

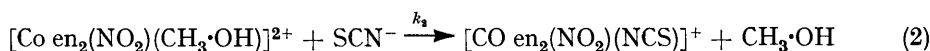
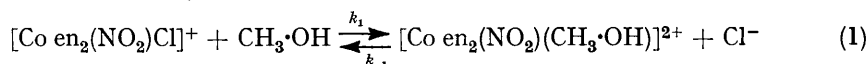
571. *Mechanism of Octahedral Substitutions. Rate of Exchange of Chlorine in cis- and trans-Chloronitrobis(ethylenediamine)cobalt(III) Ions by Radioactive Chloride in Methanol. Mechanism of Aquation.**

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The rate of exchange of chlorine by radioactive $^{36}\text{Cl}^-$ in the *trans*- and *cis*-chloronitrobis(ethylenediamine)cobalt(III) ions in absolute methanol shows only a small dependence on the chloride ion concentration and is equal to the rate of replacement of chlorine by thiocyanate ion in methanol.

The rate of aquation of the *trans*-chloronitrobis(ethylenediamine)cobalt(III) cation in formic acid as solvent is proportional to the concentration of water added, which means that the aquation is bimolecular. The mechanistic implications of these results are discussed.

It was suggested¹ that methanolysis is the rate-determining step in the replacement of chlorine by thiocyanate in the *trans*- and *cis*-chloronitrobis(ethylenediamine)cobalt(III) cation in methanolic solution and that methanolysis is followed by a fast replacement of co-ordinated methanol by thiocyanate ion:



* Reported in part at the Seventh International Conference on Co-ordination Chemistry, June 1962.

¹ Ašperger, Pavlović, and Orhanović, *J.*, 1961, 2142.

The suggested mechanism requires that the rate of exchange of chlorine with radioactive chloride in both *trans*- and *cis*-chloronitrobis(ethylenediamine)cobalt(III) cation is independent of the chloride ion concentration and that the rate of exchange in methanol is equal to the rate of replacement of chlorine by thiocyanate in methanol, which was actually observed.

The independence of the rate of replacement of chlorine by thiocyanate on the thiocyanate ion concentration, and the independence of the rate of exchange of chlorine on the chloride ion concentration in *trans*- and *cis*-chloronitro-complex ions in methanol is not only in agreement with the suggested mechanism involving methanolysis but it is also in agreement with the S_N1 mechanism. The rate¹ of replacement of chlorine by thiocyanate in the *trans*-chloronitro-complex ion in methanol is about 30 times faster than the rate of the analogous replacement of chlorine by thiocyanate in the *trans*-dichlorobis(ethylenediamine)-cobalt(III) ion in methanol (calculated for one chlorine atom). The rate of exchange of chlorine in chloronitro-complex ion in methanol is found to be about 40 times faster than the rate of exchange of chlorine in the dichloro-complex-ion² (calculated for one chlorine atom). Essentially the same accelerating influence of the nitro-group in both cases supports the mechanism involving methanolysis as rate-determining step, since the polarization of the cobalt atom, caused by the negative electromeric effect of the nitro-group, should oppose the heterolysis of the departing halogen, not facilitate it.

Evidence^{3,4} supports the view that the aquation of the chloronitrobis(ethylenediamine)-cobalt(III) ions is bimolecular and it has been suggested¹ that, because of analogous kinetic behaviour, aquation and methanolysis have the same molecularity. In seeking additional evidence for the molecularity of the aquation of chloronitrobis(ethylenediamine)cobalt(III) cations, the aquation of the *trans*-isomer was studied in formic acid as solvent. The rate of aquation increased almost proportionally with water added over the range 1.4 to 100 volume per cent of water. It appears, therefore, that the aquation of the nitrochloro-complex ion is bimolecular, the linear effect of the first few units per cent of water being relevant for kinetic order.

RESULTS

Exchange of Chlorine in trans- and cis-Chloronitrobis(ethylenediamine)cobalt(III) Cations by $^{36}\text{Cl}^-$ in Methanol.—Methanolic solutions of the complexes. The solutions were acidified with perchloric acid (0.0001M) to prevent the formation of methoxide ion which would attack the complex.² The amount of water so introduced was negligible (0.01%). Absolute methanol, dried by Lund and Bjerrum's procedure,⁵ contained about 0.05% of water (determined by Karl Fischer's method⁶). Pearson *et al.* found² that up to 0.5% of water had no effect on the rates of similar substitutions in methanol. We observed also that in the replacement of chlorine by thiocyanate in *trans*-chloronitrobis(ethylenediamine)cobalt(III) ion in methanol the addition of 0.25 and even 0.5% of water to methanol did not influence the rate. Complexes were dissolved at room temperature by prolonged shaking (8—14 hr.). The solutions were always kept in the dark since it appeared that light effects the *cis-trans* isomerisation.

Stereochemical changes during the exchange. The absorption spectra of *trans*- and *cis*-chloronitrobis(ethylenediamine)cobalt(III) cations in absolute methanol are given in Fig. 1. There is a minimum of absorption of *trans*- and *cis*-isomers at 3100 and 3075 Å, respectively (curves 1 and 2). These minima were well reproducible and therefore used for the determination of the composition of the products of the exchange. The molar extinction coefficient of the *trans*-chloronitrobis(ethylenediamine)cobalt(III) nitrate at 3100 Å amounted to 1045 and of the *cis*-chloronitrobis(ethylenediamine)cobalt(III) chloride at 3075 Å to 1355 cm.⁻¹ mole⁻¹ l. Curve 3 depicts the absorption spectrum of the product of exchange of chlorine in 0.000909M-*trans*-chloronitrobis(ethylenediamine)cobalt(III) nitrate with 0.0727M-lithium chloride in methanol at

² Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379.

³ Ašperger and Ingold, *J.*, 1956, 2862.

⁴ Ingold, *Nature*, 1960, **187**, 477.

⁵ Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

⁶ Vogel, "Quantitative Inorganic Analysis," Longmans, London, 1960, p. 698.

25° after 14 half-lives. The absorptions were measured against acidified methanolic lithium chloride solution of the mentioned concentrations. At 3100 Å curves 1 and 3 are superimposed. A difference in absorption existed only at 3400 Å but this variation was of the order of magnitude of the experimental error at that wavelength. It could be concluded that the exchange of chlorine in *trans*-chloronitro-isomer proceeds with complete retention of configuration. This

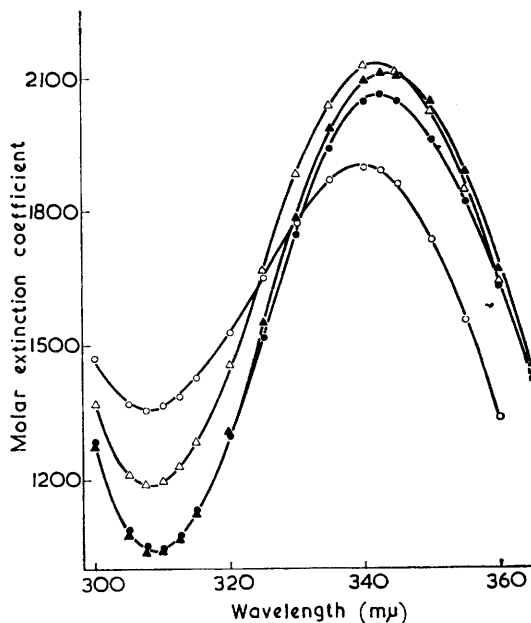


FIG. 1. Absorption spectra of $\sim 0.001M$ -complexes in methanol in the presence of $0.0004M$ -perchloric acid.

- 1, (●) *trans*-[Co en₂(NO₂)Cl]NO₃; 2, (○) *cis*-[Co en₂(NO₂)Cl]Cl; 3, (▲) mixture of *trans*-[Co en₂(NO₂)Cl]NO₃ and $0.0727M$ -LiCl at 25° after 14 half-lives; 4, (△) mixture of *cis*-[Co en₂(NO₂)Cl]Cl and $0.0182M$ -LiCl at 35.8° after 12 half-lives.

agrees well with the observation¹ that the replacement of chlorine of *trans*-chloronitrobis(ethylenediamine)cobalt(III) cation by thiocyanate ion in methanol proceeds with complete retention of configuration.

The exchange of chlorine of *cis*-chloronitrobis(ethylenediamine)cobalt(III) cation is accompanied by a partial change of configuration. This was expected since the replacement of chlorine of *cis*-chloronitrobis(ethylenediamine)cobalt(III) cation with thiocyanate ion in methanol proceeds with 80 per cent. retention of configuration. Curve 4 in Fig. 1 shows the absorption spectrum of the equilibrium mixture in the reaction of $0.000909M$ -*cis*-chloronitrobis(ethylenediamine)cobalt(III) cation and $0.0182M$ -lithium chloride in methanol at 35.8° after approximately 12 half-lives. Using the mentioned molar extinction coefficients of the *trans*- and the *cis*-isomer at 3100 and 3075 Å, respectively, it was calculated that this equilibrium mixture after 12 half-lives contained about 50% of *trans*- and 50% of *cis*-isomer.

TABLE I.

Rate constants for exchange of chlorine with ³⁶Cl⁻ in $0.000909M$ -*trans*- and *cis*-[Co en₂(NO₂)Cl]⁺ in absolute methanol at 25 and 35.8°, respectively.

[LiCl]		10 ⁵ k (sec. ⁻¹)				
0.0182M	<i>trans</i>	13.9, 13.8, 13.3, 13.7, 13.8	Average 13.7			
	<i>cis</i>	1.95, 2.02, 1.92	,, 1.96			
0.0364M	<i>trans</i>	14.2, 14.1, 14.4, 14.2, 14.0	Average 14.2			
	<i>cis</i>	1.99, 1.98, 2.00	,, 1.99			
0.0727M	<i>trans</i>	15.3, 14.8, 14.5, 15.0	Average 14.9			
	<i>cis</i>	2.00, 1.89, 2.13	,, 2.01			

Rate of exchange of chlorine. The rate in $0.000909M$ -*trans*- and *cis*-chloronitrobis(ethylenediamine)cobalt(III) cation, respectively, with radioactive lithium chloride, 20—80 times in excess of the complex, was measured at 25.0° with *trans*-isomer and at 35.8° with *cis*-isomer in absolute methanol. To measure the rate of the exchange it was necessary to separate the complex from

the radioactive chloride in a solution of relatively high activity and then to measure the activity of the complex cation. Silver nitrate has been used for separation of radioactive chloride from *cis*- and *trans*-dichlorobis(ethylenediamine)cobalt(III) cations.^{3,7} In our case, the separation of

TABLE 2.

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 25°.

KSCN (mole/l.)	0.02	0.04	0.08
10 ⁵ k (sec. ⁻¹)	10.6	11.8	13.3

the ionic chloride with methanolic solution of silver nitrate, even when using a silver electrode to avoid excess of silver nitrate, was found inadequate, because silver nitrate removed chlorine from the complex cation even at 0°, hence causing appreciable error. Much better results were obtained by using an ion-exchange column with Amberlite IRA-400 in the acetate form. Blanks showed that chloride ions from the methanolic solutions are quantitatively exchanged on the column and that at -10° the complex cation leaves the column unchanged. The reaction rate was determined by the expression (3) in which *a* and *b* are concentrations of the complex and

$$R = - \frac{2.303ab}{i(a+b)} \log \left[1 - \frac{x}{z} \left(1 + \frac{b}{a} \right) \right] \quad (3)$$

lithium chloride, respectively; *z* is the radioactivity in the solution and *x* is the activity in the complex.⁸ The first-order rate constants were calculated from the expression $k_1 = R/a$. The results are in Tables 1 and 2. It can be seen that in both isomers the rate depends very little on the concentration of lithium chloride. The rate coefficients decrease systematically during the first part of the reaction but after half completion the coefficients change little. The rate coefficients presented in Table 1 refer, therefore, to approximately 50 per cent completion of the reaction.

Table 2 contains the rates of replacement of chlorine by thiocyanate ion in methanol, determined spectrophotometrically also at 25°. (The rates in Table 2 are somewhat higher than the rates previously reported.¹) The rate of replacement of chlorine by thiocyanate shows only a small change with thiocyanate ion concentration, and this rate differs only little from the rate of exchange of chlorine with radioactive chloride.* The difference seems not to be significant and is most probably due mainly to different experimental technique. The rate coefficients in Table 2 also refer to half completion of reaction, because they show the same behaviour as the rate coefficients of the chlorine exchange.

Less good agreement is obtained when the rate of exchange of chlorine with radioactive chloride in *cis*-chloronitrobis(ethylenediamine)cobalt(III) cation ($k \sim 2.1 \cdot 10^{-5}$ sec.⁻¹ at 35.8°) is compared with the rate of replacement of chlorine with thiocyanate in the *cis*-isomer ($k \sim 1.2 \cdot 10^{-5}$ sec.⁻¹ at 35.8°). A rate of exchange of chlorine in *cis*-isomer higher than the rate of replacement of chlorine with thiocyanate is to be expected because the exchange leads to substantial isomerisation to *trans*-chloronitrobis(ethylenediamine)cobalt(III) cation which then exchanges chlorine about 20 times faster than the *cis*-isomer, as seen from the Table 1.

The small increase of the rate coefficients with thiocyanate and chloride ion concentrations, respectively, and the decrease of the rate coefficients in a specific run needs further comment. Steady-state approximation for the replacement of chlorine by thiocyanate in reactions (1) and (2) leads to eqn. (4)

$$R = \frac{k_1[\text{CH}_3\cdot\text{OH}][\text{Co en}_2(\text{NO}_2)\text{Cl}^+][\text{SCN}^-]}{k_{-1}/k_2[\text{Cl}^-] + [\text{SCN}^-]} \quad (4)$$

In determination of the rate coefficients $k_{-1}/k_2[\text{Cl}^-]$ was neglected, the concentration of the

* It was erroneously reported in the Proceedings Abstracts of the Seventh International Conference on Co-ordination Chemistry, Stockholm and Uppsala, 1962, that the rates of replacement of chlorine by ³⁶Cl⁻ in *cis*- and *trans*-chloronitrobis(ethylenediamine)cobalt(III) ions are 2.5 times higher than the rates of the analogous replacement by thiocyanate.

⁷ Brown and Ingold, *J.*, 1953, 2680.

⁸ Friedlander and Kennedy, "Introduction to Radiochemistry," J. Wiley, New York, 1960, p. 315.

chloride ion being assumed small compared with that of thiocyanate ion. The rate was taken as proportional to the concentration of the complex cation only and the first-order rate equation was applied. According to eqn. (4) the small increase of the rate with increasing thiocyanate ion concentration and the decrease of the rate with increasing chloride ion concentration is to be expected.

Unfortunately the salt effect of the thiocyanate and chloride ions could not be measured because of the very limited solubility of electrolytes in methanolic solutions.

Kinetics of the Reaction of trans-Chloronitrobis(ethylenediamine)cobalt(III) Ion with Water in Formic Acid.—The absorption spectra of *trans*-chloronitrobis(ethylenediamine)cobalt(III) nitrate and *trans*-aquaonitrobis(ethylenediamine)cobalt(III) nitrate in formic acid differ only little from the spectra of the same complexes in aqueous solution.³ The aquation in formic acid

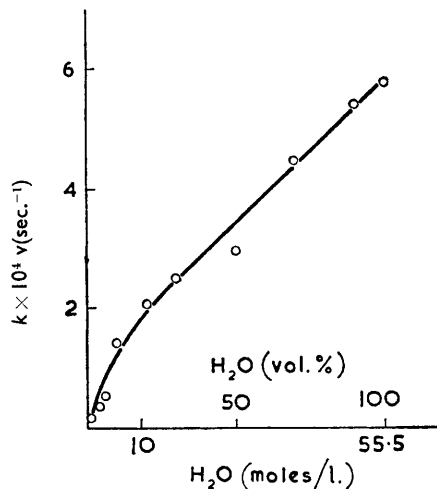


FIG. 2. Dependence of the rate of replacement of chlorine by water in 0.0005M-*trans*-[Co en₂(NO₂)Cl]NO₃ in formic acid on water concentration at 20°.

proceeded with retention of configuration. The solutions follow Beer's law. The kinetic measurements were done by measuring the absorption of the reacting solution at 329 mμ. At that wavelength the molar extinction coefficient of *trans*-chloronitrobis(ethylenediamine)cobalt(III) ion amounted to 1450 and for *trans*-aquaonitrobis(ethylenediamine)cobalt(III) ion 1150 cm.⁻¹ mole⁻¹ l. The concentration of *trans*-[Co en₂(NO₂)Cl]NO₃ was 0.0005M and the concentration of water added to formic acid, made dry with boron trioxide, varied between 0.389 and 55.5M (1.4 to 100 volume per cent of water). The reaction is of first order irrespective of mechanism, because water was always in excess of the complex. The rate constants were calculated as

$$k = (2.303/t) \log_{10} [(E_0 - E_\infty)/(E_t - E_\infty)].$$

When the concentration of water was less than 1 volume per cent the rate constants were not well reproducible. Fig. 2 shows the increase of the rate of aquation with the concentration of water. In most of the concentration interval the increase of the rate is almost linear.

DISCUSSION

It was supposed¹ that the substitution of chlorine by thiocyanate in *trans*- and *cis*-chloronitrobis(ethylenediamine)cobalt(III) cations in methanol proceeds mainly *via* methanolysis but partly that it also undergoes a simultaneous S_N2 substitution of chlorine by thiocyanate, and that the increase of the thiocyanate concentration makes this S_N2 substitution increasingly important. It appears that this assumption was not correct since the rate of replacement of chlorine by azide ion in *trans*-chloronitrobis(ethylenediamine)cobalt(III) cation in methanol depends only very little on the concentration of azide ion,⁹ the dependence being similar to that of thiocyanate and chloride ion concentration. The azide ion is more nucleophilic than thiocyanate or chloride ion. Especially,

⁹ M. Pribanić, personal communication.

the basicity of the azide is appreciably larger than that of chloride or thiocyanate ion.¹⁰ Brown and Ingold⁷ found the replacement of chlorine in *cis*-dichlorobis(ethylenediamine)cobalt(III) cation in methanol by weakly nucleophilic reagents (Cl^- , SCN^-) to follow $\text{S}_{\text{N}}1$ kinetics, but when the reagent was azide ion the substitution had $\text{S}_{\text{N}}2$ kinetics. In our case one would expect that if $\text{S}_{\text{N}}2$ substitution of chlorine proceeded at all it should have been more expressed with the strongly nucleophilic azide ion than with thiocyanate and chloride, respectively, which should result in substantial dependence of the rate of reaction on azide ion concentration, which was not the case.

EXPERIMENTAL

Preparations.—*trans*-Chloronitrobis(ethylenediamine)cobalt(III) nitrate and *cis*-chloronitrobis(ethylenediamine)cobalt(III)chloride were prepared and analysed previously.³

Radioactive lithium chloride was prepared from radioactive 2N-hydrochloric acid with specific activity of 100 μC per gram of chlorine supplied by Radiochemical Centre, Amersham. The acid was neutralized with addition of lithium hydroxide monohydrate. Lithium chloride was recrystallized from acetone, then heated at 400°, and kept dry over phosphoric oxide. The stock solution of radioactive lithium chloride in absolute methanol was 1—1.4M. The specific activity of the stock solution amounted to 6.7×10^5 counts/min.

Formic acid (Merck, 98%) was dried with powdered boron trioxide for several days, then distilled under reduced pressure.

An ion exchange column with IRA-400 in acetate form was used for the separation of ionic chlorine from the complex cations. The column was converted into acetate form by N-ammonium acetate and thoroughly washed with methanol. The column was cooled outside to -10° . At definite reaction times aliquot portions were withdrawn from the reaction solution and poured on the cooled column, which almost stopped the reaction. The methanolic solutions of the complexes exchanged ionic chlorine quantitatively while the complex cation passed unchanged. The column was washed with absolute methanol, which diluted the reaction solution about five times.

Radioactivity Measurements.—A Geiger-Müller counter for liquid samples of 10 ml. volume ("20th Century Electronics") was used with an "Ecko-Electronics" scaler. The efficiency of the counter for chlorine-36 amounted to 2.7%. Because of the dilution of the solutions passed through the ion-exchange column the activities of the counted solutions were small (0—120 counts/min. approximately). The calculated maximum value of x in eqn. (3) agreed well with the measured values.

Spectrophotometry.—The methanolic solutions of *trans*- and *cis*-chloronitro- and of *trans*- and *cis*-thiocyanatonitrobis(ethylenediamine)cobalt(III) ions obey the Beer-Lambert law. Light-absorption measurements in methanolic solutions were made with a Hilger H700 spectrophotometer and 5 mm. quartz cells. The spectral measurements in formic acid solutions were made with a Unicam S.P. 500 spectrophotometer with 10 mm. quartz cells.

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¹⁰ Basolo and Pearson, "Mechanism of Inorganic Reactions," Wiley and Sons, Inc., New York, 1958, p. 93.