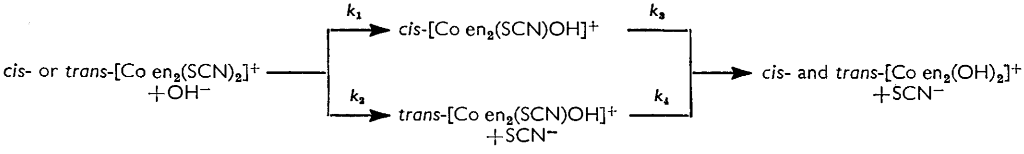
# 599. *Nucleophilic Replacement at an Octahedrally Co-ordinated Metal Atom. Part III.*[1] *The Basic Hydrolyses of* cis- *and* trans-*Di-isothiocyanato- and Isothiocyanatoammine-bisethylenediaminecobalt*(III) *Salts*

By P. J. Staples

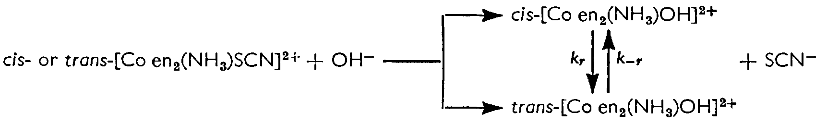
The basic hydrolyses of *cis*- and *trans*-$[\mathrm{Co\,en_2(SCN)_2}]^+$ ions and of *cis*- and *trans*-$[\mathrm{Co\,en_2(NH_3)SCN}]^{2+}$ ions have been studied at 18, 25, and 35°. Steric-course measurements have been performed: *cis*- and *trans*-$[\mathrm{Co\,en_2(SCN)_2}]^+$ ions react to yield between 70 and 80%, and 60% of *cis*-$[\mathrm{Co\,en_2(SCN)OH}]^+$ ion, respectively, whilst *cis*- and *trans*-$[\mathrm{Co\,en_2(NH_3)SCN}]^{2+}$ ions react to yield 90 and 70% of *cis*-$[\mathrm{Co\,en_2(NH_3)OH}]^{2+}$ ion, respectively. The Arrhenius parameters have been evaluated. The mechanism of these reactions is discussed.

Salts of the complex ions *cis*- and *trans*-$[\mathrm{Co\,en_2(SCN)_2}]^+$ and of *cis*- and *trans*-$[\mathrm{Co\,en_2(NH_3)SCN}]^{2+}$ are not hydrolysed in neutral or faintly acidic aqueous solutions at room temperature. However, if salts of *cis*- and *trans*-$[\mathrm{Co\,en_2(SCN)_2}]^{2+}$ ions are dissolved in dilute sodium hydroxide solution the following reactions take place:



Scheme A

When *cis*- or *trans*-$[\mathrm{Co\,en_2(NH_3)SCN}]^{2+}$ salts are dissolved in dilute sodium hydroxide solution the isothiocyanato-group is replaced by hydroxide ion, *i.e.*,



Scheme B

## Results and Discussion

*Replacement of Isothiocyanato-groups from* cis- *and* trans-*Di-isothiocyanatobisethylenediaminecobalt*(III) *Salts by Hydroxide Ions.*—(*a*) *Kinetics.* These reactions were studied by estimating the concentration of free thiocyanate ions using silver nitrate. Portions of the reaction mixture were withdrawn at timed intervals and run into an excess of dilute nitric acid. The acidified solutions were passed down an ion-exchange column (Amberlite IR-120, acid form). The effluent and washings were titrated potentiometrically with silver nitrate. Attempts to study these reactions without removing the complex cations on an ion-exchange column before the argentometric titration gave rate constants similar to those obtained by the above method, but the end-points were somewhat obscured by the subsequent formation of an addition compound between silver nitrate and the complex. Unless otherwise stated the results reported in Table 1 were obtained using ion-exchange columns.

The hydrolyses were second-order; *i.e.*, rate $= k_s[\text{complex}][\mathrm{OH^-}]$. However, as most experiments were performed using a large excess of sodium hydroxide the reactions actually studied were pseudo-first-order; *i.e.*, rate $= k_f[\text{complex}]$, where $k_f = k_s[\mathrm{OH^-}]$. As the rate constants for the second steps were of an order of magnitude similar to that for the

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[1] Part II, A. Rogers and P. J. Staples, *J.*, **1963**, 4749.

first steps, the rate constants for the *trans*-isomer were determined over one half-life only, whilst those for the *cis*-isomer were determined over three half-lives.

Runs performed in blackened vessels gave the same results within the experimental error, as those performed in clear vessels.

TABLE 1

Mean rate constants for the replacement of the first isothiocyanato-group from *cis*- and *trans*-di-isothiocyanatobisethylenediaminecobalt(III) salts in sodium hydroxide solution at various temperatures

Rate constants from the graph $\log_{10} (V_\infty - V_t)$ against time, $V_\infty$ and $V_t$ being the silver nitrate titres at times $\infty$ and $t$, respectively. The infinity value was a calculated value as the incursion of the second step prevented an experimental determination. *cis*-Isomer supplied as nitrate, *trans*-isomer as perchlorate; $10^3$[complex] = 0·90—3·80M.

| Isomer | Temp. | [OH⁻] (mole l.⁻¹) | $10^4k_f$ (sec.⁻¹) | $10^3k_s$ (l. mole⁻¹ sec.⁻¹) | Isomer | Temp. | [OH⁻] (mole l.⁻¹) | $10^4k_f$ (sec.⁻¹) | $10^3k_s$ (l. mole⁻¹ sec.⁻¹) |
|---|---|---|---|---|---|---|---|---|---|
| *trans* | 18·2° | 0·1000 | 1·35 | 1·35 | *cis* | 18·2° | 0·0500 | 6·39 | 12·8 |
| | 18·2 | 0·0500 | 0·72 | 1·44 | | 18·2 | 0·0250 | 3·45 | 13·8 |
| | 25·0 | 0·1000 | 5·00 | 5·00 | | 25·0 | 0·0500 | 20·1 | 40·2 |
| | 25·0 | 0·0500 | 3·18 | 6·36 | | 25·0 | 0·0500 | 23·2 * | 46·4 |
| | 25·0 | 0·0500 | 2·75 * | 5·50 | | 25·0 | 0·0250 | 11·3 | 45·2 |
| | 25·0 | 0·0333 | 2·46 | 7·38 | | 25·0 | 0·0250 | 12·4 * | 49·6 |
| | 35·0 | 0·0500 | 17·3 | 34·6 | | 25·0 | 0·0100 | | 46·3 |
| | 35·0 | 0·0250 | 8·9 | 35·8 | | 35·0 | 0·00995 | | 233 |
| | | | | | | 35·0 | 0·00498 | | 222 |

* Results obtained without using an ion-exchange column to remove the complex cations before the determination of free thiocyanate.

The Arrhenius parameters determined from these results are reported in Table 4.

(*b*) *Steric course.* As the second isothiocyanato-group is replaced at a rate similar to that at which the first is replaced, the steric courses could not be measured spectrophotometrically. However, since the *cis*- and *trans*-hydroxoisothiocyanatobisethylenediaminecobalt(III) ions initially formed react to liberate thiocyanate ions at quite different rates, the steric courses can still be elucidated from plots of the concentration of free thiocyanate ions against time. The steric course of the first step in Scheme A is given by $(k_1/k_2)$; this may be deduced as follows. As $k_3$ and $k_4$ are known it is possible to set up a family of hypothetical curves of [SCN⁻] against time by apportioning values of the observed rate constant for the first step between $k_1$ and $k_2$. The steric course is then evaluated by obtaining the best possible fit between the experimental and hypothetical curves of [SCN⁻] against time. The equation [2] used to calculate the hypothetical curves was

$$[\mathrm{SCN}^-]/A_0 = 2 - 2\exp(-Kt) - \frac{k_1}{k_3 - K}[\exp(-Kt) - \exp(-k_3)]$$

$$- \frac{k_2}{k_4 - K}[\exp(-Kt) - \exp(-k_4t)] \text{[cf. equation (3) in ref. 2] *}$$

where $K = k_1 + k_2$ (see Scheme A), $A_0$ = complex concentration at time $t = 0$, and $K \neq k_3$ ($K = k_3$ is a special case).

The experimental results show that the *cis*-[Co en$_2$(SCN)$_2$]$^+$ ion yields between 70 and 80% *cis*-[Co en$_2$(SCN)OH]$^+$ ion, whilst *trans*-[Co en$_2$(SCN)$_2$]$^+$ ion yields 60% *cis*-product. The experimental results are shown in Figures 1 and 2. The rate constants used to compute the theoretical curves (for 25°) are given in Table 2.

*Replacement of the Isothiocyanato-group from* cis- *and* trans-*Isothiocyanatoamminebisethylenediaminecobalt*(III) *Salts in Sodium Hydroxide Solutions.*—(*a*) *Kinetics.* The reactions were studied (i) by passing aliquot portions of the reaction mixture down an ion-exchange

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* The factor 2 in this equation arises because two thiocyanate groups are being replaced from each complex ion.

[2] P. J. Staples, *J.*, 1963, 3226.

TABLE 2

First-order rate constants used to compile the hypothetical curves of [SCN]/$A_0$ against time

| | *cis*-Nitrate | *trans*-Perchlorate |
|---|---|---|
| $[OH^-]$ (g.-ion l.$^{-1}$) | 0·0250 | 0·1000 |
| $10^2K$ (min.$^{-1}$) | 6·78 | 2·91 |
| $10^3k_3$ (min.$^{-1}$) | 3·6 * | 14·4 * |
| $10^4k_4$ (min.$^{-1}$) | 1·08 * | 4·32 * |

* From ref. 2.

column (acid form) and titrating the effluent and washings potentiometrically with silver nitrate solution and (ii) spectrophotometrically at a wavelength at which *cis*- and *trans*-$[Co\,en_2(NH_3)H_2O]^{3+}$ ions have the same extinction coefficients, *viz.*, 3900 Å. Runs performed in clear and in blackened vessels gave the same results, within the experimental error.

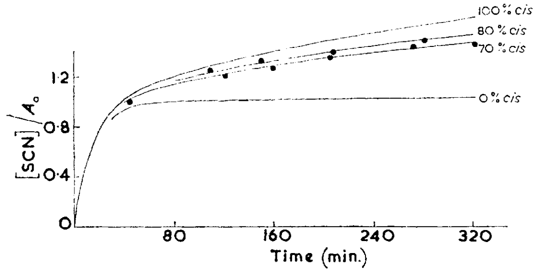

FIGURE 1. Experimental plots of $[SCN^-]/A_0$ against time (●) for the basic hydrolysis of *cis*-$[Co\,en_2(SCN)_2]NO_3$. The full lines denote the calculated curves for various hypothetical steric courses

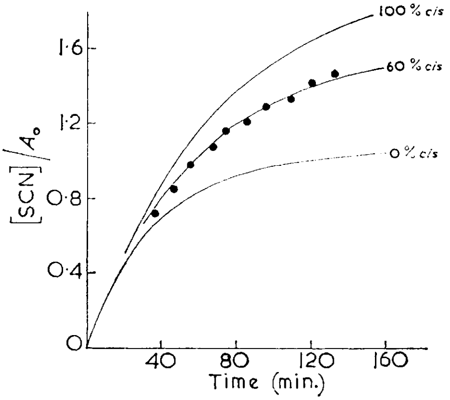

FIGURE 2. Experimental plots of $[SCN^-]/A_0$ against time (●) for the basic hydrolysis of *trans*-$[Co\,en_2(SCN)_2]ClO_4$. The full lines denote the calculated curves for various hypothetical steric courses

The hydrolyses are second-order; *i.e.*, rate = $k_s$[complex]$[OH^-]$. However, as most of the runs were performed in the presence of a large excess of sodium hydroxide, they appeared to be first-order; *i.e.*, rate = $k_f$[complex]. The results of these experiments are collected in Table 3.

TABLE 3

Mean rate constants for the replacement of thiocyanate ions from *cis*- and *trans*-isothiocyanatoamminebisethylenediaminecobalt(III) salts in the sodium hydroxide solution at various temperatures

| Isomer | Temp. | $[OH^-]$ (mole l.$^{-1}$) | $10^4k_f$ (sec.$^{-1}$) | $10^3k_s$ (l. mole$^{-1}$ sec.$^{-1}$) |
|---|---|---|---|---|
| *cis* | 15·0° | 0·1000 | 0·49 | 0·49 |
| | 15·0 | 0·0500 | 0·29 | 0·57 |
| | 25·0 | 0·1000 | 2·63 * | 2·63 |
| | 25·0 | 0·1000 | 2·94 | 2·94 |
| | 25·0 | 0·0800 | 2·17 | 2·71 |
| | 25·0 | 0·0750 | 2·07 * | 2·76 |
| | 25·0 | 0·0500 | 1·56 * | 3·12 |
| | 25·0 | 0·0500 | 1·50 | 3·00 |
| | 25·0 | 0·0333 | 0·98 * | 2·94 |
| | 35·0 | 0·1000 | 18·8 | 18·8 |
| | 35·0 | 0·0500 | 9·2 | 18·4 |

| Isomer | Temp. | $[OH^-]$ (mole l.$^{-1}$) | $10^4k_f$ (sec.$^{-1}$) | $10^3k_s$ (l. mole$^{-1}$ sec.$^{-1}$) |
|---|---|---|---|---|
| *trans* | 18·4° | 0·1000 | 1·94 | 1·94 |
| | 18·4 | 0·0500 | 0·90 | 1·80 |
| | 25·0 | 0·1000 | 5·9 | 5·9 |
| | 25·0 | 0·0625 | 3·7 | 5·9 |
| | 25·0 | 0·0500 | 3·0 | 6·0 |
| | 35·0 | 0·0525 | 19·0 | 36·2 |
| | 35·0 | 0·0333 | 12·9 | 38·7 |

* Runs followed by argentometric titration, all other runs followed by spectrophotometry.

(*b*) *Steric course*. The steric course was studied at 35° by acidifying the solution with dilute nitric acid after seven half-lives. The visible absorption spectrum was measured at 450—520 m$\mu$. The composition of the reaction mixture was deduced from the spectrum and gave an approximate measure of the steric course of the basic hydrolysis reaction. Martin and Tobe[3] have shown that *trans*-hydroxoamminebisethylenediaminecobalt(III) salts rearrange slowly to yield the other isomer. It was possible, however, to make a small correction for this rearrangement. Ingold, Nyholm, and Tobe[4] have shown that the steric course of a reaction like that shown in Scheme B can be elucidated if $k_r$ and $k_{-r}$ are known. However, as the correction was of the same order of magnitude as the experimental error (*ca.* 5%) it was neglected. The results showed that *cis*- and *trans*-[Co en$_2$(NH$_3$)SCN]$^{2+}$ salts react with hydroxide ions to yield 90 and 70% of the *cis*-[Co en$_2$(NH$_3$)OH]$^{2+}$ ion, respectively.

*Arrhenius Parameters*.—The Arrhenius parameters evaluated from the results reported in the foregoing sections are given in Table 4.

TABLE 4

Arrhenius parameters for the basic hydrolyses of isothiocyanatobisethylenediaminecobalt(III) salts

| Compound | $E$ (kcal. mole$^{-1}$) | $\log_{10} A$ |
|---|---|---|
| *cis*-[Co en$_2$(SCN)$_2$]NO$_3$ | 29·9 | 20·7 |
| *trans*-[Co en$_2$(SCN)$_2$]ClO$_4$ | 34·2 | 22·7 |
| *cis*-[Co en$_2$(SCN)NH$_3$]S$_2$O$_6$ | 31·2 | 20·3 |
| *trans*-[Co en$_2$(SCN)NH$_3$](SCN)$_2$ | 32·4 | 23·8 |

It must be pointed out that there is some disagreement in the earlier literature concerning the configurations of the two di-isothiocyanatobisethylenediaminecobalt(III) salts.[5,6] More recent workers[7–9] however, agree that the orange salts are the *cis*-series whilst the red salts have the *trans*-configuration. This assignment has been adopted in this investigation.

The results of this investigation follow those of previous work in which ammine- and isothiocyanato-groups act as directing groups in basic hydrolysis. Ingold, Nyholm, and Tobe[4] have studied the replacement of chloro- and bromo-groups from *cis*- or *trans*-ammine- and isothiocyanato-bisethylenediaminecobalt(III) salts by hydroxide ions. The steric courses for the replacement of thiocyanate and chloride ions resemble one another rather closely. In the cases studied where isothiocyanate is the directing group, the *cis*-isomer reacts faster than the *trans*-isomer, whereas the reverse is true when ammine acts as the directing group. However, the activation energies for the replacement of the thiocyanate group are considerably greater than those for the replacement of the chloro-group. One possible explanation is that the energy required to stretch the cobalt–nitrogen bond is greater than that required to stretch the cobalt–chlorine bond. However, the activation energy for the basic hydrolysis of *cis*-chloroamminebisethylenediaminecobalt(III) salts[10] is 30 kcal. mole$^{-1}$, which suggests that the explanation is more complicated.

## EXPERIMENTAL

*Preparations*.—*cis*- and *trans*-[Co en$_2$(SCN)$_2$]SCN, *cis*- and *trans*-[Co en$_2$(NH$_3$)SCN](SCN)$_2$, and *cis*- and *trans*-[Co en$_2$(NH$_3$)H$_2$O]Br$_3$ were all prepared by Werner's methods. *cis*-[Co en$_2$(SCN)$_2$]NO$_3$, *trans*-[Co en$_2$(SCN)$_2$]ClO$_4$, and *cis*-[Co en$_2$(NH$_3$)SCN]S$_2$O$_6$ were obtained by

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[3] D. F. Martin and M. L. Tobe, *J.*, 1962, 1388.

[4] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J.*, 1956, 1691; R. S. Nyholm and M. L. Tobe, *J.*, 1956, 1707.

[5] A. Werner, *Annalen*, 1912, **386**, 1.

[6] F. Braunlich, *Annalen*, 1912, **386**, 193.

[7] A. V. Ablov and N. I. Lobanov, *Zhur. neorg. Khim.*, 1959, **4**, 148.

[8] M. E. Baldwin, private communication.

[9] R. Larsson, *Acta Chem. Scand.*, 1962, **16**, 931.

[10] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, 1955, **59**, 304; R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 2673; *J. Inorg. Nuclear. Chem.*, 1955, **1**, 342.

adding the appropriate sodium salt to an aqueous solution of the corresponding thiocyanate. Analyses are given in Table 5.

*Thiocyanate analyses.* Accurately weighed portions of the complex (*ca.* 0·1 g.) were treated with hot sodium hydroxide (1·0M); after a few minutes the solutions were acidified with dilute nitric acid, and the thiocyanate ions present estimated potentiometrically with standard silver nitrate (0·025M).

TABLE 5

Di-isocyanotobisethylenediaminecobalt(III) salts and related compounds

| | Found (%) | | | | | Requires (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | C | H | N | S | Equiv. | C | H | N | S | Equiv. |
| *cis*-[Co en$_2$(SCN)$_2$]NO$_3$ * | 20·25 | 4·6 | 27·4 | 18·05 | | 20·1 | 4·5 | 27·5 | 17·9 | |
| *trans*-[Co en$_2$(SCN)$_2$]ClO$_4$ † | 18·4 | 4·2 | 21·1 | 16·2 | | 18·3 | 4·1 | 21·3 | 16·3 | |
| *cis*-[Co en$_2$(NH$_3$)SCN)]S$_2$O$_6$ | 14·7 | 4·6 | 20·3 | 23·0 | 211 | 14·5 | 4·6 | 20·3 | 23·1 | 207 |
| *trans*-[Co en$_2$(NH$_3$)SCN](SCN)$_2$ | 22·65 | 5·3 | 30·2 | 26·0 | 185 | 22·6 | 5·2 | 30·2 | 26·0 | 185 |
| *cis*-[Co en$_2$(NH$_3$)H$_2$O]Br$_3$ | 10·6 | 4·7 | 15·4 | — | 156 | 10·6 | 4·6 | 15·4 | — | 151 |
| *trans*-[Co en$_2$(NH$_3$)H$_2$O]Br$_3$ | 10·55 | 4·8 | 15·4 | — | 153 | 10·6 | 4·6 | 15·4 | — | 151 |

* Found: SCN, 32·2. Requires SCN, 32·5%. † Found: SCN 29·0. Requires SCN, 29·3%.

*Measurement of Equivalent.*—Accurately weighed samples of the complex (*ca.* 0·2 g.) were dissolved in water and passed through a column of Amberlite IR-120 (hydrogen form). The effluent and washings were titrated with borax (0·025M).

*Spectrophotometric Runs.*—Portions of the reaction mixture were withdrawn at timed intervals and run into a measured excess of dilute nitric acid (*e.g.*, 5 ml. of 0·25N). The optical density at the wavelength 3900 Å was measured using silica cells in a Unicam S.P. 500 spectrophotometer.

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