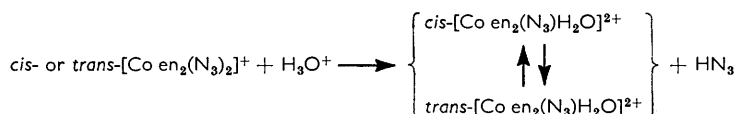


**147.** *The Acid-catalysed Reactions of Transition-metal Complexes. Part I. The Acid-catalysed Aquations of cis- and trans-Diazidobisethylenediaminecobalt(III) Salts.*

By P. J. STAPLES.

The acid-catalysed aquations of *cis*- and *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> have been studied at 25° at ionic strengths 2.0 and 3.5, over a wide range of acid concentrations. Over the intermediate range the rate of aquation is directly proportional to the stoichiometric acid concentration; deviations from linearity occur at the highest and the very lowest acid concentrations. Studies of the steric courses at suitable acid concentrations show that these aquations proceed mainly with retention of configuration. The rearrangement of *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub> has been studied at various ionic strengths and acid concentrations. The mechanism of these reactions is discussed.

NEUTRAL or faintly acidic solutions of *cis*- or *trans*-diazidobisethylenediaminecobalt(III) perchlorate are stable for long periods. If, however, either of these compounds is dissolved in an aqueous solution of a strong acid, one of the azido-groups is replaced by water and the aquoazidobisethylenediaminecobalt(III) salts, formed initially, rearrange to give their equilibrium mixture. The replacement of the second azido-group is very slow compared with that of the first. Except at the highest acid concentrations there was no evidence that the second azido-group was replaced, and thus the effective overall reaction schemes may be written:



#### RESULTS

*Acid-catalysed Replacement of an Azido-group in cis- and trans-Diazidobisethylenediaminecobalt(III) Perchlorate at Ionic Strength 2.0.—(a) Kinetics.* These reactions have been studied over a wide range of perchloric acid concentrations. The salt used to maintain constant ionic strength was sodium perchlorate. Two methods were used: the nitritometric method

previously described<sup>1</sup> (for both isomers), and the spectrophotometric method at the wavelength (5330 Å) at which *cis*- and *trans*-aquoazidobisethylenediaminecobalt(III) perchlorate have the same molar extinction coefficient. In the case of the *trans*-diazidobisethylenediaminecobalt(III) salt the spectra of reactant and products were too similar to allow an accurate determination of the rate constant; for the *cis*-isomer results obtained by the two methods agree quite well. Separate experiments in darkened and clear vessels showed that the reactions were not photocatalysed. The two sets of experiments gave the same rate constants.

For acid concentrations 2.00–0.05M the reaction is first-order in both acid and complex concentration, *viz.*,

$$\text{Rate} = k_s[\text{HClO}_4][\text{Complex}]$$

However, except at the lowest acid concentrations, the acid was in large excess and thus the reactions studied were pseudo-first-order, *i.e.*,

$$\text{Rate} = k_t[\text{Complex}]$$

TABLE I.

Mean first- and second-order rate constants for the replacement of the first azido-group of *cis*- and *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> at ionic strength 2.0, at various acid concentrations at 25.0° ([Complex] = 1.00 × 10<sup>-3</sup>M or 0.50 × 10<sup>-3</sup>M).

| <i>cis</i> -Isomer                                |   |  | <i>cis</i> -Isomer                                |   |  | <i>trans</i> -Isomer                              |   |  |
|---|---|--|---|---|--|---|---|--|
| [HClO <sub>4</sub> ]<br>(moles l. <sup>-1</sup> ) | 10 <sup>4</sup> k <sub>t</sub><br>(sec. <sup>-1</sup> ) | 10 <sup>4</sup> k <sub>s</sub><br>(l. mole <sup>-1</sup><br>sec. <sup>-1</sup> ) | [HClO <sub>4</sub> ]<br>(moles l. <sup>-1</sup> ) | 10 <sup>4</sup> k <sub>t</sub><br>(sec. <sup>-1</sup> ) | 10 <sup>4</sup> k <sub>s</sub><br>(l. mole <sup>-1</sup><br>sec. <sup>-1</sup> ) | [HClO <sub>4</sub> ]<br>(moles l. <sup>-1</sup> ) | 10 <sup>4</sup> k <sub>t</sub><br>(sec. <sup>-1</sup> ) | 10 <sup>4</sup> k <sub>s</sub><br>(l. mole <sup>-1</sup><br>sec. <sup>-1</sup> ) |
| 2.00  | 5.16  | 2.58 *   | 0.80  | 1.88  | 2.35 *   | 2.00  | 3.50  | 1.75   |
| 1.80  | 4.31  | 2.39 *   | 0.80  | 1.79  | 2.24 †   | 1.60  | 2.93  | 1.83   |
| 1.60  | 4.00  | 2.50 *   | 0.60  | 1.56  | 2.60 *   | 1.40  | 2.52  | 1.80   |
| 1.60  | 4.25  | 2.66 †   | 0.50  | 1.25  | 2.50 *   | 1.20  | 1.91  | 1.59   |
| 1.40  | 3.08  | 2.20 *   | 0.40  | 0.94  | 2.36 *   | 0.80  | 1.27  | 1.51   |
| 1.20  | 2.81  | 2.34 *   | 0.30  | 0.69  | 2.30 *   | 0.70  | 1.17  | 1.67   |
| 1.20  | 3.30  | 2.52 †   | 0.20  | 0.51  | 2.55 *   |   |   |  |
| 1.00  | 2.14  | 2.14 *   | 0.0976  | 0.217   | 2.20 *   |   |   |  |
| 1.00  | 1.94  | 1.94 †   | 0.0488  | 0.120   | 2.46 *   |   |   |  |

\* Followed spectrophotometrically. † Followed nitritometrically.

At lower acid concentrations, however, the kinetics became much more complicated. The reactions could no longer be treated as strictly second-order and there appeared to be a shift towards first-order kinetics. Also, the addition of small amounts of hydrazoic acid retarded the reaction.

(b) *Steric course*. As the replacement of the second azido-group is very slow compared with that of the first, it was possible to determine the steric courses of these reactions by spectrophotometry. Ingold, Nyholm, and Tobe<sup>2</sup> have shown that the steric course of a reaction such as that shown in the above Scheme may be elucidated as follows. If  $K_a$  = rate of aquation,  $K_r$  = rate of rearrangement of the aquo-products,  $F_a$  = fraction of initial complex aquated at time  $t$ ,  $f$  = fraction of the aquated complex which has the *cis*-configuration at time  $t$ ,  $f_\infty$  = fraction of the aquated complex which has the *cis*-configuration at  $t = \infty$ , and  $f_0$  = fraction of the aquated complex which has the *cis*-configuration at  $t = 0$ , then

$$\frac{f - f_\infty}{f_0 - f_\infty} = \frac{K_a}{K_r - K_a} \left[ \frac{(1 - F_a)}{F_a} - \frac{(1 - F_a)^{K_r/K_a}}{F_a} \right]$$

The steric course is given by  $f_0$ . All the quantities in the equation except  $f_0$  have been measured. By substituting hypothetical values for  $f_0$  we can calculate a set of theoretical curves of  $f$  against  $F_a$ . The experimental results are plotted on the same graph and the best fits between theory and experiment are obtained.

The results for the *cis*-isomer are shown in Fig. 1. At  $\mu = 2.0$ , [HClO<sub>4</sub>] = 2.00M, *cis*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> is aquated to give 100% of *cis*-[Co en<sub>2</sub>(N<sub>3</sub>)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub>, whilst the *trans*-compound is aquated at  $\mu = 2.0$ , [HClO<sub>4</sub>] = 1.00M, mainly with retention of configuration.

<sup>1</sup> Staples, *Chem. and Ind.*, 1960, 1210.

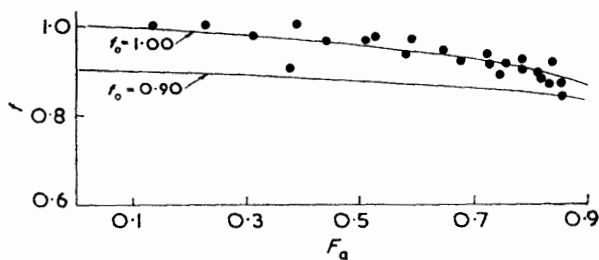
<sup>2</sup> Ingold, Nyholm, and Tobe, *J.*, 1956, 1691.

It was not possible to determine the steric courses at the same acid concentration because the relative values of  $K_f$  and  $K_a$  were not suitable at similar values of  $[\text{HClO}_4]$ .

*Acid-catalysed Replacement of an Azido-group in cis- and trans-Diazidobisethylenediaminecobalt(III) Perchlorate at Ionic Strength 3.5.*—These reactions have been studied by the methods described above, the *cis*-isomer by spectrophotometry and the *trans*-isomer by nitritometry. At this, the higher ionic strength, the ion-exchange columns used in the nitritometric method had a very short working life, and after this period the resin did not exchange completely with the complex cations. Basolo *et al.*<sup>3</sup> reported similar difficulties. For this reason the rate constants for the *trans*-diazido-system at  $\mu = 3.5$  must be considered as less accurate than the others reported in the present paper.

The results (Table 2) show the same behaviour as those at ionic strength 2.0, except that at the highest acid concentrations the increase in rate constant is considerably greater than

FIG. 1. Product analyses during the acid-catalysed aquation of *cis*- $[\text{Co en}_2(\text{N}_3)_2]\text{ClO}_4$ . The lines represent hypothetical steric courses, the dots (●) represent the experimental results.



the increase in acid concentration (see Fig. 2). Possible explanations for this are: (i) that the aquoazido-product was protonated and the incursion of the replacement of the second azido-group gave rise to an apparent increase in the rate of the first step; (ii) that both azido-groups of the substrate were protonated; this would give rise to the same effect as case (i); (iii) that a considerably greater stationary concentration of the intermediate *cis*- or *trans*- $[\text{Co en}_2(\text{N}_3\text{H})\text{N}_3]^{2+}$  was formed in more concentrated acid. An attempt was made to distinguish between these hypotheses by spectrophotometry. The spectra of solutions of

TABLE 2.

Mean pseudo-first-order and second-order rate constants for the acid-catalysed aquation of *cis*- and *trans*- $[\text{Co en}_2(\text{N}_3)_2]\text{ClO}_4$  at ionic strength 3.5 at 25.0° ( $10^3[\text{Complex}] = 1.00$  or 0.50).

| <i>cis</i> -Isomer                            |                                     |  | <i>cis</i> -Isomer                            |                                     |  | <i>trans</i> -Isomer                          |                                     |  |
|---|-------------------------------------|--|---|-------------------------------------|--|---|-------------------------------------|--|
| $[\text{HClO}_4]$<br>(mole l. <sup>-1</sup> ) | $10^4 k_f$<br>(sec. <sup>-1</sup> ) | $10^4 k_a$<br>(l. mole <sup>-1</sup><br>sec. <sup>-1</sup> ) | $[\text{HClO}_4]$<br>(mole l. <sup>-1</sup> ) | $10^4 k_f$<br>(sec. <sup>-1</sup> ) | $10^4 k_a$<br>(l. mole <sup>-1</sup><br>sec. <sup>-1</sup> ) | $[\text{HClO}_4]$<br>(mole l. <sup>-1</sup> ) | $10^4 k_f$<br>(sec. <sup>-1</sup> ) | $10^4 k_a$<br>(l. mole <sup>-1</sup><br>sec. <sup>-1</sup> ) |
| 3.50  | 23.9                                | 6.82   | 1.00  | 4.5                                 | 4.50   | 3.00  | 25                                  | 8  |
| 3.20  | 17.3                                | 5.40   | 0.80  | 2.56                                | 3.20   | 2.80  | 26                                  | 9  |
| 3.00  | 16.5                                | 5.50   | 0.60  | 2.36                                | 3.93   | 2.50  | 11                                  | 4.4  |
| 2.80  | 15.3                                | 5.45   | 0.40  | 1.48                                | 3.70   | 2.00  | 10                                  | 5.0  |
| 2.50  | 13.1                                | 5.24   | 0.20  | 0.79                                | 3.95   | 1.50  | 6.3                                 | 4.2  |
| 2.00  | 9.45                                | 4.73   |   |                                     |  | 1.00  | 4.7                                 | 4.7  |
| 1.60  | 6.8                                 | 4.25   |   |                                     |  | 0.70  | 3.0                                 | 4.3  |
| 1.20  | 4.8                                 | 4.00   |   |                                     |  | 0.50  | 2.3                                 | 4.6  |
|   |                                     |  | <i>trans</i> -Isomer                          |                                     |  |   |                                     |  |
|   |                                     |  | 3.50  | 71                                  | 20   |   |                                     |  |
|   |                                     |  | 3.30  | 55                                  | 16   |   |                                     |  |

The reactions of the *cis*-isomer were studied spectrophotometrically, and those of the *trans*-isomer nitritometrically.

*cis*- and *trans*-aquoazidobisethylenediaminecobalt(III) perchlorate were studied in the following solvents: (a)  $[\text{HClO}_4] = 0.010\text{M}$ ,  $\mu = 3.5$ ; (b)  $[\text{HClO}_4] = 3.50\text{M}$ ,  $\mu = 3.5$ . The absorption spectra of solutions (a) and (b) in the range 205—600  $\text{m}\mu$  were very similar and thus did not indicate a sharp rise in the degree of protonation of the aquoazidobisethylenediaminecobalt(III) perchlorates. However, as the degree of protonation is almost certainly very small, no firm conclusions should be drawn from these observations. It would not be surprising if an already doubly-charged species, *viz.*, *cis*- or *trans*- $[\text{Co en}_2(\text{N}_3\text{H})\text{N}_3]^{2+}$  or *cis*- or *trans*- $[\text{Co en}_2(\text{H}_2\text{O})\text{N}_3]^{2+}$

<sup>3</sup> Basolo, Matoush, and Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 4883.

ions, were not protonated further. Attempts to detect a marked increase in the concentration of the much more likely intermediate species, *viz.*, *cis*- or *trans*-[Co en<sub>2</sub>(N<sub>3</sub>H)N<sub>3</sub>]<sup>2+</sup>, by spectrophotometry were frustrated by the speed of the overall reactions.

*Aquation of cis- and trans-Diazidobisethylenediaminecobalt(III) Perchlorate at Different Ionic Strengths.*—These reactions have also been studied by the methods mentioned above. The results are summarised in Table 3.

TABLE 3.

Pseudo-first-order rate constants for acid-catalysed aquation of *cis*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> in 2.00M perchloric acid at 25.0° at different ionic strengths.

|  |      |      |      |     |     |
|--|------|------|------|-----|-----|
| Ionic strength (g.-ion l. <sup>-1</sup> ) .....            | 4.0  | 3.5  | 3.0  | 2.5 | 2.0 |
| 10 <sup>4</sup> k <sub>t</sub> (sec. <sup>-1</sup> ) ..... | 20.2 | 15.1 | 11.1 | 9.3 | 5.2 |

TABLE 4.

First-order rate constants for the rearrangement of *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub> at various ionic strengths and acid concentrations at 25.0° (% of *cis*-product = 77, in each case).

|  |      |      |      |      |      |
|--|------|------|------|------|------|
| Ionic strength (g.-ion l. <sup>-1</sup> ) .....            | 2.00 | 2.00 | 2.00 | 1.50 | 1.00 |
| [HClO <sub>4</sub> ] (moles l. <sup>-1</sup> ) .....       | 2.00 | 1.50 | 1.00 | 1.00 | 1.00 |
| 10 <sup>4</sup> k <sub>t</sub> (sec. <sup>-1</sup> ) ..... | 3.11 | 2.65 | 2.40 | 2.15 | 1.88 |

*Rearrangement of trans-Aquoazidobisethylenediaminecobalt(III) Perchlorate at 25.0°.*—This reaction has been studied at various ionic strengths and perchloric acid concentrations by spectrophotometry (Table 4). *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub> was chosen because the changes in optical density were greater than for the *cis*-isomer.

## DISCUSSION

Two methods were used to analyse the results obtained in these investigations. First, log<sub>10</sub> k<sub>t</sub> was plotted against log<sub>10</sub> [HClO<sub>4</sub>] and secondly log<sub>10</sub> k<sub>t</sub> was plotted against acidity function.

Over the intermediate range of acid concentrations the graphs of log<sub>10</sub> k<sub>t</sub> against log<sub>10</sub> [HClO<sub>4</sub>] have unit slope (Fig. 2); at ionic strength 3.5 g.-ion l.<sup>-1</sup> the slope is 1.02 for the *cis*- and 1.00 for the *trans*-isomer, and at ionic strength 2.0 g.-ion l.<sup>-1</sup> the slopes are 1.00 and 1.06, respectively.

Although the graphs of log<sub>10</sub> k<sub>t</sub> against acidity function, H<sub>0</sub>, were roughly linear, the slopes were too low (*ca.* 0.67) to agree with Hammett's hypothesis<sup>4</sup> for reactions in which the rate-determining step is the rearrangement of the protonated intermediate without participation of a water molecule. It should be pointed out, however, that H<sub>0</sub> was used instead of H<sub>+</sub> as insufficient data were available for the latter. Bonner and Lockhart<sup>5</sup> have shown that these two acidity functions, H<sub>0</sub> and H<sub>+</sub>, are parallel over a wide range of acid concentrations, so that no significant error is introduced by this procedure. A more serious drawback was that the values of H<sub>0</sub> had been determined using aromatic bases when obviously, in these investigations, those measured with bases structurally similar to the substrates were required. The values of H<sub>0</sub> for perchloric acid were taken from Long and Paul.<sup>6</sup>

Basolo, Matoush, and Pearson<sup>3</sup> have shown that the rate of the acid-catalysed aquation of the *trans*-[Co en<sub>2</sub>F<sub>2</sub>]<sup>+</sup> ion is linearly dependent on the stoichiometric acid concentration, and they claim that the plot has unit slope. The results quoted in their paper, however, actually give a slope of 1.3 which is rather high and may be due to a neglect of the ionic strength effect; they do not mention whether the ionic strength was kept constant. There is, therefore, general agreement between the two investigations.

<sup>4</sup> Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 273.

<sup>5</sup> Bonner and Lockhart, *J.*, 1957, 364.

<sup>6</sup> Long and Paul, *Chem. Rev.*, 1957, 57, 12.

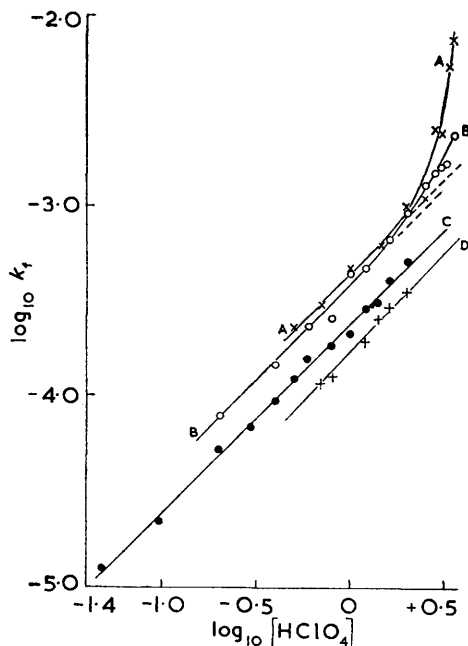
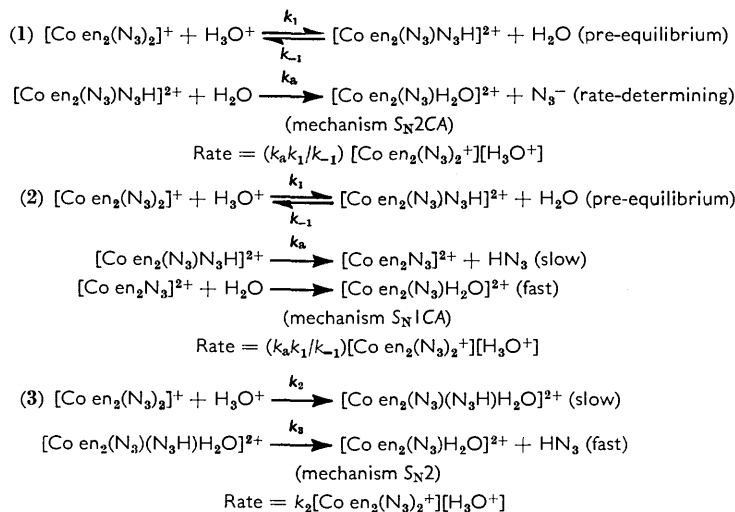


FIG. 2. The relationship between the first-order rate constant for aquation and the stoichiometric acid concentration.

A, *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> at  $\mu = 3.5$  ( $\times$ ).  
 B, *cis*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> at  $\mu = 3.5$  ( $\circ$ ).  
 C, *cis*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> at  $\mu = 2.0$  ( $\bullet$ ).  
 D, *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> at  $\mu = 2.0$  ( $+$ ).

Three possible mechanisms may be envisaged for these acid-catalysed aquations, *viz.*:



Mechanism (3) may be ruled out on the grounds that the unfavourable entropy factor for the rate-determining step ( $k_2$ ) would lead to a very slow reaction whereas, in fact, these reactions are relatively fast at room temperature.

Mechanisms (1) and (2) lead to the same kinetic equation, and other criteria are therefore required. It has already been shown that the graph of  $\log_{10} k_t$  against acidity function has a slope much less than unity, this suggests that mechanism (2) does not operate. The steric-course measurements show that the acid-catalysed aquations of *cis*- and *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> proceed mainly with retention of configuration. This suggests that these reactions proceed by a bimolecular mechanism  $S_N2CA$  ( $CA = \text{conjugate acid}$ ), since it is difficult to see how a five-co-ordinate intermediate could fail to

give rise to an appreciable amount of stereo-change. Basolo *et al.*<sup>3</sup> postulated a similar mechanism for the acid-catalysed aquation of *trans*-[Co en<sub>2</sub>F<sub>2</sub>]NO<sub>3</sub>.

More recently, Haim and Wilmarth<sup>7</sup> have shown that the acid-catalysed aquation of the [Co(CN)<sub>5</sub>N<sub>3</sub>]<sup>3-</sup> ion proceeds by a unimolecular S<sub>N</sub>1 mechanism [cf. mechanism (2)]. The relatively complicated dependence of the measured rate-constant on the acid concentration is a consequence of the high degree of protonation of the substrate, as would be expected for an anion. Essentially, however, the mechanism of a pre-equilibrium followed by a slow step is similar to the findings of this investigation. The main difference is in the mechanism postulated for the rate-determining step. Haim and Wilmarth prefer a unimolecular process, whilst the evidence in the case of the [Co en<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations favours a bimolecular process. However, the electronic structures of the ions in question are so dissimilar that any correlation on this point would not be expected.

No firm conclusions can be made at this stage about the mechanism at high acid concentrations, except that the postulated mechanism (1) appears to break down.

#### EXPERIMENTAL

Previously described methods<sup>8</sup> were used for the preparation of *cis*- (Found: C, 13.2; H, 4.4; N, 38.3%) and *trans*-diazidobisethylenediaminecobalt(III) perchlorate {Found: C, 13.5; H, 4.5; N, 38.35. [Co(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> requires C, 13.2; H, 4.4; N, 38.6%}, and *trans*-chloroazidobisethylenediaminecobalt(III) perchlorate {Found: Cl, 10.0; N<sub>3</sub><sup>-</sup>, 11.7. [Co(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(N<sub>3</sub>)Cl]ClO<sub>4</sub> requires Cl, 10.0; N<sub>3</sub><sup>-</sup>, 11.8%}; the compounds were recrystallised to constant absorption spectrum.

Solutions of *trans*-aquoazidobisethylenediaminecobalt(III) perchlorate were prepared by the method previously described.<sup>8</sup> *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)Cl]ClO<sub>4</sub> was dissolved in water, one or two drops of a dilute solution of mercuric nitrate were added, and the resulting solution of *trans*-[Co en<sub>2</sub>(N<sub>3</sub>)H<sub>2</sub>O](ClO<sub>4</sub>)<sub>2</sub> was passed through a column of Amberlite IR-A 400 (OH<sup>-</sup> form), which caused the mercuric ions in the solution to be precipitated as mercuric oxide. The effluent was then neutralised to pH 4.

*Spectrophotometric Runs.*—Aliquot portions of the reaction mixture were withdrawn and "frozen," and the optical density at 5330 Å was measured as quickly as possible on a Unicam S.P. 500 spectrophotometer. The rate constant was calculated from the slope of a graph of log<sub>10</sub> (D<sub>t</sub> - D<sub>∞</sub>) against time, where D<sub>t</sub> = optical density at time *t*, and D<sub>∞</sub> = optical density of the solution after ten half-lives. At low acid concentrations this value was in good agreement with the calculated figure. At the highest acid concentrations a calculated infinity reading was used because of slight interference from the slow second step. It was shown that the differences between the spectra in water and in 2M-sodium perchlorate of any one of these compounds were within the experimental error of the method.

*Nitritometric Runs.*<sup>1</sup>—Aliquot portions of the reaction mixture were withdrawn and neutralised with borax solution (0.2N) and the resultant solutions were passed through columns of Amberlite IR 120 ion-exchange resin (Na form). The effluent and washings were treated with an excess of standard sodium nitrite solution and acidified. After a few minutes the excess of sodium nitrite was estimated using sulphanilic acid and 1-naphthylamine.

The author thanks Dr. A. M. Staples for valuable discussion.

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BRADFORD 7, YORKS. [Received, May 31st, 1963.]

<sup>7</sup> Haim and Wilmarth, *Inorg. Chem.*, 1962, **1**, 583.

<sup>8</sup> Staples and Tobe, *J.*, 1960, 4812.