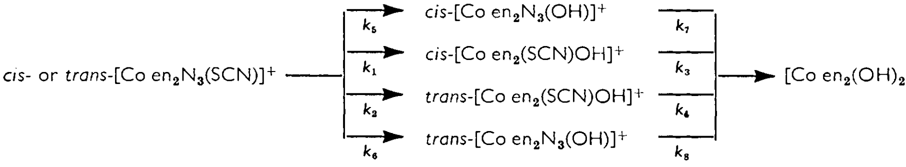
600. *Nucleophilic Replacement at an Octahedrally Co-ordinated Metal Atom. Part I. The Basic Hydrolyses of* cis- *and* trans-*Azidoisothiocyanatobisethylenediaminecobalt*(III) *Ions.*

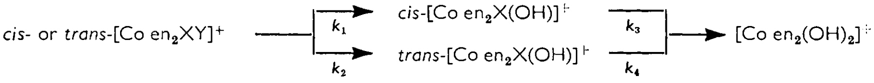
By P. J. Staples.

The basic hydrolyses of *cis*- and *trans*-[Co $en_2(SCN)N_3]^+$ ions have been studied at 24·9°. In each case the azido- and the isothiocyanato-groups are replaced competitively. For both *cis*- and *trans*-[Co $en_2(SCN)N_3]^+$ ions the rates of replacement of the azido- and of the isothiocyanato-group are of the same order of magnitude. In each case, however, the rate of displacement of the azido-group is greater than that of the isothiocyanato-group. The steric courses of the replacement of both the azido- and the isothiocyanato-group have been determined. In those substitutions in which the isothiocyanato-group is displaced in the first step, the *cis*- and the *trans*-isomer yield 100% and between 60% and 90% of *cis*-[Co $en_2(N_3)OH]^+$, respectively. When the azido-group is replaced in the first step, the *cis*- and the *trans*-isomer yield 65—70% and 70% of *cis*-[Co $en_2(SCN)OH]^+$, respectively. The mechanisms of these reactions are discussed.

Neutral or weakly acidic solutions of *cis*- and *trans*-azidoisothiocyanatobisethylenediaminecobalt(III) salts are not hydrolysed. If, however, these salts are dissolved in sodium hydroxide solution, both azide and thiocyanate groups are displaced by hydroxyl, as shown in scheme I. This is interesting since most other diacido-complexes of this series are hydrolysed in two successive steps (scheme II) which are kinetically very easy to separate.



Scheme I.



Scheme II.

It was also shown during these investigations that light had no measurable effect on the rates of reaction. Experiments performed in darkened reaction vessels gave the same rate constants as those performed in clear vessels.

1. *The Replacement of Azide Groups from* cis- *and* trans-*Azidoisothiocyanotobisethylenediaminecobalt*(III) *ions.*—(*a*) *Kinetics.* These hydrolyses were followed by estimating the concentration of free azide ion by means of standard sodium nitrite solution.[1]

The complex ions present in the solution were first removed by passing each aliquot portion through an ion-exchange column (sodium form). This was essential because the excess of nitrite ion reacts with co-ordinated azide groups.[1,2] The hydrolyses were of second order, *i.e.*,

$$\text{Rate} = k_S[\text{Complex}][\text{OH}^-].$$

In the replacement experiments, however, a large excess of sodium hydroxide was used so that the reactions were of the first order, *i.e.*,

$$\text{Rate} = k\,[\text{Complex}].$$

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[1] Staples, *Chem. and Ind.*, 1960, 1210.

[2] Staples, Thesis, London, 1960.

Some rate constants for the replacement of azide groups from these two complexes are given in Table 1.

TABLE 1.

Rate constants for the basic hydrolyses of *cis-* and *trans-*azidoisothiocyanatobisethylenediaminecobalt(III) cations at 24·9°. [Rate constants, measured by means of nitrite, were derived graphically, by plotting $\log_{10} (C_\infty - C_t)$ against time, C_∞ and C_t being the concentrations of azide ion after forty half-lives and at time t, respectively ($k_f = 2{\cdot}303 \times$ slope). The *trans*-isomer was supplied as perchlorate and *cis*-isomer as dithionate.]

	10^3[Complex] (mole $l.^{-1}$)	$[OH^-]$ (mole $l.^{-1}$)	$10^4 k_f$ (sec.$^{-1}$)	$10^3 k_s$ (l. mole^{-1} sec.$^{-1}$)		10^3[Complex] (mole $l.^{-1}$)	$[OH^-]$ (mole $l.^{-1}$)	$10^4 k_f$ (sec.$^{-1}$)	$10^3 k_s$ (l. mole^{-1} sec.$^{-1}$)
cis	0·449	0·1000	5·53	5·53	*trans*	0·515	0·1000	3·62	3·62
cis	0·920	0·1000	5·56	5·56	*trans*	0·953	0·1000	3·32	3·32
cis	1·30	0·1000	5·61	5·61	*trans*	2·45	0·1000	3·31	3·31
cis	1·04	0·0750	4·12	5·50	*trans*	1·27	0·0750	2·56	3·43
cis	0·876	0·0750	4·62	6·17	*trans*	1·67	0·0500	1·64	3·28
cis	0·511	0·0500	3·01	6·02	*trans*	1·04	0·0500	1·65	3·30
cis	0·834	0·0500	3·01	6·02					

(*b*) *Steric Course.* As there were seven coloured species present in the solution at any given time, it was not possible to determine the steric course by a spectrophotometric method. In scheme I the steric course of replacement of azide groups is given by k_1/k_2. If the two initial products, *cis-* and *trans-*hydroxoisothiocyanatobisethylenediaminecobalt(III) ions, react with hydroxide ions to yield free thiocyanate ions at sufficiently different rates, it is possible to determine the steric course of replacement of the azido-group. The system is, however, complicated by the presence of thiocyanate ions which have been displaced directly from the azidoisothiocyanato-complex. Nevertheless, provided that the rate constant for the latter displacement is known, the steric course can still be deduced.

The differential equation governing the concentration of free thiocyanate ions in solution at a time t is:

$$d[SCN^-]/dt = (K + K')A - dC/dt - dT/dt, \tag{1}$$

where $K = k_1 + k_2$, $K' = k_5 + k_6$, A = concentration of *cis-* or *trans-*$[Co\ en_2N_3(SCN)]^+$ at time t, C = concentration of *cis-*$[Co\ en_2(OH)SCN]^+$ at time t, and T = concentration of *trans-*$[Co\ en_2(OH)SCN]^+$ at time t. Integration of equation (1) gives

$$[SCN^-]/A_0 = 1 - \exp(-Kt - K't) - \frac{k_1}{K + K' - k_3}[\exp(-k_3t) - \exp(-Kt - K't)] - \frac{k_2}{K + K' - k_4}[\exp(-k_4t) - \exp(-Kt - K't)], \tag{2}$$

where A_0 = concentration of *cis-* or *trans-*$[Co\ en_2N_3(SCN)]^+$ at time $t = 0$. k_1, k_2, etc., follow the notation of scheme I.

The corresponding relation between free thiocyanate ion concentration and time given by the simpler reaction scheme II is

$$[SCN^-]/A_0 = 1 - \exp(-Kt) - \frac{k_2}{K - k_4}[\exp(-k_4t) - \exp(-Kt)] - \frac{k_1}{K - k_3}[\exp(-k_3t) - \exp(-Kt)], \tag{3}$$

where in scheme II X = SCN and Y = N_3.

It is of interest that in scheme I the steric course of the replacement of the azido-group, as the first step, is found by plotting the concentration of thiocyanate ion against time, whereas the steric course of the replacement of the isothiocyanato-group, as the first step, may be obtained by plotting the concentration of azide ion against time.

The values of K (section 1), K' (section 2), and k_3 and k_4 (section 3) have been determined. By assigning arbitrary values to k_1 and k_2 such that $K = k_1 + k_2$ it is possible to construct a family of curves of $[SCN^-]/A_0$ against time for all possible steric courses. The experimental results were plotted on the same graph and the best fit between theory and experiment was determined. The results are shown in Figs. 1 and 2. The steric courses obtained are given in Table 6 (p. 3231). The values of the rate constants used to calculate the steric courses are given in Table 2.

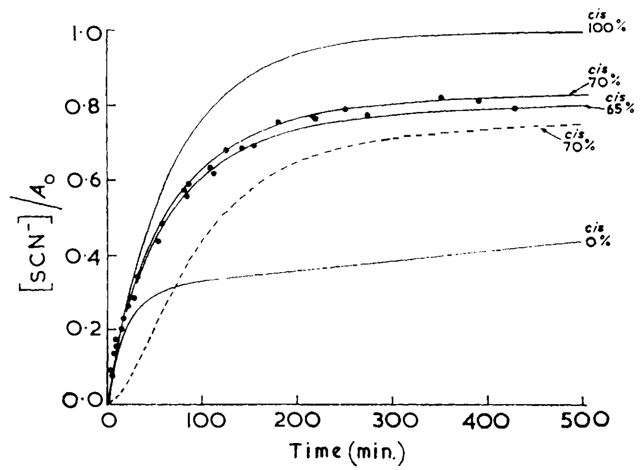

FIG. 1. Experimentally determined values of $[SCN^-]/A_0$ (●), plotted against time for the basic hydrolysis of *cis*-$[Co\ en_2(SCN)N_3]^+$. The full lines show the various possible steric courses calculated from equation 2. The broken line was calculated from equation 3.

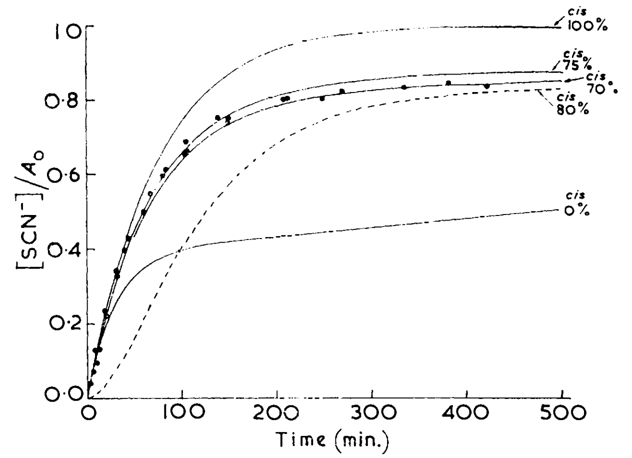

FIG. 2. Experimentally determined values of $[SCN^-]/A_0$ (●), plotted against time for the basic hydrolysis of *trans*-$[Co\ en_2(SCN)N_3]^+$. The full lines show the various possible steric courses calculated by equation 2. The broken line was calculated from equation 3.

2. *The Replacement of Isothiocyanate Groups from* cis- *and* trans-*Azidoisothiocyanatobisethylenediaminecobalt*(III) *Salts*.—(*a*) *Kinetics*. The rates of replacement of isothiocyanate groups from these salts were determined by acidifying aliquot portions with dilute nitric

TABLE 2.

The pseudo-first-order rate constants used to calculate the steric courses of replacement of azide ions at 24·9°.

cis-$[Co\ en_2N_3(SCN)]_2S_2O_6$	*trans*-$[Co\ en_2N_3(SCN)]ClO_4$
$[OH^-] = 0{\cdot}1000$N	$[OH^-] = 0{\cdot}1000$N
$10^4K = 6{\cdot}00$ sec.$^{-1}$	$10^4K = 3{\cdot}33$ sec.$^{-1}$
$10^4K^1 = 2{\cdot}66$ sec.$^{-1}$	$10^4K^1 = 2{\cdot}17$ sec.$^{-1}$
$10^4k_3 = 2{\cdot}30$ sec.$^{-1}$	$10^4k_3 = 2{\cdot}30$ sec.$^{-1}$
$10^4k_4 = 0{\cdot}070$ sec.$^{-1}$	$10^4k_4 = 0{\cdot}070$ sec.$^{-1}$

acid and titrating the thiocyanate ions present in the solution with standard silver nitrate. If the complex ions were removed on an ion-exchange column (sodium form) before the thiocyanate determination the plot of thiocyanate ion against time was the same as that obtained without such treatment. This showed that the silver ions did not catalyse replacement of the isothiocyanato-group in the complex during the determination and that silver nitrate did not form an addition compound with the complex. It was not possible to evaluate the rate constants from the experimental data by means of a logarithmic plot of $\log_{10}(a - x)$ against time since the replacement of isothiocyanate was the slower of two competing first steps. The logarithmic plots obtained were non-linear. To overcome this difficulty the rate constants were evaluated from the initial slopes of curves of thiocyanate ion concentration against time. The mean values of the rate constants obtained by this method are given in Table 3.

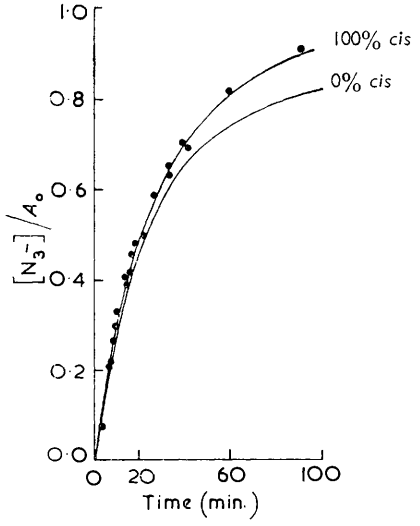

FIG. 3.

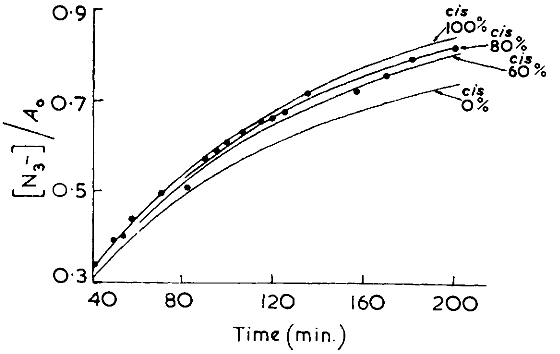

FIG. 4.

FIG. 3. Experimentally determined values of $[N_3^-]/A_0$ (●), plotted against time for the basic hydrolysis of *cis*-$[Co\ en_2N_3(SCN)]^+$. The full lines show the possible steric courses calculated by equation 4.

FIG. 4. Experimentally determined values of $[N_3^-]/A_0$ (●), plotted against time for the basic hydrolysis of *trans*-$[Co\ en_2N_3(SCN)]^+$. The full lines show the possible steric courses calculated by equation 4.

TABLE 3.

Second-order rate constants for the replacement of isothiocyante groups from *cis*- and *trans*-azidoisothiocyanatobisethylenediaminecobalt(III) salts at 24·9°.

cis: $10^3k_s = 2{\cdot}66$ l. mole^{-1} sec.$^{-1}$
trans: $10^3k_s = 2{\cdot}17$ l. mole^{-1} sec.$^{-1}$

(*b*) *Steric course.* As in the replacement of the azido-group, it was not possible to determine the steric course of isothiocyanate replacement by spectrophotometry and a method analogous to that described in section 1(*b*) was used. By plotting $[N_3^-]/A_0$ against time it was possible to deduce the steric course of the replacement of the isothiocyanato-group by hydroxide ions. However, as the rates of the second steps involved, *viz.*, the basic hydrolyses of *cis*- and *trans*-hydroxoazidobisethylenediaminecobalt(III) ions, were somewhat similar, it was not possible to attain the high accuracy obtained in section 1(*b*). Nevertheless, the accuracy sufficed to show that the *cis*-reactant yielded almost 100% of *cis*-hydroxoazidobisethylenediaminecobalt(III) ion whilst the *trans*-reactant yielded between 60% and 90% of *cis*-product. The experimental results are shown in Figs. 3 and 4.

The expression used to calculate the change of azide ion concentration with time for possible steric courses was:

$$[\mathrm{N_3}^-]/A_0 = 1 - \exp(-Kt - K't) - \frac{k_5}{K + K' - k_7}[\exp(-k_7t) - \exp(-Kt - K't)] - \frac{k_6}{K + K' - k_8}[\exp(-k_8t) - \exp(\;Kt - K't)], \quad (4)$$

where $k_5 + k_6 = K'$. The rate constants used to calculate the possible steric courses are given in Table 4.

TABLE 4.

Pseudo-first-order rate constants used in the calculation of the steric courses of replacement of isothiocyanate groups in *cis*- and *trans*-azidoisothiocyanatobisethylenediaminecobalt(III) salts at 24·9°.

cis-$[\mathrm{Co\ en_2N_3(SCN)}]_2\mathrm{S_2O_6}$	*trans*-$[\mathrm{Co\ en_2N_3(SCN)}]\mathrm{ClO_4}$
$[\mathrm{OH}^-] = 0{\cdot}1000$N	$[\mathrm{OH}^-] = 0{\cdot}0500$N
$10^4K = 6{\cdot}00$ sec.$^{-1}$	$10^4K = 1{\cdot}67$ sec.$^{-1}$
$10^4K' = 2{\cdot}66$ sec.$^{-1}$	$10^4K' = 1{\cdot}08_5$ sec.$^{-1}$
$10^4k_7 = 2{\cdot}80$ sec.$^{-1}$ (ref. 3)	$10^4k_7 = 1{\cdot}40$ sec.$^{-1}$ (ref. 3)
$10^4k_8 = 1{\cdot}21$ sec.$^{-1}$ (ref. 3)	$10^4k_8 = 0{\cdot}60_5$ sec.$^{-1}$ (ref. 3)

3. *The Replacement of the Isothiocyanate Group from* cis- *and* trans-*Hydroxoisothiocyanatobisethylenediaminecobalt*(III) *Salts*.—The rates of replacement of isothiocyanate groups from these salts were determined as in section 2. There was no evidence that silver nitrate formed an addition compound with these complex ions at the concentrations used. This was shown by removing the complex ions on an ion-exchange column (sodium form) before determination of thiocyanate: the rate constants calculated were the same as those obtained without this treatment. A spectrophotometric study of these two complex ions at pH 10 and 11 showed that rearrangement between them was immeasurably slow. This possible rearrangement was not, therefore, a significant factor in the steric courses reported in sections (1) and (2). Some rate constants for the replacement of isothiocyanate groups from these complexes are given in Table 5.

4. *Summary and Discussion*.—The results reported in the foregoing sections are collected in Table 6. The relative rates of replacement, *viz.*, *cis*/*trans* and $\mathrm{N_3}$/SCN, do not give much information about the mechanism of these reactions. The steric courses are much more informative. Two mechanisms have been postulated for the basic hydrolyses of diacidobisethylenediaminecobalt(III) salts, namely, S_N2 and S_N1CB. For each, several transition states can be envisaged. These experiments alone do not give enough information to distinguish between the two mechanisms but they help to clarify the situation concerning possible transition states.

For a bimolecular reaction four transition states may be considered, comprising severally a pentagonal bipyramid, an augmented octahedron, a face-centred trigonal antiprism,

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[3] Staples and Tobe, *J.*, 1960, 4803.

TABLE 5.

Rate constants for the replacement of isothiocyanate groups from *cis*- and *trans*-hydroxoisothiocyanatobisethylenediaminecobalt(III) salts at 24·9°. {Rate constants derived graphically by plotting $\log_{10}$ ($[SCN]_\infty - [SCN]_t$) against time. The infinity thiocyanate-ion concentration was determined experimentally after ten half-lives ($k_f = 2{\cdot}303 \times$ slope). *cis*-complex supplied as *cis*-[Co $en_2(H_2O)SCN]S_2O_6$; *trans*-complex as *trans*-[Co $en_2(OH)SCN]SCN$.}

	10^3[Complex] (mole $l.^{-1}$)	[OH^-] (mole $l.^{-1}$)	10^4k_f (sec.$^{-1}$)	10^3k_s (l. mole^{-1} sec.$^{-1}$)		10^3[Complex] (mole $l.^{-1}$)	[OH^-] (mole $l.^{-1}$)	10^4k_f (sec.$^{-1}$)	10^3k_s (l. mole^{-1} sec.$^{-1}$)
cis	2·46	0·1000	2·18	2·18	*trans*	2·15	0·1000	0·068	0·068
cis	6·44	0·1000	2·21	2·21	*trans*	4·79	0·1000	0·076	0·076
cis	2·32	0·0500	1·23	2·46	*trans*	2·39	0·1000	0·070	0·070
cis	3·76	0·0500	1·18	2·36	*trans*	4·47	0·0750	0·054	0·072

TABLE 6.

Rate constants and products of hydrolyses of azido- and isothiocyanato-bisethylenediaminecobalt(III) salts in alkaline solution at 24·9°.

Compound	Displaced group	10^3k_s (l. mole^{-1} sec.$^{-1}$)	*cis*-Product (%)
cis-N_3(SCN)	N_3	6·00	65—70
trans-N_3(SCN)	N_3	3·33	70
cis-N_3(OH)	N_3	2·80 (ref. 3)	—
trans-N_3(OH)	N_3	1·21 (ref. 3)	—
cis-N_3(SCN)	SCN	2·66	100
trans-N_3(SCN)	SCN	2·17	60—90
cis-(SCN)OH	SCN	2·30	—
trans-(SCN)OH	SCN	0·070	—

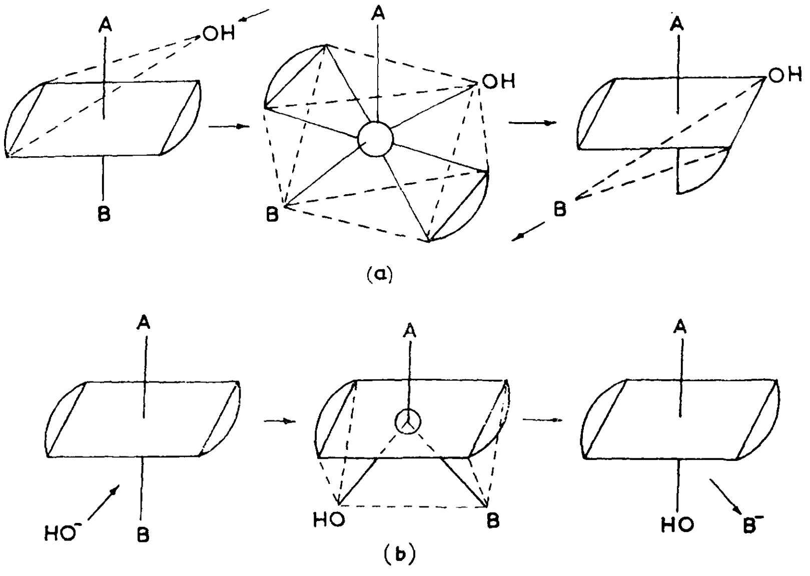

FIG. 5 (a) The face-centred trigonal antiprismatic transition state for back-face attack. (b) The face-centred trigonal prismatic transition state for front-face attack.

and a face-centred trigonal prism. It is possible to exclude the pentagonal bipyramid because it requires a hybridisation, $p_xp_yp_z^2d_\epsilon d_\gamma^2$, which involves so much orbital promotion as to be most improbable: it also implies an edge attack on the octahedron which is electrostatically unfavourable. The augmented octahedron is not really a transition state as the orbitals of the seventh bond are not hybridised into the system; it is, however, a good method of approaching either of the remaining two transition states. The face-centred trigonal antiprism (C_{3v} symmetry) is a feasible transition state for a back-face attack (*i.e.*, attack remote from the leaving group) on the octahedron; such an attack would not contravene the principle of microscopic reversibility; this is shown in Fig. 5a. It is, however, not an allowed transition state for front-face attack as the entering and the leaving group do not have the same symmetry with respect to the rest of the molecule. The face-centred trigonal prism, which has C_{2v} symmetry, is equivalent to the transition state discussed by Basolo and Pearson;[4] this is an allowed transition state for front-face attack only; it is disallowed for back-face attack on microscopic-reversibility considerations, just as the C_{3v} structure is disallowed for front-face attack. The face-centred trigonal prism should always lead to retention of configuration, this is shown in Fig. 5b. Both these transition states require d^3sp^3 hybridisation. Referred to the octahedral symmetry, the *d*-orbitals concerned are not the same; they are $d_\gamma^2 d_\epsilon$ (C_{3v}) and $d_\gamma d_\epsilon^2$ (C_{2v}). This distinction does not, of course, hold for seven-co-ordinate structures.

In unimolecular reactions two possible transition states are the tetragonal pyramid, d^2sp^2, and the trigonal bipyramid, dsp^3. The tetragonal pyramid should always lead to retention of configuration, whilst the trigonal bipyramid should give a product in which the *cis*-isomer predominates.

The results reported in this paper show that the replacement of the azido-group proceeds to give virtually the same product from both isomers. If the mechanism were straighforwardly of the S_N2 type it would require a face-centred trigonal antiprismatic transition state, in the case of the *trans*-isomer, and a face-centred prismatic intermediate for the *cis*-isomer. It is most unlikely that the two isomers would react through different transition states. The most obvious explanation is that both isomers react through the same intermediate, *i.e.*, by the unimolecular mechanism, S_N1CB. To draw such a conclusion would be premature at this stage, as the agreement between the two experimental results may be fortuitous.

In the replacement of the isothiocyanato-group from these complexes the *cis*-isomer gives almost 100% of *cis*-product, whilst the *trans*-isomer gives a large proportion of *cis*-product. Once again there are at least two possibilities for the mechanism. The first is S_N2 in which back-face attack predominates (a little front-face attack would be necessary to explain the experimental result). Another is S_N1CB in which the intermediate is a trigonal bipyramid. The very large proportion of *cis*-product observed may arise because the attacking water molecule forms a hydrogen bond to the azido-group, giving a preferred configuration.

EXPERIMENTAL

Preparations.—*cis*- and *trans*-Azidoisothiocyanatobisethylenediaminecobalt(III) salts[5] and *cis*-[6] and *trans*-hydroxoisothiocyanatobisethylenediaminecobalt(III)[7] salts were prepared by the methods described in the literature. The criteria used to determine purity were analyses and full agreement of the visible absorption spectra with those of specimens of known purity.

Determination of Azide Ion.[1]—An aliquot portion of the reaction mixture was passed through a column of Amberlite IR-120 cation-exchange resin in the sodium form. (If the resin is in the hydrogen form the co-ordinated azide is replaced by water and appears in the effluent.[2]) The effluent and washings were passed into a solution containing an excess of standard sodium nitrite and 1·0 ml. of 0·5M-acetic acid was added. After 2 or 3 min. the excess of sodium nitrite was determined by Ridd's method.[8]

Determination of Thiocyanate Ion.—An aliquot portion of the reaction mixture was acidified

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[4] Basolo and Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958, pp. 238—239.

[5] Staples, *J.*, 1963, 138.

[6] Ingold, Nyholm, and Tobe, *J.*, 1956, 1691.

[7] Werner, *Annalen*, 1912, **386**, 1.

[8] Ridd, Thesis, London, 1951.

with dilute nitric acid and cooled in ice. The thiocyanate ions present were then determined by potentiometric titration with standard silver nitrate solution (0·025M); a silver wire and a calomel half-cell with an agar-agar ammonium nitrate bridge were used. In some runs the aliquot portion was first passed through a column of Amberlite IR-120 resin in the sodium form, and the effluent and washings were acidified and titrated potentiometrically with the standard silver nitrate solution. The two sets of results were concordant, showing that the silver nitrate did not catalyse the replacement of thiocyanate ions during the determination nor did it form an addition compound with the complex.

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