min. C, at time* 24 *hr.*

FIG. 9.



Substitution in cis-$[\text{Co en}_2\text{Cl}_2]^+$ *by* MeO^- *at* 0°. (*Run* 33.)

(5) *Action of Methoxide and Hydroxide Ions on the* cis-*Dichloro-cation.*

(5*a*) *Displacement of Chlorine in Methyl-alcoholic Sodium Methoxide.*—An attempt has been made to study the rate of the first of the two possible substitutions,

$$[\text{Co en}_2\text{Cl}_2]^+ \xrightarrow{\text{OMe}^-} [\text{Co en}_2\text{Cl(OMe)}]^+ + \text{Cl}^- \xrightarrow{\text{OMe}^-} [\text{Co en}_2(\text{OMe})_2]^+ + 2\text{Cl}^-$$

The reaction is not well adapted for quantitative investigation, but even our qualitative or semi-quantitative results are significant in relation to the general pattern of kinetic data recorded in this paper. The difficulties in the way of quantitative study are, first, that it was not found possible to employ the methyl-alcoholic solvent in so dry a state that our small concentrations of alkali could with certainty be regarded as methoxide ion entirely, without any hydroxide ion; and secondly, that even at 0° the substitution was inconveniently fast for the analytical method.

The methyl-alcoholic solvent, though carefully dried before use, could have acquired between 0·01 and 0·1% of water by the time the manipulations involved in its employment were completed. Theoretically this could allow from about 5 to 45% of the introduced methoxide ion to suffer conversion into hydroxide ion, and thus to lead to a hydroxy-substitution product in place of the wanted methoxy-substitution product. If the much greater complexing power of water than of methyl alcohol provides a reliable analogy, we might expect the hydroxy-substitution product to be formed, in place of the methoxy-substitution product, nearly to the stoicheiometrically permitted extent.

Owing to the great rates of substitution, we employed about millimolar concentrations, and worked at 0°. Our lack of knowledge of the physical properties of the substitution products precluded the use of physical methods of following the kinetics. The disappearance of alkali was not followed directly, because the substitution products themselves are bases. Therefore we used potentiometric titration of the liberated halide ion. However, as the process of substitution had to be stopped by destroying the substituting agent with acid and as the substitution products were unstable in acid, as will be noted below, the analytical procedure, despite the utmost expedition and the use of low temperatures, was inexact.

Part of the evidence that both hydroxy- and methoxy-substitution products are formed is that, when a small amount of water was deliberately added to the methyl alcohol, then a large proportion of chlorine was liberated instantaneously, whilst any remaining chlorine was thereafter set free in a reaction having a rate of the order of magnitude of that observed in the most carefully dried solvents. With well-dried solvents the instantaneous liberation of chloride ion could be cut down to small proportions, as illustrated for Run 33 in Fig. 9, while the kinetically followed liberation pursued a course, which, to within the considerable experimental error, could be represented as a second-order reaction. The high rate itself shows that the rate depends on the anion, as well as on the dichloro-cation. For the second-order rate constant at 0° we find $k_2^{\text{anal-OMe}} = 1{\cdot}8 \pm 0{\cdot}2$ $\text{sec.}^{-1}\ \text{mole}^{-1}\ \text{l.}$

(5*b*) *Effect of Acid on the Product of Methoxide Substitution.*—In an attempt to discover something of the properties of the cation $[\mathrm{Co\,en_2Cl(MeOH)}]^{++}$, a methyl-alcoholic solution of the product of a methoxide-ion substitution was acidified with methyl-alcoholic hydrogen chloride. It was found that one equivalent of chloride ion rapidly disappeared from the solution : more than half of this one equivalent had gone before the first measurement could be made, while the rest disappeared more gradually, sufficiently so to suggest that the solution before acidification contained two acid-sensitive products (Run 35). It is a surmise that the cation formulated above accepts chlorine in place of methyl alcohol very quickly, while the aquo-cation $[\mathrm{Co\,en_2Cl(H_2O)}]^{++}$ undergoes an analogous displacement of water more slowly. Contemporaneously with these effects, a slow change commenced in the colour of the solution, which changed from violet to green. The final green product was shown by its absorption spectrum to be *trans*-$[\mathrm{Co\,en_2Cl_2}]^+$. The following scheme is consistent with these observations :

$$[\mathrm{Co\,en_2Cl(OMe)}]^+ \xrightarrow[\text{fast}]{\mathrm{H^+}} [\mathrm{Co\,en_2Cl(MeOH)}]^{++} \xrightarrow[\text{fast}]{\mathrm{Cl^-}}$$

$$\textit{cis-}\text{ and }\textit{trans-}[\mathrm{Co\,en_2Cl_2}]^+ \xrightarrow[\text{slow}]{} \textit{trans-}[\mathrm{Co\,en_2Cl_2}]^+$$

(6) *Action of Nitrate Ion on the* cis-*Dichloro-cation.*

A brief polarimetric study has been made of the action of nitrate ions, introduced mainly as lithium nitrate, on the *cis*-dichlorobisethylenediaminecobalt(III) ion, introduced as its nitrate, in solvent methyl alcohol. In these conditions chloride ion was liberated, but a large excess of nitrate ion was always present. The colour changes are instructive. When chloride ion is the only anion acting on the violet *cis*-dichloro-cation, then the final product is the green *trans*-dichloro-cation. However, in the initial presence of excess of nitrate ions, the final product is purple-red. This can only be due to the formation of $[\mathrm{Co\,en_2Cl(NO_3)}]^+$ or $[\mathrm{Co\,en_2(NO_3)_2}]^+$. Accompanying this change of colour, there is a loss of optical rotation, closely similar to that which accompanies substitution by chloride ion or by thiocyanate ion (Sections 2*a* and 3*a*). The rotation loss accompanying the nitrate reaction is of first order in the dichloro-cation, and of zero order in nitrate ion. It shows the same slow increase with ionic strength, as that already described in connexion with substitution by chloride ion, and by thiocyanate ion. Furthermore, as far as the conditions allow comparison, the absolute rate of the first-order polarimetric change accompanying nitrate substitution is the same as the corresponding rates for the chloride and thiocyanate substitutions (cf. Fig. 1). The figures are in Table 7. The comparison of absolute rates cannot be made quite precise, because in these experiments 0·5% of water was added to the methyl alcohol in order to avoid difficulties due to low solubility of some of the nitrates in dry methyl alcohol. However, the comparison between the last two experiments noted in Table 7 is straightforward. The ionic strengths are nearly the same, but in one of the experiments about half the nitrate ion present in the other has been replaced by chloride ion. In the experiment with added nitrate only, the final colour was purple-red. In the experiment with both nitrate and chloride, the final colour was an impure, very pale green. Evidently in this experiment there has been substitution by both nitrate and chloride. Yet the rates in the two experiments are practically identical.

TABLE 7. *Rates of loss of optical activity from solutions of* [Co en$_2$Cl$_2$]$^+$NO$_3^-$ *and* LiNO$_3$ *in* MeOH *at* 35·8°.

Run No.	36	37	38	39	40
[{Co en$_2$Cl$_2$}$^+$NO$_3^-$] (mmole/l.)	0·73	0·75	1·47	1·49	0·74
[LiNO$_3$] (mmole/l.)	9·2	43·4	312	733	367
[LiCl] (mmole/l.)	—	—	—	—	350
$10^3\mu$ (μ = ionic strength)	10	44	313	734	717
[NO$_3^-$]/[{Co en$_2$Cl$_2^+$}]	14	59	213	492	497
[Cl$^-$]/[{Co en$_2$Cl$_2^+$}]	—	—	—	—	473
$10^4k_1^{\text{pol-NO}_3}$ (with k_1 in sec.)	1·15	1·37	1·68	1·87	1·91

(7) *Action of Bromide Ion on the* cis-*Dichloro-cation.*

A similar short study has been made of the action of bromide ions introduced as lithium bromide, on the dichloro-cation, introduced as nitrate, the conditions being the same as in the experiments described in the immediately preceding Section. Chlorine is liberated as chloride ion, and bromine enters the complex. The solution changes colour from violet to yellow-green, which is the colour of *trans*-[Co en$_2$ClBr]$^+$. Accompanying this bromide substitution there is a loss of optical rotatory power closely similar to that which accompanies substitutions by chloride, thiocyanate, and nitrate ions. It is of first order in the complex cation, but of zero order in bromide ion. It shows the usual positive salt effect. As far as comparison is possible its absolute rate is the same as that associated with the other substitutions mentioned (cf. Fig. 1). The figures are in Table 8.

TABLE 8. *Rate of loss of optical activity from solutions of* [Co en$_2$Cl$_2$]$^+$NO$_3^-$ *and* LiBr *in* MeOH *at* 35·8°.

Run No.	41	42	43
[{Co en$_2$Cl$_2$}$^+$NO$_3^-$] (mmole/l.)	1·77	1·78	1·83
[LiBr] (mmole/l.)	2·76	10·4	57·5
$10^3\mu$ (μ = ionic strength)	3·5	12	59
[Br$^-$]/[{Co en$_2$Cl$_2$}$^+$]	1·6	5·8	31·4
$10^4k_1^{\text{pol-Br}}$ (with k_1 in sec.$^{-1}$)	1·08	1·20	1·52

(8) *Action of Nitrite Ion on the* cis-*Dichloro-cation.*

We have made a short examination of the action of nitrite ions introduced as sodium nitrite, on the *cis*-dichloro-cation, introduced in the form of its nitrate, the conditions being as in the experiments of the two immediately preceding Sections. It emerged that this substitution by nitrite ion is mechanistically marginal, and has a mixed kinetic form. Having observed this, we did not pursue the matter closely, since a quantitative kinetic analysis would have involved much detailed work, and it seemed that the qualitative deduction from the experiments mentioned was likely to be the most interesting of any conclusions that a comprehensive study might have yielded.

When nitrite ion acts on the dichloro-cation in methyl alcohol, chloride ion is liberated, and nitrite ion enters the complex, to form, finally, dinitro-cations. The colour changes from violet to golden-yellow. Solutions of both *cis*- and *trans*-[Co en$_2$(NO$_2$)$_2$]$^+$ are yellow. The substitution is accompanied by a first-order loss of optical rotation, which, however, is dependent (apart from salt effects) on the concentration of nitrite ion. By the use of high proportions of nitrite ions, the rates are raised considerably above the first-order rate associated, at given ionic strength, with substitutions by chloride, thiocyanate, nitrate, and bromide ion. The illustration in Table 9 is an extreme one, in which, by the use of a 300-fold excess of nitrite ion, the rate is built up to 3·5 times the common first-order rate at the same ionic strength, of any of the substitutions mentioned. We assume the incursion, in general of some, and in this example of a predominating amount, of bimolecular substitution by nitrite ion. Such substitution would produce an increased rate of loss of optical activity whether the immediate bimolecular product were the *trans*-, the racemic *cis*-, or an optically active *cis*-form of [Co en$_2$Cl(NO$_2$)]$^+$, because the last has only a small rotatory power for yellow light relatively to that of the original dichloro-compound. By neglecting the possible small rotatory power of the bimolecular product, we can, after making an estimated allowance for the part of the rate which does not depend on nitrite ion, compute an approximate value for the second-order rate of substitution by nitrite ion, as is done in Table 9.

TABLE 9. *Rate of loss of optical activity from a solution of* [Co en$_2$Cl$_2$]$^+$NO$_3^-$ *and* [NaNO$_2$] *in* MeOH *at* 35·8°. (*Run* 45.)

[{Co en$_2$Cl$_2$}$^+$NO$_3^-$] (mmole/l.)	0·576
[NaNO$_2$] (mmole/l.)	165
$10^4k_1^{\text{pol}\cdot\text{NO}_2}$ (composite) (k_1 in sec.$^{-1}$)	6·0
$10^4k_1^{\text{pol}\cdot\text{NO}_2}$ (estimated unimolecular part)	1·7
$k_2^{\text{pol}\cdot\text{NO}_2}$ (sec.$^{-1}$ mole^{-1} l.) (by difference)	0·0026

(9) *Discussion : The Two Mechanisms of Substitution.*

We have now described nucleophilic substitutions by seven anions each displacing chlorine from the *cis*-dichlorobisethylenediaminecobalt(III) ion in solvent methyl alcohol. For four of these anionic reagents, the nitrate, chloride, bromide, and thiocyanate ion, substitution proceeds according to a first-order law : the rates depend on the concentration of the cation undergoing substitution, but not on that of the substituting agent; and thus the rates are the same for all these substituting agents (the medium and temperature being the same), as shown by the graphical conspectus in Fig. 1. This common rate is also the rate at which the cobalt cation loses optical activity in the absence of any stronger nucleophilic reagent than those mentioned. We interpret these reactions as unimolecular nucleophilic substitutions, involving loss of asymmetry in the rate-determining solvent-assisted dissociation :

$$[\text{Co en}_2\text{Cl}_2]^+ \xrightarrow{\text{slow}} \underset{\substack{\text{(optically}\\\text{inactive)}}}{[\text{Co en}_2\text{Cl}]^{++}} \xrightarrow[\text{X}^-]{\text{fast}} [\text{Co en}_2\text{ClX}]^+ \quad . \quad . \quad . \quad . \quad . \quad (S_{\text{N}}1)$$

Certain detailed kinetic observations fit this interpretation. An ionic-strength acceleration of the somewhat large order of magnitude of those observed in organic unimolecular substitutions has been found; and a mass-law retardation, which, when it can be observed, is the most diagnostic kinetic character of the unimolecular mechanism, has been observed in these substitutions.

Three of the anionic reagents substitute partly or wholly according to a second-order law. Substitution by nitrite ion shows mixed kinetics, but a considerable part of the rate may depend on the concentration of the anions. The faster substitution by azide ion proceeds mainly according to a second-order law, the rate depending not only on the cation substituted but also on the substituting agent, though a small background reaction of first-order form appears to be present. The still faster substitution by methoxide ion follows a second-order law, as closely as could be ascertained in face of difficulties due to the high rate. We interpret these second-order reactions as bimolecular nucleophilic substitutions :

$$\text{X}^- + [\text{Co en}_2\text{Cl}_2]^+ \longrightarrow [\text{Co en}_2\text{ClX}]^+ + \text{Cl}^- \quad . \quad . \quad . \quad . \quad . \quad (S_{\text{N}}2)$$

The second-order substitutions differ so widely with respect to rate that they could not all be kinetically investigated at the same temperature. However, having determined the temperature coefficient of the rate of the azide substitution, we can compare this rate, on the one hand, with that of the nitrite substitution at 35·8°, and, on the other, with that of the methoxide substitution at 0°. We thus estimate that, at a common temperature, the second-order rates of reaction of the three substituting agents, OMe^-, N_3^-, NO_2^-, would stand approximately in the ratio 30,000 : 100 : 1.

These relations show that the second-order reactions are not conjugate-base substitutions S_N1cB or S_N2cB, rate-controlled by the extraction of a proton from an ethylenediamine ligand. If they were, the rates would depend on the basicity of the reagent, not on nucleophilic power apart from this specific form. We should expect to be able to make a Brönsted plot, demonstrating a linear free-energy relation between rate and basicity. Now OMe^- is more basic than N_3^- by a ratio of something like 10^{12}, while N_3^- is more basic than NO_2^- by one of only about $10^{1 \cdot 5}$. These factors bear no kind of linear-logarithmic relation to the rate ratios, $10^{2 \cdot 5}$ from OMe^- to N_3^-, and 10^2 from N_3^- to NO_2^-. Obviously these reagents are not attacking a proton, and therefore they must be attacking the cobalt atom, as assumed in our interpretation of the reactions as S_N2 substitutions.

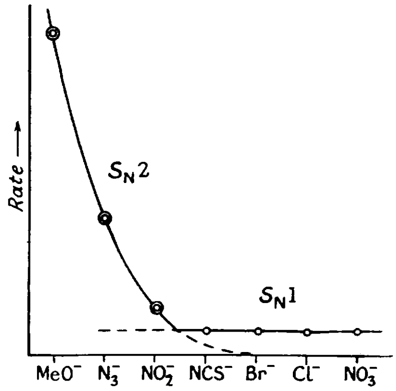


FIG. 10.

Summary of kinetic relations applying to nucleophilic substitution in cis-$[Co\,en_2Cl_2]^+$. *(Schematic.)*

Our mechanistic deductions have support from analogy; for the kinetic situation is not unprecedented. It was shown in 1935 for nucleophilic substitution at carbon, that, if substituting agents, arranged in order of diminishing nucleophilic power, are considered with respect to their substitutions in the same alkyl compound, then, on passage through the series, the reaction order at first remains second, while the absolute rates diminish strongly from case to case, until a point of change is reached, whereafter the reaction order becomes first, and the rates maintain a constant value in the successive cases. Gleave, Hughes, and Ingold represented these relations in a schematic diagram (*J.*, 1935, 236). Their conclusion, that the change of kinetic form, and of rate trend, betrays a change of mechanism from S_N2 to S_N1, is to-day well understood. The present study of nucleophilic substitutions at octahedrally bonded cobalt has revealed a similar pattern of results, which we may likewise represent schematically, as in Fig. 10. Our deduction concerning the co-existence of mechanisms S_N2 and S_N1 in this range of substitution is only an extension of the old conclusion; but we emphasise the extension, believing that the idea of duplexity of mechanism has a notable part to play in the future study of inorganic substitutions, just as it has been basic to the growth in recent decades of our knowledge of organic substitutions.

(10) *Experimental Methods and Illustrative Data.*

(10*a*) *Preparations.*—*trans*-Dichlorobisethylenediaminecobalt(III) chloride was prepared and converted into the *cis*-isomer, and the latter was resolved through the (+)-α-bromocamphor-π-sulphonate, from which the optically active chloride was regenerated, essentially as described in "Inorganic Syntheses," Vol. II, p. 222. For optical measurements the *trans*-isomer had to be freed from accompanying, less soluble, trisethylenediaminecobalt(III) chloride: this was accomplished by extracting the dichloro-salt with water, and, after filtering, causing it to crystallise by the addition of ethyl alcohol, and then extracting it with, and crystallising it from, dry methyl alcohol (Found: C, 16·9; N, 19·7; Cl, 37·1. Calc.: C, 16·8; N, 19·6; Cl, 37·3%). The *cis*-isomer, prepared from the crude *trans*-isomer, became purified during its resolution (Found, for the *l*-*cis*-bromocamphorsulphonate: N, 10·0. Calc.: N, 10·0%). The *l*-*cis*-chloride (Found: C, 16·8; N, 19·6%), freed from the bromocamphorsulphonate by treatment, repeated as necessary, with cold alcoholic-ethereal hydrogen chloride followed by alcohol, was converted into the nitrate (Section 6) by precipitation with lithium nitrate from methyl-alcoholic solution.

The *trans*-dichloro-chloride was converted by treatment with potassium thiocyanate into *trans*-chlorothiocyanatobisethylenediaminecobalt(III) thiocyanate and *cis*-chlorothiocyanatobisethylenediaminecobalt(III) chloride, and the latter was resolved to give the *l*-*cis*-chlorothiocyanato-(+)-α-bromocamphor-π-sulphonate, and thence the *l*-*cis*-chlorothiocyanato-perchlorate, essentially as described by Werner (*Annalen*, 1912, **386**, 133). For optical measurements the bromocamphorsulphonate was crystallised from methyl alcohol with addition of ether (Found: C, 30·6; N, 12·0. Calc.: C, 30·8; N, 12·0%). The *trans*-chlorothiocyanato-thiocyanate was purified by crystallisation from water (Found: C, 22·1; H, 4·8; N, 25·2. Calc.: C, 21·8; H, 4·9; N, 25·4%), and, by means of potassium iodide, was converted into the iodide, which was crystallised from water (Found: C, 14·9; N, 17·7. Calc.: C, 15·0; N, 17·5%). The dithiocyanato-thiocyanate was obtained as a final product of one of the investigated substitutions, as noted in Section 3*b* (Found: C, 24·2; H, 4·6. Calc.: C, 23·8; H, 4·6%).

Most of the required simple reagents were prepared or purified by standard methods. It was found more satistactory to prepare lithium thiocyanate from purified lithium sulphate and purified barium thiocyanate, than to try to purify commercial lithium thiocyanate. Methyl alcohol was dried by reaction with magnesium, and subsequent storage over magnesium perchlorate, followed by distillation. Lithium radio-chloride was prepared by a Szilard–Chalmers separation from potassium perchlorate, which had been irradiated for one month in the Harwell pile, under a flux of 10^{10} neutrons per cm.^{2} per sec., and kept for a further month in order to allow decay of most of the potassium activity. To a solution of this material in water, a small amount of sodium chloride was added as carrier, and then the chloride was precipitated as silver chloride, converted by reduction with hydrogen at red heat into hydrogen chloride, and thence into lithium chloride, which was purified with the aid of acetone, and dried. Lithium chloride, both ordinary and radioactive, as well as other lithium salts, were stored in solution in dry methyl alcohol suitably protected in the reservoir of an automatic burette.

(10*b*) *Apparatus*.—Measurements of rotatory dispersion were made on a spectropolarimeter with monochromator by Schmidt and Haentsch. For polarimetrically-followed kinetic runs a polarimeter by Hilger (Mk. 11) was employed along with a sodium lamp. Both for measurements of absorption spectra, and for spectrophotometrically-followed kinetic runs, the Unicam quartz spectrophotometer (SP 500) was used. For measurements of radioactivity, a Geiger counter tube of type M6, by Twentieth Century Electronics, was employed, pulses from the counter being amplified and fed into a Morley and Duke scaling unit, there to be magnetically counted and recorded. The potentiometric titration equipment was standard.

(10*c*) *Polarimetric Kinetics*.—The first measurements of the rate of loss of optical activity from *cis*-dichlorobisethylenediaminecobalt(III) salts were made by maintaining the sample continuously in a jacketed polarimeter tube at the experimental temperature. However, it was discovered that the light passing through the polarimeter tube accelerated the reaction appreciably, and therefore all recorded runs of the final series were made by the following method which excludes the action of light.

The experimental solution was prepared, with the aid of solvent and salt solutions delivered from the automatic burettes, in a dry nitrogen-filled flask connected through a sealed-in sintered-glass filter to the dry nitrogen-filled reservoir of an automatic pipette, into which the solution was transferred by suction. From there it was delivered under nitrogen and sealed into ten tubes, which were cooled to −80°, blackened, and transferred to the blackened thermostat. After an allowance of 2 minutes for warming up, the first tube, representing the time zero of the kinetic run, was cooled to −80°, and at known subsequent times the other tubes were similarly cooled. For measurement of the optical rotations, the contents of each tube were transferred in turn to a jacketed polarimeter tube held at 0°. The change of rotation at this temperature is too small to be observed in 30 minutes, and thus plenty of time was available for making the readings as precise as the equipment permitted. A sample run is recorded in Table 10.

TABLE 10. *Loss of optical rotation of l-cis-*$[\text{Co en}_2\text{Cl}_2]^+\text{Cl}^-$ *in* MeOH *at* 35·8° (*Run no.* 1.)

Initially $[\{\text{Co en}_2\text{Cl}_2\}^+\text{Cl}^-] = 1{\cdot}745 \times 10^{-3}$M; α = observed rotation in a 10-cm. tube at 0° for Na light; $k_1 = (2{\cdot}303/t) \log_{10} (\alpha_0/\alpha_t)$.

t (min.)	0	16	38	58·5	77·5	103·5	146	187·5	249·5
α (deg.)	0·417	0·378	0·324	0·297	0·256	0·220	0·176	0·129	0·080
% Reaction	0	9·3	22·3	28·8	38·6	47·2	57·8	69·1	80·8
$10^4 k_1$ (min.$^{-1}$)	—	61	66	58	63	62	59	63	66

Mean $k_1 = 0{\cdot}0063$ min.$^{-1}$.

(10*d*) *Spectrophotometric Kinetics.*—The optical density $\log_{10} (I_0/I) = \varepsilon c d$, where I_0 is the intensity of the incident and I that of the emergent light, and ε is the extinction coefficient, c the concentration, and d the cell thickness, has been used to follow, for example, the conversion of the dichloro-cation, through substitution by the thiocyanate ion, into the chlorothiocyanato-cation. Most of the optical-density measurements were made on the solution which had been used for the rotation measurements, some of the solution, still at 0°, being transferred to the absorption cell of the spectrophotometer. A specimen run is given in Table 11.

TABLE 11. *Change of optical density at* 5400 Å *during the reaction of cis-*$[\text{Co en}_2\text{Cl}_2]^+\text{Cl}^-$ *with* LiNCS *at* 35·8° *in* MeOH. (*Run no.* 23.)

Initially $[\{\text{Co en}_2\text{Cl}_2\}^+\text{Cl}^-] = 0{\cdot}718 \times 10^{-3}$M, and $[\text{LiNCS}] = 13{\cdot}7 \times 10^{-3}$M.
D = optical density in a 4-cm. cell for λ 5400 Å; $k_1 = (2{\cdot}303/t) \log_{10} (D_\infty - D_0)/(D_\infty - D_t)$.

t (min.)	0	10·5	20	30	41·3	52·5	63·8	79	103·5	140
D_t	0·277	0·286	0·292	0·300	0·306	0·314	0·322	0·331	0·341	0·355
% Reaction	0	5·0	8·3	12·6	15·9	20·3	24·8	29·7	35·1	42·9
$10^4 k_1$ (min.$^{-1}$)	—	49	43	45	42	43	45	45	42	40

From absorption spectrum $D_\infty = 0{\cdot}459$. Extrapolated $k_1 = 0{\cdot}0047$ min.$^{-1}$.

(10*e*) *Kinetics of Chlorine Exchange by Radioactivity.*—A solution of weighed *cis*-dichlorobisethylenediaminecobalt(III) chloride in methyl alcohol was made up in the dry, nitrogen-filled reservoir of an automatic sampling apparatus, immersed in a darkened thermostat at 35·8°, and a known volume of methyl-alcoholic lithium radio-chloride was added. After 3 minutes the first measured sample, representing the time-zero of the kinetic run, was expelled into a cooled beaker, brought as quickly as possible to −20°, and treated with methyl-alcoholic silver nitrate in slight excess over the equivalent of the ionic chlorine. The solution was immediately filtered, and the precipitate quickly washed with ice-cold water, into a standard flask, and the filtrate, after the addition of a few drops of concentrated aqueous ammonia, was then made up to the volume mark. Counts were made on this solution at convenience. Other portions of solution from the sampling apparatus at known subsequent times were treated similarly. Because of the large excess of lithium chloride used, a first-order equation was applied. An illustrative run is recorded in Table 12.

TABLE 12. *Exchange of chlorine between cis-*$[\text{Co en}_2\text{Cl}_2]^+$ *and* Cl^- *in* MeOH *at* 35·8°. (*Run no.* 18.)

Initially $[\{\text{Co en}_2\text{Cl}_2\}^+\text{Cl}^-] = 1{\cdot}77 \times 10^{-3}$M; $[^{36}\text{Cl-labelled LiCl}] = 38{\cdot}05 \times 10^{-3}$M. Y_t = count per 100 min., corrected for background, on 5·98 c.c. of solution, after precipitation with 0·80 c.c. of 0·3079N-AgNO_3, filtration, and making the filtrate up to 10 c.c. with water. $k_1 = (2{\cdot}303/t) \log_{10} \{(\frac{1}{2}Y_\infty - Y_0)/(\frac{1}{2}Y_\infty - Y_t)\}$.

t (min.)	0	19·3	32·5	61·8	110	∞
Y_{t_4}	300	920	1310	2130	3400	7200
$10^4 k_1$ (k_1 in min.$^{-1}$)	—	107	112	131	413	—
% of 1 Cl exchanged	8·3	25·5	36·2	59·0	94·0	(200)

(10*f*) *Kinetics by Potentiometric Titration of Chloride Ion.*—This form of analysis was used, for example, to follow displacement of chlorine by means of azide ion from the *cis*-dichlorobisethylenediaminecobalt(III) ion. One electrode was provided by a silver wire dipping in the solution, which was connected by a saturated potassium nitrate, agar-agar, salt-bridge to a calomel half-cell. The titrant was methyl-alcoholic silver nitrate, while the solvent of the titrated solution was a mixture of 2 vols. of methyl alcohol and 3 vols. of acetone, to which was added a little nitric acid.

The reacting solutions were made up as usual under nitrogen and with exclusion of moisture, and reaction was allowed to proceed in a darkened thermostat. Measured samples were delivered into the acidified acetone at −80°, and, after the titration vessel had then been surrounded with ice-water, were titrated as rapidly as possible. A sample run is recorded in Table 13.

Table 13. *Titrimetrically followed reaction of cis*-$[\mathrm{Co\,en_2Cl_2}]^+\mathrm{Cl}^-$ *with* $\mathrm{NaN_3}$ *in* MeOH *at* 25·9. (*Run no.* 31.)

Initially $[\{\mathrm{Co\,en_2Cl_2}\}^+\mathrm{Cl}^-] = 0{\cdot}775 \times 10^{-3}$M, and $[\mathrm{NaN_3}] = 1{\cdot}93 \times 10^{-3}$M. Titres are in c.c. of $1{\cdot}00 \times 10^{-3}$N-$\mathrm{AgNO_3}$ for 10 c.c of reaction solution, and so the calculated initial titre is 7·75 c.c., while the calculated final titre for one chlorine atom replaced is 15·5 c.c. From the titre at the time of taking the first sample, $t = 0$, it follows that 16·14% of reaction has by then occurred. Therefore at $t = 0$, $[\{\mathrm{Co\,en_2Cl_2}\}^+\mathrm{Cl}^-] = 0{\cdot}650 \times 10^{-3} = a$ and $[\mathrm{NaN_3}] = 1{\cdot}068 \times 10^{-3}\mathrm{M} = b$. In terms of titres, $a = 6{\cdot}50$ c.c. and $b = 10{\cdot}68$ c.c. The rate constant is calculated from $k_2 = \{2{\cdot}303/t(b-a)\} \log_{10} \{a(b-x)/(b(a-x)\}$.

t (min.)	0	8·25	22·5	62	87·5	139·5	171	207	261	321	446
Titre (c.c.)	9·0	9·45	9·8	11·05	11·6	12·55	12·90	13·35	13·85	14·1	14·65
x (c.c.)	0	0·45	0·80	2·05	2·60	3·55	3·90	4·35	4·85	5·10	5·65
k_2 (min.$^{-1}$ mole^{-1} l.)	—	8·4	5·8	6·4	6·4	6·6	6·5	6·8	7·0	6·6	6·9
% 1 Cl replaced	16·1	21·9	26·4	42·6	49·6	62·0	66·5	72·3	78·7	82·0	89·0

Mean $k_2 = 6{\cdot}7$ min.$^{-1}$ mole^{-1} l.

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