407. *Mechanism of Replacement of Chlorine in* cis- *and* trans-*Chloronitrobis(ethylenediamine)cobalt*(III) *Ions by Thiocyanate in Methanol.*

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The rate of replacement of chlorine by thiocyanate in the *cis*-chloronitrobis(ethylenediamine)cobalt(III) ion in methanol solution is independent of the thiocyanate concentration, but that in the *trans*-isomer shows a slight dependence on the thiocyanate concentration and is 14 times (or 28 times if calculated for one chlorine atom only) greater than the rate of the similar replacement in the *trans*-dichlorobis(ethylenediamine)cobalt(III) ion in methanol. The accelerating influence of the nitro-group suggests that this substitution is an S_N2 process involving methanol as the nucleophilic reagent. The negative electromeric effect of the nitro-group causes polarisation of the cobalt atom. The polarisation demand of the binding of the methanol seems to be more important than the loosening of the displaced chlorine which the nitro-group makes more difficult. An analogy is drawn with the aquation of the same complexes.

THE kinetics of octahedral substitutions have been studied by several authors, most of the work being done in aqueous solutions because of the insolubility of complex ions in most other solvents. It has been shown that water is not a very suitable solvent, except for very strongly nucleophilic reagents, *e.g.*, hydroxide ion, because it has a higher complex-forming power towards the ions of transition metals than any other solvent except liquid ammonia, so that an intermediate hydrolysis step takes place.[1,2]

Methanol has been considered as a suitable solvent in which a number of direct reactions seem to occur. Brown and Ingold[3] studied the rates of reactions of *cis*-dichlorobis-(ethylenediamine)cobalt(III) ion in methanol with seven anions which displace chlorine. They found that four of them (NO_3^-, Br^-, SCN^-, and $*Cl^-$), all weakly nucleophilic, showed first-order kinetics; for three more strongly nucleophilic anions (NO_2^-, N_3^-, and OMe^-) substitution showed second-order kinetics, with the rates differing widely in order of nucleophilic power. However, Brown and Ingold's kinetic results on the basis of which the S_N1 mechanism was predicted are also in agreement with an S_N2 mechanism involving the solvent methanol as the nucleophilic reagent.

The reactions of *cis*- and *trans*-chloronitrobis(ethylenediamine)cobalt(III) ions with thiocyanate in methanol which we investigated also showed first-order kinetics (complete independence of the rate on the thiocyanate calculated for the *cis*-complex and slight dependence for the *trans*-complex). The comparison of the rates of replacement of chlorine by thiocyanate in methanol in *trans*-chloronitrobis(ethylenediamine)cobalt(III) ion and in *trans*-dichlorobis(ethylenediamine)cobalt(III) ion showed that the replacement in the former complex is about 14 times (or 28 times if calculated for one chlorine atom) faster than in the dichloro-complex. This is not in accordance with a dissociation mechanism, since the polarisation of the cobalt atom by the nitro-group should oppose the heterolysis of the departing halogen, not facilitate it.[2]

Comparison of the rates of replacement of chlorine by thiocyanate in *cis*- and *trans*-chloronitro- and *cis*- and *trans*-dichloro-bis(ethylenediamine)cobalt(III) ions with the corresponding rates of aquation also lends support to the idea that the replacement of chlorine by thiocyanate requires two stages, the first being a rate-determining methanolysis.

[1] Brown, Ingold, and Nyholm, *J.,* 1953, 2674.
[2] Ašperger and Ingold, *J.,* 1956, 2862.
[3] Brown and Ingold, *J.,* 1953, 2680.

RESULTS

Kinetics and Products of the Reaction of trans-*Chloronitrobis(ethylenediamine)cobalt*(III) *Ion with Thiocyanate Ion in Methanol.*—The spectral method was used for measuring the rates of substitutions. For this it was necessary to prepare the complexes in crystalline form and to determine their absorption spectra in methanolic solution. *trans*-Chloronitrobis(ethylene-diamine)cobalt(III) nitrate, *cis*-chloronitrobis(ethylenediamine)cobalt(III) chloride, and *trans*- and *cis*-thiocyanatonitrobis(ethylenediamine)cobalt(III) thiocyanate were prepared. Solutions of these complexes were made in absolute methanol dried by Lund and Bjerrum's method.[4] Analyses showed that methanol contained about 0·05% of water. Pearson *et al.* previously found [5] that up to 0·5% of water had no effect on the measured rates for some *trans*-[CoA$_2$Cl$_2$]$^+$ complexes in methanol (A = ethylenediamine, propylenediamine, 1,2-dimethyl-ethylenediamine, diaziridine, and tetramethylethylenediamine, respectively).
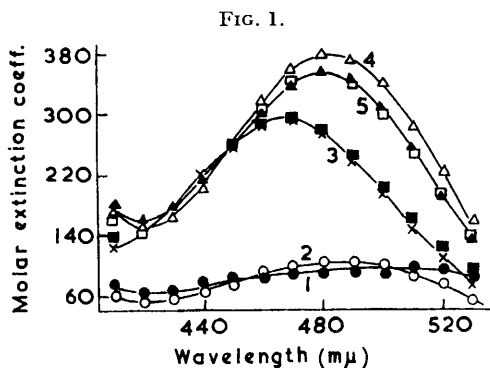

FIG. 1.

FIG. 2.

FIG. 1. *Absorption spectra of* 0·001M-*methanolic solutions, acidified by toluene*-p-*sulphonic or perchloric acid.*

(1) *cis*-[Co en$_2$(NO$_2$)Cl]Cl. (2) *trans*-[Co en$_2$(NO$_2$)Cl]NO$_3$. (3) *trans*-[Co en$_2$(NO$_2$)(NCS)]SCN; ×, *of the crystallised complex*; ■, *of the reaction product of* 0·001M-*trans*-[Co en$_2$(NO$_2$)Cl]NO$_3$ *and* 0·04M-KSCN *after a few days.* (4) *cis*-[Co en$_2$(NO$_2$)(NCS)]SCN. (5) ▲, *of the reaction product of* 0·001M-*cis*-[Co en$_2$(NO$_2$)Cl]Cl *and* 0·02—0·08M-KSCN; □, *of the calculated spectrum supposing 80% of cis*-[Co en$_2$(NO$_2$)(NCS)]$^+$ *and* 20% *of its trans-isomer.*
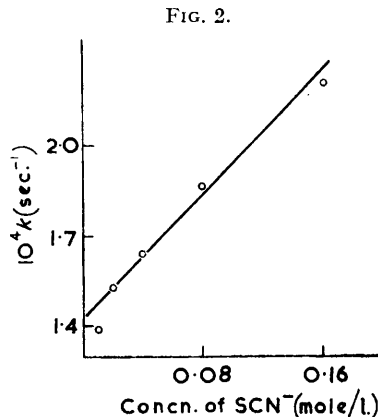
FIG. 2. *The dependence of the pseudo-first-order rate constant of the substitution of chlorine by thiocyanate in* trans-[Co en$_2$(NO$_2$)Cl]$^+$ *on the concentration of* SCN$^-$ *at* 30°.

The methanolic solutions of the complexes were acidified by addition of toluene-*p*-sulphonic acid or perchloric acid, to prevent the formation of methoxide ion, which will atack the complex.[5] The water introduced by addition of acids was found to be negligible (0·01%).

The addition of perchloric acid markedly reduced the solubility of the complex. The spectral measurements showed that the addition of only small quantities of these acids, just sufficient to ensure acidity, did not influence their spectra. Larger quantities of toluene-*p*-sulphonic acid added to *trans*-thiocyanatonitrobis(ethylenediamine)cobalt(III) thiocyanate solutions produced a violet colour; the same colour is obtained when *trans*-chloronitrobis-(ethylenediamine)cobalt(III) nitrate, potassium thiocyanate, and a larger quantity of toluene-*p*-sulphonic acid are dissolved in methanol.

A plot of absorption spectra of *trans*- and *cis*-chloronitrobis(ethylenediamine)cobalt(III) ions and *trans*- and *cis*-thiocyanatonitrobis(ethylenediamine)cobalt(III) ions is given in Fig. 1. The absorptions were measured against dry methanol containing the same quantity of the acid as the test solution. The differences in light absorptions of the starting compound and the reaction products are so great that the reaction rate and even the stereochemistry of the products can be determined. It was found that between 400 and 530 mμ the absorption spectrum of

[4] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[5] Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379.

the freshly prepared 0·001M-solution of *trans*-thiocyanatonitrobis(ethylenediamine)cobalt(III) thiocyanate in methanol was identical with that of the mixture of 0·001M-*trans*-chloronitro-bis(ethylenediamine)cobalt(III) nitrate and 0·04M-potassium thiocyanate in methanol after storage for ten half-lives. Fig. 1 (curve 3) contains these results. It is obvious that the replacement of chlorine by thiocyanate in *trans*-chloronitrobis(ethylenediamine)cobalt(III) ion proceeds with complete retention of configuration and that the product is the *trans*-thiocyanato-nitro-ion. Basolo *et al.*[6] found for the same substitution in 95% methanol that the substitution proceeds " largely " by retention of configuration.

The greatest difference of absorption between the *trans*-chloro- and the *trans*-thiocyanato-nitrobis(ethylenediamine)cobalt(III) ion occurs at 470 mμ where is also the maximum of absorption of the latter ion. This, therefore, was the wavelength used for following the kinetics. The initial concentration of *trans*-chloronitrobis(ethylenediamine)cobalt(III) ion was in all cases 0·001M, and that of potassium thiocyanate was varied between 0·01 and 0·16M. Again, toluene-*p*-sulphonic acid or perchloric acid was used for obtaining acid methanolic solutions. It was found that in the weakly acid solutions the reaction rate was independent of the hydrogen-ion concentration. The methanolic solutions of *trans*-chloronitro- and of *trans*-thiocyanato-nitro-bis(ethylenediamine)cobalt(III) ion obeyed the Beer–Lambert law. Therefore the concentration of the latter ion was calculated from the expression $(E - E_0) \times 0.001/(E_\infty - E_0)$, where E_0 and E_∞ are the extinctions of the reaction mixture at $t = 0$ and $t = \infty$, respectively. [E_∞ agreed with the extinction of a 0·001M-solution of *trans*-thiocyanatonitrobis(ethylene-diamine)cobalt(III) thiocyanate at the same wavelength.] The pseudo-first-order rate constants were calculated up to 50% completion of reaction. In a particular run the first-order rate constant decreased by about 10—20%. Table 1 shows that the pseudo-first-order rate con-

TABLE 1. *Rates of replacement of chlorine by* SCN⁻ *in* 0·001M-trans-[Co en₂(NO₂)Cl]⁺ *to give* trans-[Co en₂(NO₂)(NCS)]⁺ *in methanol at* 30°.

KSCN (mole/l.)	0·01	0·02	0·04	0·08	0·16
10^4k (sec.⁻¹)	1·39	1·53	1·64	1·87	2·20

stants changed also with the initial concentration of potassium thiocyanate. The dependence of the rates on temperature is given in Table 2. From the data of Table 2 a good Arrhenius plot was obtained by the method of least squares, so that the rate constant could be expressed in the form $k = 3.44 \times 10^{11}$ exp $(-21,300/RT)$ sec.⁻¹ over the temperature range studied.

TABLE 2. *Temperature-dependence of the rates of substitution of chlorine by* 0·08M-SCN⁻ *in* 0·001M-trans-[Co en₂(NO₂)Cl]⁺ *in methanol.*

Temperature	20°	25°	30°	35°
10^5k (sec.⁻¹)	5·04	8·41	18·7	26·8

The content of water in methanol was also varied. It was mentioned that absolute methanol contained about 0·05% of water; this was increased to 0·25 and to 0·5%, and the rates of replacement of chlorine by thiocyanate were measured at 30°. The rates remained unchanged. It is therefore most unlikely that water present in absolute methanol takes part in this reaction.

Kinetics and Products of the Reaction of cis-*Chloronitrobis(ethylenediamine)cobalt*(III) *Ion with Thiocyanate Ion in Methanol.*—Ultraviolet light caused partial isomerisation of *cis*-chloro-nitrobis(ethylenediamine)cobalt(III) ion to its *trans*-isomer, so its methanolic solutions were always kept in the dark. Methanolic solutions were acidified by perchloric acid to a concentration of 0·0001M. The initial concentration of *cis*-chloronitrobis(ethylenediamine)cobalt(III) chloride was always 0·001M. With potassium thiocyanate concentrations of 0·02, 0·04, and 0·08M, at 35·8°, equilibrium was reached in about 4 days.

The absorption spectrum of the reaction product does not correspond to that of either pure *cis*- or pure *trans*-thiocyanatonitrobis(ethylenediamine)cobalt(III) ion but to that of a mixture of the two. The maximum absorption of the *cis*-thiocyanate is at 480 mμ. At that wave-length the extinction coefficients are:

cis-[Co en₂(NO₂)(NCS)]⁺, 380; *trans*-[Co en₂(NO₂)(NCS)]⁺, 275 cm.⁻¹ mole⁻¹ l.

⁶ Basolo, Stone, and Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 819.

It was shown that at this wavelength, and at the concentrations involved, salts of both these cations obey the Beer–Lambert law, so that concentrations and compositions can be calculated with the aid of the usual linear relations. The molar extinction coefficient of the reaction mixture was found to be 357 cm.$^{-1}$ mole^{-1} l. (arithmetic mean of several measurements at different thiocyanate concentrations); hence the equilibrium mixture contained about 80% of the *cis*- and 20% of the *trans*-ion. (Basolo *et al.*[6] found for the same reaction in 95% methanol " largely " retention of configuration.) For some unknown reason increase of the initial concentration of potassium thiocyanate slightly increased the initial and the final extinctions (E_0 and E_∞) of the reaction mixture. This, however, did not influence the above-mentioned ratio of the *cis*- and *trans*-ions since the differences ($E_\infty - E_0$) remained constant.

The measured absorption spectrum of the reaction products corresponded exactly to the calculated spectrum on the assumption of 80% of *cis*-thiocyanatonitrobis(ethylenediamine)-cobalt(III) ion and 20% of its *trans*-isomer (Fig. 1, curve 5). The first-order rate constants were calculated from the changes of extinctions of the reaction mixtures at 480 mμ. The equation $k = (2 \cdot 303/t) \log_{10}[(E_\infty - E_0)/(E_\infty - E)]$ gave consistent values for the rate constant in every run, and this was independent of the initial concentration of potassium thiocyanate, as shown in Table 3.

TABLE 3. *Rates of replacement of chlorine by* SCN$^-$ *in* 0·001M-cis-[Co en$_2$(NO$_2$)Cl]$^+$ *to give 80% of* cis- *and* 20% *of* trans-[Co en$_2$(NO$_2$)(NCS)]$^+$ *in methanol at 35·8°.*

KSCN (mole/l.)	0·02	0·04	0·08
$10^5 k$ (sec.$^{-1}$)	1·24, 1·23	1·24, 1·21, 1·27	1·24, 1·24

Measurements were also made at 450 mμ, where the difference of molar extinction co-efficients of *cis*-chloronitro- and *cis*-thiocyanatonitro-complexes is much smaller than at 480 mμ, so that the precision of measurements was decreased, but at that wavelength the molar extinction coefficients of *cis*- and *trans*-thiocyanatonitro-complexes are identical so that, regardless of the reaction mechanism, reliable kinetic data could be obtained. It was found that the kinetic data obtained at 480 mμ and at 450 mμ were identical. It is therefore very probable that the replacement of chlorine by thiocyanate gave only the *cis*-product which subsequently underwent isomerisation. Experiments also showed that the *cis*-thiocyanato-nitro-complex—under the conditions of the reaction—slowly isomerised to its *trans*-isomer and in 5 days (time needed for completion of the reaction) 10% of the latter had been formed.

The dependence of the rates on temperature is given in Table 4. The Arrhenius para-meters, calculated therefrom by the method of least squares, were 24·6 kcal./mole for the activation energy and 3·21 × 10^{12} sec.$^{-1}$ for the frequency factor. The entropy of activation was calculated to be −3·4 e.u.

TABLE 4. *Temperature-dependence of the rates of substitution of chlorine by* 0·04M-SCN$^-$ *in* 0·001M-cis-[Co en$_2$(NO$_2$)Cl]$^+$ *in methanol.*

Temperature	35·8°	40·1°	45·1°	50·2°
$10^5 k$ (sec.$^{-1}$)	1·24	2·12	3·66	7·57

SUMMARY AND DISCUSSION

The main results reported in the preceding section are collected in Table 5 together with the rates of replacement of chlorine in *trans*- and *cis*-dichlorobis(ethylenediamine)-cobalt(III) ions, reported by previous investigators. Although these comparisons of rate constants should be made by using values extrapolated to zero thiocyanate concentration, the inaccuracies involved in such extrapolations would outweigh the advantages gained. We have therefore tried to compare all data at a fixed concentration of thiocyanate.

Table 5 shows that the rate of replacement in *trans*-chloronitrobis(ethylenediamine)-cobalt(III) ion by thiocyanate is 28 times faster than in *trans*-dichlorobis(ethylenediamine)-cobalt(III) ion (calculated for one chlorine atom). If the S_N1 mechanism operated one would expect slower reaction in the *trans*-chloronitro- than in the *trans*-dichloro-complex because the polarisation of the cobalt atom, caused by the nitro-group, should oppose heterolysis, as discussed in the first section. Table 6 contains the rates of aquation of the

same complexes. It can be seen that very similar ratios of rates to those in the replacements by thiocyanate are obtained in the aquations (see Table 6).

TABLE 5. *Rates of replacement of chlorine in bis(ethylenediamine)cobalt(III) ions by* SCN^- *in methanol.*

Co en$_2$ complex	Co en$_2$ complex (M)	SCN^- (M)	10^5k (sec.$^{-1}$) 25°	35·8°	Note
trans-[Co en$_2$(NO$_2$)Cl]$^+$	0·001	0·08	8·41		
cis-[Co en$_2$(NO$_2$)Cl]$^+$	0·001	0·08	0·29 *	1·24	
trans-[Co en$_2$Cl$_2$]$^+$	0·001—0·002	0·08	0·30		a
cis-[Co en$_2$Cl$_2$]$^+$	0·0007	0·05	1·82 †		b

a Pearson, Henry, and Basolo's data [5] have been halved since the displacement of one chlorine is required for comparison with the other rate figures in Tables 5 and 6. *b* Brown and Ingold's data have also been halved.

* Calc. from the rate at 35·8° and the activation energy of 24·6 kcal./mole.

† Calc. from the rate at 35·8° and the assumed activation energy of 22·0 kcal./mole.

TABLE 6. *Rates of aquation in bisethylenediaminecobalt(III) complexes at 25°.*

Complex	10^5k (sec.$^{-1}$)	Mechanism suggested	Note
trans-[Co en$_2$(NO$_2$)Cl]$^+$	81·85	S_N2	a
cis-[Co en$_2$(NO$_2$)Cl]$^+$	11·0	S_N2	b
trans-[Co en$_2$Cl$_2$]$^+$	3·16	S_N1	c
cis-[Co en$_2$Cl$_2$]$^+$	14·0	S_N1	d

a Calc. from the rate at 30° and the activation energy of 21·5 kcal./mole reported by Ašperger and Ingold.[2] *b* Calc. from the rate at 30° and the activation energy of 22·35 kcal./mole reported by Ašperger and Ingold.[2] *c* Rate data by Mathieu [7] at 30° have been multiplied by 2·303 and halved, since the displacement of one chlorine is required for comparison with the other rate figures in the Table. In calculation of the rate, the activation energy of 24·2 kcal./mole was used, as given by Mathieu. *d* Rate data by Mathieu [7] have been multiplied by 2·303 and halved.

Ratios of rates of substitution of chlorine by SCN^- *in methanol at 25°:*

(a) k for *trans*-[Co en$_2$(NO$_2$)Cl]$^+$/k for *trans*-[Co en$_2$Cl$_2$]$^+$ ≈ 28

(b) k for *cis*-[Co en$_2$(NO$_2$)Cl]$^+$/k for *cis*-[Co en$_2$Cl$_2$]$^+$ ≈ 0.16

Ratios of rates of aquations at 25°:

(a) k for *trans*-[Co en$_2$(NO$_2$)Cl]$^+$/k for *trans*-[Co en$_2$Cl]$^+$ ≈ 26

(b) k for *cis*-[Co en$_2$(NO$_2$)Cl]$^+$/k for *cis*-[Co en$_2$Cl$_2$]$^+$ ≈ 0.8

The ratios of rates of replacement of chlorine by thiocyanate in the *trans*- and *cis*-chloronitro-complexes and *trans*- and *cis*-dichloro-complexes are also similar to the ratios of the rates of aquations of the same complexes.
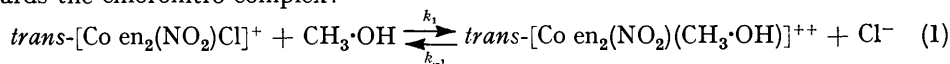
Ratios of rates of replacement of chlorine by SCN^- *in methanol at 25°.*

(a) k for *trans*-[Co en$_2$(NO$_2$)Cl]$^+$/k for *cis*-[Co en$_2$(NO$_2$)Cl]$^+$ ≈ 29

(b) k for *trans*-[Co en$_2$(Cl$_2$)]$^+$/k for *cis*-[Co en$_2$Cl$_2$]$^+$ ≈ 0.17

Ratios of rates of the aquations at 25°:

(a) k for *trans*-[Co en$_2$(NO$_2$)Cl]$^+$/k for *cis*-[Co en$_2$(NO$_2$)Cl]$^+$ ≈ 7.4

(b) k for *trans*-[Co en$_2$Cl$_2$]$^+$/k for *cis*-[Co en$_2$Cl$_2$]$^+$ ≈ 0.23

The accelerating influence of the nitro-group and the above-mentioned similarities of the rate ratios for the reaction with thiocyanate in methanol and the solvolytic aquation lead us to believe that the rate-determining step in the replacement of chlorine by thiocyanate in the *trans*- (and possibly *cis*-) chloronitrobis(ethylenediamine)cobalt(III) cation is a bimolecular methanolysis, which is followed by a fast replacement of co-ordinated methanol by thiocyanate. The equilibrium of the reaction (1) is shifted very much towards the chloronitro-complex:

$$\text{\textit{trans}-[Co en}_2\text{(NO}_2\text{)Cl]}^+ + \text{CH}_3\text{·OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons} } \text{\textit{trans}-[Co en}_2\text{(NO}_2\text{)(CH}_3\text{·OH)]}^{++} + \text{Cl}^- \quad (1)$$

[7] Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 2152.

Therefore the absorption spectra of the methanolic solutions of this complex are unchanged. In the presence of the thiocyanate ions reactions (2) and (3) take place:

$$trans\text{-}[Co\ en_2(NO_2)(CH_3 \cdot OH)]^{++} + SCN^- \xrightarrow{k_2}$$
$$trans\text{-}[Co\ en_2(NO_2)(NCS)]^+ + CH_3 \cdot OH \quad . \quad (2)$$

$$trans\text{-}[Co\ en_2(NO_2)Cl]^+ + SCN^- \xrightarrow{k_3} trans\text{-}[Co\ en_2(NO_2)(NCS)]^+ + Cl^- \quad . \quad (3)$$
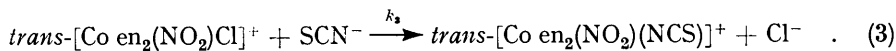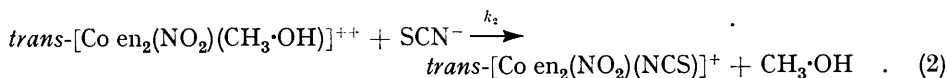
The rate constant k_2 must be greater than k_1. The rate of formation of the trans-[Co en$_2$(NO$_2$)(NCS)]$^+$ ion is given by:

$$\text{Rate} = \{k_1' + k_3[SCN^-]\}[trans\text{-}[Co\ en_2(NO_2)Cl^+] \quad . \quad . \quad . \quad (4)$$

$k_1' + k_3[SCN^-]$ is equal to the pseudo-first-order rate constant k determined experimentally. In Fig. 2 the values of k from Table 1 are plotted as a function of the thiocyanate concentration. The straight line enabled a rough determination of k_1' (intercept) and k_3 (slope); k_1' was found to be 1.42×10^{-4} sec.$^{-1}$ and k_3 to be 5.2×10^{-4} sec.$^{-1}$ mole^{-1} l. The increase of the thiocyanate concentration makes the S_N2 substitution of chlorine increasingly important; *e.g.*, when the thiocyanate was 0.04M (40-fold excess), k was 1.6×10^{-4} sec.$^{-1}$. It follows that 13% of the product was formed by S_N2 substitution of chlorine by the thiocyanate ion and 87% *via* methanolysis.

The accelerating influence of the nitro-group can now be understood. The rate-determining step in the substitution by the thiocyanate ion is the methanolysis, which occurs as an S_N2 reaction; S_N2 reactions are in general less sensitive to electron-displacement than S_N1 reactions, since the release of electrons towards the reaction centre assists bond breaking and thus makes the bond formation more difficult. Since methanol is a weak nucleophilic reagent it needs help from polarisation to be brought into reaction. Therefore the polarisation demand of the binding of the methanol is more important than the loosening of the displaced chlorine. This is analogous to the influence of the nitro-group in aquation of the *trans*-chloronitrobis(ethylenediamine)cobalt(III) ion studied by Ašperger and Ingold.[2] They suggested that $4d$-orbitals of cobalt play an intermediate rôle in the binding of water, which is greatly assisted when the underlying $3d$-shell is pulled out of the way by the nitro-substituent. It seems very likely that the $4d$-orbitals of cobalt also play an intermediate rôle in the binding of methanol. The rate of exchange of *cis*- and *trans*-chloronitrobis(ethylenediamine)cobalt(III) ion with radioactive chlorine is now being studied and compared with the rate of isomerisation in order to obtain more accurate information about the mechanism and steric course of these reactions.

It should be pointed out that the first-order kinetic form observed for the weakly nucleophilic reagents could arise from a rate-determining methanolysis followed by a fast replacement of co-ordinated methanol by the reagent. This would only be a serious objection to Brown and Ingold's mechanism if the methanolysis were bimolecular. Comparison of methanolysis with aquation, however, would lead us to believe that the methanolysis of *cis*- and *trans*-dichlorobis(ethylenediamine)cobalt(III) ion is unimolecular and that the reactive [Co en$_2$Cl(MeOH)]$^{2+}$ appears only because the methanol is suitably placed to occupy the position vacated.

<h2 style="text-align:center">EXPERIMENTAL</h2>

Preparations.—*trans*-Chloronitrobis(ethylenediamine)cobalt(III) nitrate and the chloride of the *cis*-isomer were used from a stock previously prepared.[2] *trans*- and *cis*-Thiocyanato-nitrobis(ethylenediamine)cobalt(III) thiocyanates were prepared by Werner's method[8] (Found: ionic SCN$^-$, 17.03 in *trans*- and 16.85% in *cis*-[Co en$_2$(NO$_2$)(NCS)]SCN. Calc.: 17.02%).

Reagent-grade absolute methanol was further dehydrated by Lund and Bjerrum's method.[4]

[8] Gmelin's " Handbuch der anorganischen Chemie," No. 58, Berlin, 1930, p. 270.

Analyses by the Karl Fischer method showed that the dried methanol contained about 0·05% of water.

Spectroscopy.—Light-absorption intensity measurements were made with a Hilger H 700 quartz spectrophotometer and 10 mm. cells.

Kinetics.—The methanol was acidified by toluene-*p*-sulphonic acid or 60% perchloric acid. 0·001M-Solutions of the chloronitro-complexes were prepared by short warming or by prolonged shaking at room temperature. The solutions were always kept in the dark to prevent isomerisation. The solution of the complex was thermally equilibrated in a water thermostat ($\pm 0·01°$) and a weighed quantity of dried sodium thiocyanate was added, which dissolved readily.

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