

973. *Mechanisms of Substitution Reactions of Octahedral Bis(ditertiary arsine) Complexes. Part I. Isomerisation and Thiocyanate Substitution Reactions of cis-Dichlorobis-(o-phenylenebisdimethylarsine)-cobalt(III) Perchlorate.*

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The isomerisation of *cis*-[Co diars₂ Cl₂]⁺ (diars = *o*-phenylenebisdimethylarsine) to the *trans* isomer has been studied in anhydrous methanol at 54.9°. The rate has a first-order dependence on the concentration of complex and is independent of chloride over a wide range of concentration. Light and unidentified impurities catalyse the reaction and there is evidence, at higher complex concentrations, for the production of a catalyst in the course of the reaction. The replacement of co-ordinated chlorine by thiocyanate has been studied spectrophotometrically. The final product of the reaction is the same isomer of [Co diars₂ (SCN)₂]⁺ as that formed by thiocyanate substitution in the *trans*-dichloro-complex. Spectrophotometric analysis indicates that the substitution proceeds in two stages and the properties of the intermediate, which could not be isolated, were examined. Its spectrum is similar in many respects to that of the *trans*-[Co diars₂ Cl₂]⁺ complex but there are significant differences in the range 370—430 mμ. The rate at which this intermediate reacts with thiocyanate is faster than that of the *trans*-dichloro-complex. This is probably a chlorothiocyano-complex but further investigation is required. The rate constant for the entry of the first thiocyanate is very similar to that for the isomerisation of the *cis* complex in the absence of thiocyanate. Studies of substitution by thiocyanate in competition with an excess of chloride indicate prior formation of the *trans*-dichloro-complex, and possibly some of the intermediate but the rate of disappearance of the *cis*-dichloro-complex is the same as in the non-competitive experiments.

ONE of the most important aspects of the substitution mechanisms of octahedral inorganic complexes that has received insufficient attention is the part played by the central metal ion in determining the rates and mechanism of the reaction. Taube¹ was the first to formulate a relationship between the lability of the transition-metal complex and the electronic configuration of the metal ion but this was a non-quantitative relationship. It still presents interesting implications regarding the role played by the metal in determining the mechanism, as distinct from the lability. More recently, Basolo and Pearson² attempted to provide a semiquantitative relationship by applying simplified crystal field theory to the computation of activation energies of the substitution reactions. Although the treatment was far from rigorous and to some extent oversimplified, it has inspired a number of workers to measure and compare the activation parameters of a series of

¹ Taube, *Chem. Revs.*, 1952, **50**, 69.

² Basolo and Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958, p. 109.

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reactions where the only variable is the central metal ion and many of the data obtained have been in rough agreement with the calculations. In most cases these studies have had to be confined to a series of not more than four or five metals, the limit being set by the availability of suitable ligands. Those which have proved most convenient are 1,10-phenanthroline,³ $\alpha\alpha'\alpha''$ -terpyridyl,⁴ and ethylenediaminetetra-acetate but, in most of these cases, the multidentate nature of the ligand makes any assignment of mechanism to the individual acts of substitution either equivocal or impossible. Water, as a ligand, will obviously offer the widest selection of metals with a constant ligand environment but it limits, to some extent, the choice of oxidation states. The problems of measuring the normally fast rates have been largely overcome but the deduction of mechanism is not easy because there is little scope for studying the effects of the possible variables.

The ligand, *o*-phenylenebis(dimethylarsine), [diars], forms a large number of octahedral complexes of the type $[M \text{ diars}_2 X_2]$ which may be cationic or neutral.⁵ Ligand X may be chosen such that it is much more labile than the arsine chelate and studies of the replacement of the unidentate ligand X under non-solvolytic conditions should provide information about the effect of the nature, the electron configuration, and the oxidation state of the metal upon the rates and Arrhenius parameters of the substitutions and possibly upon the mechanism.

In this Series it is proposed to discuss the substitution reactions of these complexes. At present only one pair of stereoisomers have been characterised^{6,7} but it is hoped that, in time, studies can also be made of the steric courses of these reactions.

cis- and *trans*- $[\text{Co diars}_2 \text{Cl}_2]^+$ provide a suitable starting point since they can readily be obtained pure, they are soluble in a range of weakly co-ordinating organic solvents, and are of known configuration. The proof of configuration rests, at the moment, upon the interpretation of spectroscopic data⁷ and requires final confirmation either by optical resolution of the *cis*-isomer or from the study of their X-ray diffraction. A great deal of information is available about the behaviour of octahedral cobalt(III) complexes that contain at least four nitrogen donors⁸ and a comparison of the arsenic and nitrogen systems will throw more light on the part played by the ligands in determining the rates and mechanism of substitution.

We now report the reactions of the *cis*-complex. Those of the *trans*-complex will be reported later.

(1) *Isomerisation of cis-Dichlorobis-(o-phenylenebisdimethylarsine)cobalt(III) Perchlorate in Anhydrous Methanol at 54.9°*.—The colour of a solution of *cis*- $[\text{Co diars}_2 \text{Cl}_2]\text{ClO}_4$ in methanol slowly changes from a brownish-violet to green. The final spectrum is identical with that of a freshly prepared solution of *trans*- $[\text{Co diars}_2 \text{Cl}_2]\text{ClO}_4$ indicating that the complex has isomerised. The rate of this reaction can be very variable and, unless special precautions are taken, depends upon the light intensity and the previous history of the complex. If the complex is purified by repeated recrystallisation and light is rigorously excluded, a much slower, completely reproducible, rate of reaction can be observed. The reaction was followed spectrophotometrically and Fig. 1 shows the change in the absorption spectrum of the solution as the reaction proceeds and the two isobestic points at 437 and 366 μ are found in all the experiments for up to $3\frac{1}{2}$ half-lives of reaction and correspond exactly to the points at which the spectra of the pure *cis*- and *trans*-dichloro-complexes cross. We conclude, therefore, that the isomerisation does not involve the formation of measureable quantities of any *intermediate*. The kinetics of the isomerisation were followed

³ Ellis and Wilkins, *J.*, 1959, 299.

⁴ Hogg and Wilkins, *J.*, 1962, 341.

⁵ Nyholm, *J.*, 1950, 851, 857, 2061; 1951, 2602; Nyholm and Parish, *Chem. and Ind.*, 1956, 470; Nyholm and Sutton, *J.*, 1958, 560, 567, 572; Curtis, Fergusson, and Nyholm, *Chem. and Ind.*, 1958, 625; Lewis, Nyholm, and Smith, *J.*, 1962, 2592.

⁶ Nyholm, *J.*, 1950, 2071.

⁷ Dunn, Nyholm, and Yamada, *J.*, 1962, 1564.

⁸ Ref. 2, pp. 114—167; Tobe, *Sci. Progress*, 1960, 48, 483.

by measuring the rate of change of optical density at 490 $m\mu$ where the absorption of the *trans*-complex is negligible compared with that of the *cis* (Fig. 2). The isomerisation is of first order in the complex provided that its concentration is less than $2 \times 10^{-4}M$. At higher concentrations, the semilogarithmic plot of $\log_{10} D_t/D_0$ against time, where D_0 and D_t are the optical densities measured at the start of the reaction and after time t ,

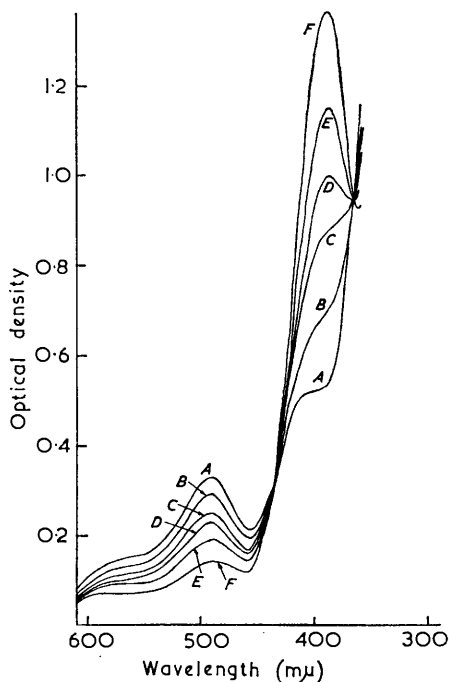


FIG. 1. Changes in the absorption spectrum of a solution of *cis*-[Co diars₂ Cl₂]⁺ ($8.9 \times 10^{-5}M$) in methanol at 54.9° after 0 (A), 1075 (B), 2490 (C), 3890 (D), 5385 (E), and 8240 (F) minutes.

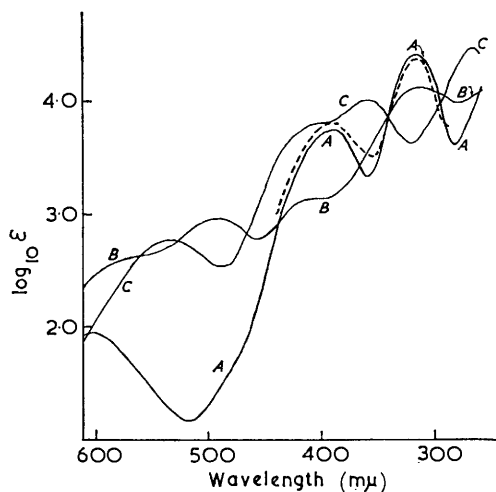


FIG. 2. Visible and ultraviolet absorption spectra of

(A), *trans*-[Co diars₂ Cl₂]⁺,
(B), *cis*-[Co diars₂ Cl₂]⁺, and
(C), [Co diars₂ (SCN)₂]⁺.

The calculated spectrum of the intermediate formed in the reaction between *cis*-[Co diars₂ Cl₂]⁺ and thiocyanate is indicated by the broken line.

respectively, shows a curvature that indicates an acceleration as the reaction proceeds. Furthermore, the initial slope tends to increase at complex concentrations $>10^{-3}M$. An identical, but more marked effect can be found in the reaction with thiocyanate.

The isomerisation was also studied in the presence of a large excess of chloride, added as anhydrous lithium chloride, and the first-order dependence in complex was maintained. The first-order rate constants, determined from the slopes of the semilogarithmic plots, are in Table I; the rate is essentially independent of the concentration of chloride, apart from a very small salt effect.

TABLE I.

First-order rate constants for the isomerisation of *cis*-[Co diars₂ Cl₂]ClO₄ in anhydrous methanol at 54.9°.

$\pm 10^4$ [Complex] (M)	0.89	0.90	1.35	1.59	1.90	1.04	1.03
10^4 [LiCl]	0	0	0	0	0	207	500
$10^4 k$ (sec. ⁻¹)	1.67	1.63	1.73	1.63	1.67	1.83	1.85

Small quantities of water (1–2 vol %) do not affect the rate or the kinetic form of the reaction but small quantities of [Co diars₂]Cl₂ (the corresponding Co^{II} derivative) catalyse the reaction and greatly increase its sensitivity to photocatalysis. At first sight it appears

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that this catalytic effect is not large enough for the $[\text{Co diars}_2]\text{Cl}_2$ as added to be the cause of the catalysis that is observed in the isomerisation of the "pure" *cis*-complex. This catalytic reaction is being studied in more detail.

(2) *Substitution by Thiocyanate in cis-Dichlorobis-(o-phenylenebisdimethylarsine)cobalt(III) Perchlorate in Anhydrous Methanol.*—A study of the change in the spectrum of a solution originally containing *cis*- $[\text{Co diars}_2 \text{Cl}_2]\text{ClO}_4$ and excess of phenyltrimethylammonium thiocyanate (or potassium thiocyanate) (Fig. 3) shows that, although the final spectrum corresponds very closely to that of $[\text{Co diars}_2 (\text{SCN})_2]^+$ already characterised⁶ the absence of isosbestic points at 466, 528, and 560 $m\mu$ (cf. Fig. 2) indicates that a coloured intermediate is formed in significant quantities. In spite of much effort, it was not possible to isolate and characterise this intermediate and so it was necessary, knowing only the spectra of the initial complex and the final dithiocyanato complex, to

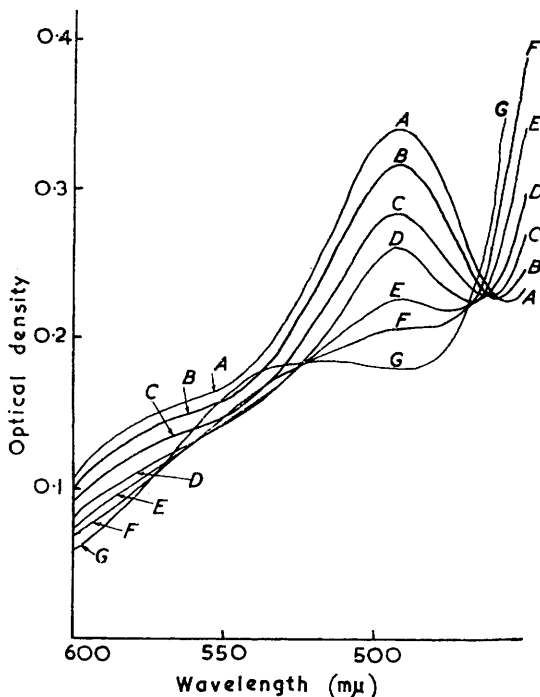


FIG. 3. Spectra of a solution originally containing *cis*- $[\text{Co diars}_2 \text{Cl}_2]^+$ ($9.25 \times 10^{-5}\text{M}$) and potassium thiocyanate ($1.565 \times 10^{-2}\text{M}$) in methanol at 54.9° , (A) on mixing and after 970 (B), 2395 (C), 3870 (D), 5300 (E), 6745 (F), and 9605 (G) minutes.

determine the concentration of all three species in solution at the different stages of reaction, and to attempt to calculate the spectrum of this intermediate. Owing to favourable circumstances it was possible to do both, by the following procedure. It was observed that, in the earlier stages of the reaction, the spectra, over the wavelength range 480—520 $m\mu$, remained parallel with one another, *i.e.*, for any pair of wavelengths within this range, λ_1 and λ_2 , the ratio of the optical densities, $D_{\lambda_1}/D_{\lambda_2}$, is independent of time and also the ratio of the optical densities at a particular wavelength at two different times is independent of wavelength. It is known, from the final spectrum, that the dithiocyanato-complex has extinction coefficients that are significantly smaller than those of the dichloro-complex, especially in the centre of this region. Consequently in the early stages of the reaction, when the concentration of the dithiocyanato-complex is small, it will not contribute significantly to the light absorption of the solution in this region. In order to observe parallel spectra it is, therefore, necessary that either the intermediate has a spectrum that is identical in shape and position to that of the *cis*-dichloro-complex but with smaller extinction coefficients (*i.e.*, $\epsilon_{cis}/\epsilon_{intermed.}$ is independent of the wavelength), or the intermediate does not absorb light sufficiently in this region to contribute to the light absorption

of the solution. It was assumed that the latter possibility was the most likely and the consistency of the resultant spectrophotometric analyses made on the basis of this assumption supports it. At 528 $m\mu$, cis -[Co diars₂ Cl₂]⁺ and the [Co diars₂ (SCN)₂]⁺ product have identical absorption, $\epsilon = 566 \text{ mole}^{-1} \text{ l. cm.}^{-1}$ and it was, therefore, possible to calculate the concentration of the intermediate by means of the expression

$$[\text{intermediate}] = \frac{D_0 - D_t}{D_0} \times [\text{total complex}]$$

where D_0 and D_t are the optical densities of the solutions at 528 $m\mu$ at the start of the reaction and time t , respectively. If $l = \text{cell length}$, $D_0 = 566[\text{total complex}]l$. At 490 $m\mu$ there is a large difference between the absorption of the cis -dichloro- and the dithiocyanato-complexes ($\epsilon = 912$ and 339 , resp.), and the absorption of the intermediate is negligible. Therefore

$$D/l = 912[cis\text{-Cl}_2] + 339[(\text{SCN})_2] \quad (1)$$

$$\text{and} \quad [\text{total complex}] = [cis\text{-Cl}_2] + [(\text{SCN})_2] + [\text{intermediate}] \quad (2)$$

and elimination of $[(\text{SCN})_2]$ gives,

$$[cis\text{-Cl}_2] = \frac{D/l - 339([\text{total complex}] - [\text{intermediate}])}{573}$$

where D is the optical density at 490 $m\mu$.

Using this type of analysis it was possible to determine the amounts of the three species in solution. The analysis of the spectra in Fig. 2 is given in Table 2.

TABLE 2.

Spectrophotometric analysis of the reaction mixture at various stages of the reaction.

Run N 136. [Complex] = $9.25 \times 10^{-5}M$, [SCN⁻] = $1.565 \times 10^{-2}M$.

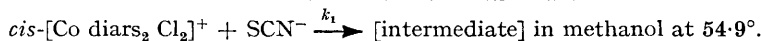
Time (min.)	$10^5[cis\text{-Cl}_2]$	$10^5[\text{intermediate}]$	$10^5[(\text{SCN})_2]$	Time (min.)	$10^5[cis\text{-Cl}_2]$	$10^5[\text{intermediate}]$	$10^5[(\text{SCN})_2]$
0	9.25	0.00	0.00	6745	4.46	1.67	3.12
970	8.49	0.51	0.26	9605	3.15	1.40	4.70
2395	7.38	1.14	0.73	12,605	1.65	0.85	6.70
3870	6.27	1.65	1.33	15,710	1.35	0.55	7.30
5300	5.23	1.85	2.17				

The results, treated in this way, can be used to calculate the rate constants for the processes involved. This disappearance of the cis -dichloro-species follows a first-order rate law provided the initial concentration of the complex species is less than $10^{-4}M$. At higher concentrations, the slope of the semilogarithmic plot increases with time although the initial slope is virtually independent of complex concentration. We believe that this is the result of a side reaction that is quite distinct from the direct substitution process and is catalytic, probably involving redox changes, the catalyst being produced during the reaction. We have tried, without success, to identify this catalyst. The cobalt(II) species [Co diars₂ Cl₂] in the form added does not appear to have the necessary catalytic power.

The first-order rate constants for the disappearance of the cis -dichloro-complex in the presence of excess of thiocyanate are in Table 3.

TABLE 3.

First-order rate constants for the reaction



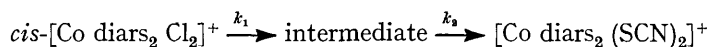
10^4 Initial [complex]	0.773	0.560	0.820	0.645	0.925	0.930	0.920	0.920
10^4 Initial [SCN ⁻]	23.0	31.0	43.4	51.5	156.5	200.0	257.0	320.0
$10^4 k_1$ (sec. ⁻¹)	2.0	1.8	1.9	2.0	1.8	1.8	1.9	2.0

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(3) *The Nature of the Intermediate.*—Since the intermediate of the reaction could not be isolated and studied separately, a series of experiments were carried out to learn more about it. First the spectrum was calculated by measuring the spectrum of the reaction mixture when the concentration of the intermediate was maximum and then subtracting the contributions made to the absorption by the unchanged *cis*-dichloro-complex and the dithiocyanato-product. The spectrum so derived indicates no absorption in the region 490—520 $m\mu$ (this is the initial assumption fed into the calculation) and the general shape of the rest is rather similar to that of *trans*-[Co diars₂ Cl₂]⁺ but has a significantly stronger absorption in the region 360—390 $m\mu$ (Fig. 2).

We have considered three possible structures for the intermediate: (a) It can be *trans*-[Co diars₂ Cl₂]⁺; this would explain the similarity of the spectra and also the similarity of the rate constants for isomerisation and thiocyanate substitution. (b) It can be an isomer of the [Co diars₂ NCS Cl]⁺ cation, and (c) it can be the less stable isomer of the cation [Co diars₂ (NCS)₂]⁺, which would require that the second chlorine is replaced considerably faster than the first in order to explain the kinetic observations.

The rate constants for the conversion of the intermediate to the dithiocyanato-product could be calculated from the analytical results. Assuming that the process consists of two consecutive first-order (or pseudo-first-order) steps, *i.e.*,



we can calculate a value for k_2 from the maximum concentration attained by the intermediate, using the expression

$$\frac{[\text{intermediate}]_{\text{max.}}}{[\text{total complex}]} = \left(\frac{k_2}{k_1} \right)^{k_2/(k_1 - k_2)}$$

and the values of k_1 obtained independently. This method is not particularly accurate since small errors in determining the maximum concentration of intermediate have a significant effect upon the value of k_2 . The values obtained for this constant are in Table 4.

TABLE 4.

	First-order rate constants for the reaction intermediate $\xrightarrow[\text{(possibly + SCN}^-)]{k_2}$ [Co diars ₂ (SCN) ₂] ⁺ in methanol at 54.9°.						
	0.773	0.820	0.845	0.925	0.930	0.920	0.920
10 ⁴ Initial [complex]	0.773	0.820	0.845	0.925	0.930	0.920	0.920
10 ⁴ Initial [SCN ⁻]	23.0	43.4	51.5	156.5	200.0	257.0	320.0
10 ⁶ k ₂ (sec. ⁻¹)	5.0	4.3	4.5	4.9	3.3	4.3	4.8

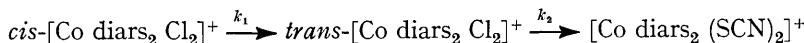
These constants are rather widely scattered because of the inaccuracy of the method and also because they rely on data gathered at the later stages of the reaction when the possibility of spurious catalysis cannot be ignored. It is likely that the lower values should be given much more weight than the higher ones.

Preliminary studies of the substitution of thiocyanate in *trans*-[Co diars₂ Cl₂]⁺ indicate that the rate constant for the first step, at 54.9° in methanol, is approximately 1.2 × 10⁻⁶ sec.⁻¹. Further, there is no spectrophotometric indication of the formation of any significant quantities of a light-absorbing intermediate. Even if we assume that the intermediate has a similar spectrum to the *trans*-dichloro-complex, the absence of a spectrophotometric induction period rules out its presence.

Although the rate constants suggest that the intermediate is not *trans*-[Co diars₂ Cl₂]⁺ a further test was applied by deliberately adding some of the *trans*-dichloro-complex to the reaction mixture at the beginning of the reaction. This did not interfere with the spectrophotometric analysis because the *trans*-dichloro-complex does not contribute significantly to the light absorption of the reaction mixture at the wavelengths involved in the analysis and it was still possible to determine the concentrations of the unchanged *cis*-dichloro-complex and the final dithiocyanato product. The analysis could not distinguish between

the reaction intermediate and the *trans*-dichloro-complex and it was possible to determine only the sum of their concentrations.

If the intermediate were *trans*-[Co diars₂ Cl₂]⁺ then this addition will not alter the scheme of two successive first-order reactions:



then $d[trans-Cl_2]/dt = k_1[cis-Cl_2] - k_2[trans-Cl_2]$

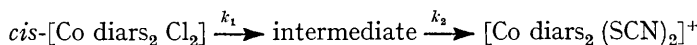
and when $[trans-Cl_2]$ is maximum $d[trans-Cl_2]/dt = 0$

so that $k_1[cis-Cl_2]^* = k_2[trans-Cl_2]_{max.}$

or $[cis-Cl_2]^*/[trans-Cl_2]_{max.} = k_2/k_1$

where $[cis-Cl_2]^*$ is the concentration of the *cis*-dichloro-complex at the time when the *trans* complex achieves its maximum concentration. In the absence of a gradually increasing catalytic component to the reaction one would expect that the ratio $[cis-Cl_2]^*/[trans-Cl_2]_{max.}$ would be independent of the amount of *trans*-dichloro-complex added at the beginning of the reaction. The experimental values are collected in Table 5, where it will be seen that this ratio changes considerably with the amount of extra *trans* complex which suggests that this is not the intermediate but does not rule out a progressive catalytic enhancement of the reaction rate as the reaction proceeds.

If the intermediate is not the *trans*-dichloro-complex then we are studying two independent reaction schemes:



and $trans-[Co\ diars_2\ Cl_2]^+ \xrightarrow{k_2} [Co\ diars_2\ (SCN)_2]^+$

The second process has been studied independently and k_3 found to be $\sim 1.2 \times 10^{-6}$ sec.⁻¹. The spectrophotometric analysis enables us to determine the sum of the concentrations of the *trans*-dichloro-complex and the intermediate and, by subtracting the amount of *trans*-dichloro-complex present, calculated from the expression

$$[trans-Cl_2]_t = [trans-Cl_2]_0 \exp(-1.2 \times 10^{-6}t)$$

the concentration of the intermediate at time t can be determined. For this reaction scheme the maximum amount of intermediate, expressed as a fraction of the initial concentration of the *cis*-dichloro-complex, should be independent of the amount of *trans*-dichloro-complex added at the beginning of the reaction and, furthermore,

$$[\text{intermediate}]_{max.}/[cis-Cl_2]_0 = \left(\frac{k_2}{k_1}\right)^{k_2/(k_1-k_2)}$$

The value of the ratio of the rate constants so calculated are in Table 5.

TABLE 5.

The reaction between *cis*-[Co diars₂ Cl₂]⁺ and SCN⁻ in the presence of varying amounts of *trans*-[Co diars₂ Cl₂]⁺ in methanol at 54.9°.

$10^4[cis-Cl_2]_0$	$10^4[trans-Cl_2]_0$	$10^4[SCN^-]_0$	k_2/k_1 (case 1) †	k_2/k_1 (case 2) ‡
0.82	0	43.4	2.1	2.2 ‡
0.71	0.169	100	1.42	1.8
0.56	0.235	31	1.04	1.9

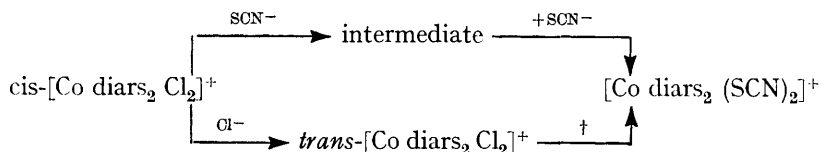
† Case 1 assumes that the intermediate is the *trans*-dichloro-complex; Case 2 assumes that they are different species. ‡ Calculated from rate constants in Tables 3 and 4.

The values of k_2/k_1 calculated according to case 2 are sensibly constant whereas those calculated according to case 1 vary widely and this constitutes good proof that the reaction between the *trans*-dichloro-complex and thiocyanate is not subject to a progressive catalysis under these circumstances and indicates that the higher rate constant derived

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from the reaction of the intermediate species shows that this is not the *trans*-dichloro-complex but a more reactive entity.

Having concluded that the intermediate is probably not *trans*-[Co diars₂ Cl₂]⁺ it is now necessary to decide whether it is a chlorothiocyanato-complex or whether it is an unstable dithiocyanato-isomer, which subsequently isomerises. In the absence of data for the release of halogen and uptake of thiocyanate it was necessary to study the reaction under conditions where there was insufficient thiocyanate to displace all the co-ordinated chlorine. The spectrophotometric analysis was made in the usual way and there are two points of interest. First, the disappearance of the *cis*-dichloro-complex followed a first-order rate law and went to completion. The first-order rate constants determined from the analyses are shown in Table 6 and appear to be some 10% larger than those determined in the presence of a large excess of thiocyanate. Why this should be so is not clear. The reaction sequence, under these conditions, appears to be:



† Although the reaction *trans*-[Co diars₂ Cl₂]⁺ → [Co diars₂ (SCN)₂]⁺ is observable it is not yet clear whether or not this goes in part through the intermediate. Present indications are that the second step of the reaction is much faster than the first.

At the early stages of the reaction [SCN⁻] ≫ [Cl⁻] and the thiocyanate substitution is predominant. At the later stages, [Cl⁻] ≫ [SCN⁻] and the main reaction is the isomerisation,



and isosbestic points appear at 437 and 366 mμ indicating that no more dithiocyanato-complex is forming. Analyses of the reaction mixture at the end of the reaction are given in Table 6, where it will be seen that the amount of dithiocyanato-complex is insufficient

TABLE 6.

Rate constants for the disappearance of *cis*-[Co diars₂ Cl₂]⁺ in the presence of small quantities of SCN⁻, and the composition of the product.

10 ⁴ [<i>cis</i> -Cl ₂] _{init.}	10 ⁴ [SCN ⁻] _{init.}	10 ⁴ <i>k</i> ₁ (sec. ⁻¹)	10 ⁴ [CoD ₂ (SCN) ₂] _{final}	$\frac{\frac{1}{2}[\text{SCN}^-]_{\text{final}}}{[\text{CoD}_2(\text{SCN})_2]_{\text{initial}}}$
0.880	0.123	1.8	0.00	0.0
0.880	0.210	2.1	0.050	0.48
0.825	0.245	2.1	0.080	0.65
0.875	0.305	2.1	0.088	0.58
0.778	0.415	2.1	0.135	0.65
0.861	0.610	2.1	0.190	0.62

to account for all the thiocyanate that had been added and it must be concluded that another thiocyanate-containing complex is present. This, in our opinion, is reasonable evidence for concluding that the intermediate is a [Co diars₂ NCS Cl]⁺ isomer.

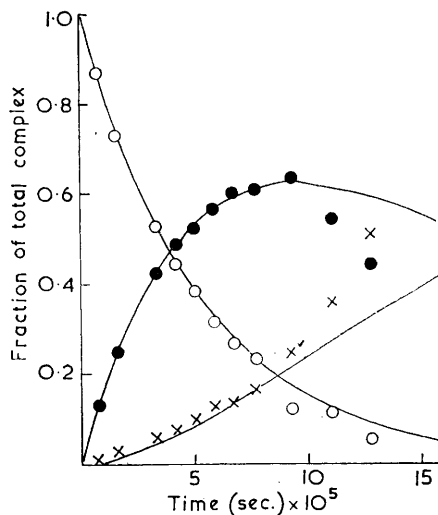
In the absence of detailed competition studies it is not possible to calculate whether the ratio appearing in the last column of Table 6 is in agreement with that calculated using the appropriate rate constants. Work is in progress using radioactive SCN⁻ and Cl⁻ to study the rates of uptake of SCN⁻ and the rates of release of Cl⁻.

(4) *Competition Studies.*—Thiocyanate substitution was studied in the presence of a large excess of chloride ions. The spectrophotometric analysis was carried out in the usual way and the results are shown in Fig. 4. The disappearance of the *cis*-[Co diars₂ Cl₂]⁺ cation follows a first-order rate law and the rate constant, *k*₁ = 1.9 × 10⁻⁶ sec.⁻¹, is in close agreement with the values determined in the absence of excess of chloride. The appearance

of the dithiocyanato-complex is delayed and the maximum concentration of intermediate species (61.3%) is far in excess of that found in the absence of excess of chloride (23.5%). These observations can be interpreted as follows. The 24-fold excess of chloride over thiocyanate allows effective competition for the highly reactive first product of the

FIG. 4. Composition of the reaction mixture as a function of time when *cis*-[Co diars₂ Cl₂]⁺, O (9.30×10^{-5} M) reacts with potassium thiocyanate (3.95×10^{-2} M) in the presence of excess of chloride (9.60×10^{-3} M).

Intermediate + *trans*-[Co diars₂ Cl₂]⁺, ●.
[Co diars₂ (SCN)₂]⁺, ×.



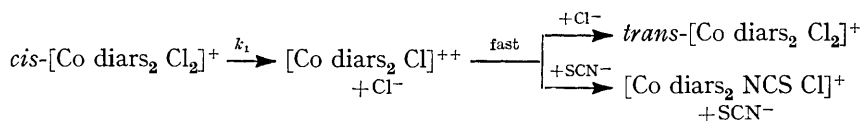
rate-determining stage so that a considerable part of the substrate is first converted into the *trans*-dichloro-complex. It should be remembered that the spectrophotometric analysis cannot distinguish the *trans*-dichloro-complex from the chlorothiocyanato-intermediate. It has already been seen that the *trans*-dichloro-complex reacts more slowly with thiocyanate, $k_3 = 1.2 \times 10^{-6} \text{ sec.}^{-1}$, and if this is now the second stage of the reaction and this constant is unaffected by the excess of chloride that has been added, it can be calculated, by using the expression discussed previously, that the maximum concentration of intermediate (*trans*-dichloro-complex) should be 45% of the total amount of complex. The higher value of 61% observed for

$$\frac{\{[trans\text{-Cl}_2] + [\text{Cl-SCN}]\}_{\text{max.}}}{[\text{total complex}]} \times 100$$

suggests, not surprisingly, that chloride competition operates here as well and that it is indicated, not by chemical change (isomerisation), but by an apparent reduction in the reaction rate, *i.e.*, mass-law retardation. The values in Fig. 4 follow very closely the curves calculated for two consecutive first-order processes with constants, $1.9 \times 10^{-6} \text{ sec.}^{-1}$ and $5.2 \times 10^{-7} \text{ sec.}^{-1}$, respectively, departing only at the later stages of the reaction where the general catalytic acceleration, noted previously, becomes important.

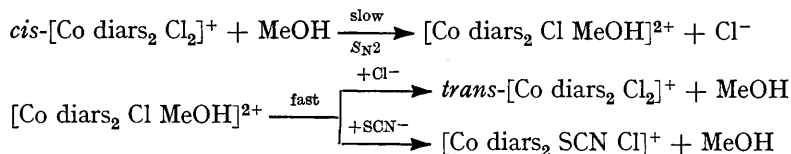
Discussion.—The kinetic data for substitution of the chlorine in *cis*-[Co diars₂ Cl₂]⁺ by chloride (measured by isomerisation studies) and by thiocyanate clearly indicate that the anion plays no significant part in the rate-determining step. Two possible mechanisms are suggested:

(i) A unimolecular (S_N1) process:



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(ii) A rate-determining bimolecular solvolysis by methanol followed by a very fast displacement of the solvent by chloride or thiocyanate:



The second stage of the substitution should be mechanistically similar to the first. Kinetically it is not possible to distinguish these two mechanisms, even by competition studies, which only demonstrate the presence of a reactive intermediate. Nothing is known about the methanolo-complexes of the cobalt(III) bis(diarsine) series and there is no evidence for their presence in noticeable amount even when the perchlorate of the complex is heated in methanol. This suggests that the stability of the methanolo-complex is very small and this is in accord with preliminary observations in aqueous solution where the *trans*-complex appears to be able to exchange its chlorines without any noticeable solvolysis taking place.⁹ Certainly, no complexes of $[\text{Co}^{\text{III}} \text{diars}_2 \text{X Y}]^{n+}$ have been isolated where X or Y is a neutral ligand, except $[\text{Co diars}_3]^{3+}$.¹⁰

From what is known of the nucleophilicity of methanol, even if the nucleophilicity scale is quite different from that found for substitution at carbon, the second mechanism seems rather unlikely and the unimolecular mechanism is preferred. Mechanistically the reaction between *cis*- $[\text{Co diars}_2 \text{Cl}_2]^+$ and chloride or thiocyanate is similar to the analogous reactions of the *cis*- $[\text{Co en}_2 \text{Cl}_2]^+$ cation (en = ethylenediamine). The reactivity is less, however; $k_1 = 1.9 \times 10^{-6} \text{ sec.}^{-1}$ at 54.9° for the diarsine complex and $k_1 = 7.6 \times 10^{-5} \text{ sec.}^{-1}$ at 35.0° for the free ion of the ethylenediamine analogue.¹¹ (This is a 400-fold difference if one uses a reasonable activation energy, 23 kcal./mole, for the ethylenediamine complex)

A very interesting observation is that the first-order rate constant for the isomerisation or thiocyanate substitution is virtually independent of the concentration of the anionic reagent over a very wide range. In the ethylenediamine analogue there is a marked dependence upon the reagent concentration at low concentrations which has been attributed to ion-association with the ion-aggregate having a different reactivity to the free ion.¹¹ Therefore, either the free ion and the ion aggregate of the arsine complex have identical reactivities or the arsine complex does not form an intimate ion-aggregate. The latter seems most likely and conductivity studies are in progress to examine this point and to determine the importance of the N-H group in the formation of ion-aggregates.

The competition studies in Section 4 can give some indication of the relative affinities of SCN^- and Cl^- for the reactive pentaco-ordinate $[\text{Co diars}_2 \text{Cl}]^{2+}$ intermediate. The very close agreement of the experimental results in Fig. 4 with the curves calculated for a simple two-step consecutive first-order process might, at first sight, suggest that the intermediate was homogeneous and not a mixture of *trans*- $[\text{Co diars}_2 \text{Cl}_2]^+$ and $[\text{Co diars}_2 \text{SCN Cl}]^+$. This, however, would give rise to a paradoxical situation for, if the intermediate were *trans*- $[\text{Co diars}_2 \text{Cl}_2]^+$, chloride, in 25-fold excess over thiocyanate, would have to compete successfully with thiocyanate for the pentaco-ordinate intermediate. But the value for k_2 ($5.2 \times 10^{-7} \text{ sec.}^{-1}$) for the second step refers to the successful competition by thiocyanate for the pentaco-ordinate intermediate derived from the *trans*-dichloro-complex. Although the acts of successful competition by chloride are not marked by chemical change they will be observable in a mass-law retardation and this is observed in the reduction of the rate constant for thiocyanate substitution in the *trans*-dichloro-complex from $1.2 \times 10^{-6} \text{ sec.}^{-1}$ (measured in the absence of excess of chloride) to $5.2 \times 10^{-7} \text{ sec.}^{-1}$. This

⁹ Graziano, Peloso, and Ricevuto, personal communication.

¹⁰ Burstall and Nyholm, *J.*, 1952, 3570.

¹¹ Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, 79, 5382; Bosnich, Ingold, and Tobe, *J.*, in the press.

reduction enables us to calculate the relative efficiencies of Cl^- and SCN^- for this pentacoordinated species by using the expression

$$\frac{\text{Effectiveness of } \text{SCN}^-}{\text{Effectiveness of } \text{Cl}^-} = \frac{5.2 \times 10^{-7}}{(12.0 - 5.2) \times 10^{-7}} \times \frac{[\text{Cl}^-]}{[\text{SCN}^-]} = 18.6$$

suggesting that thiocyanate is considerably more reactive than chloride, ion for ion, for the pentacoordinated intermediate derived from the *trans*-dichloro-complex. The original premise for this possibility, that chloride competed effectively for the pentacoordinated intermediate derived from the *cis*-dichloro-complex, is not readily compatible with the above deduction. We can take the opposite view, that the intermediate is all $[\text{Co diars}_2 \text{SCN Cl}]^+$, but the same paradox will be encountered from the opposite direction. The effectiveness of thiocyanate would have to be 1000 times that of chloride for the first step and only three times for the second step.

Until the reactions of the *trans*-dichloro-complex are studied in detail, the accurate data for the competitive abilities of chloride and thiocyanate will not be available. In all probability the initial assumption that the intermediate is homogeneous is false and we have, coincidentally, a mixture of the *trans*-dichloro- and chlorothiocyanato-complexes in such proportions as to give rise to a homogeneous kinetic form. Whatever the situation, however, it appears that thiocyanate is a better reagent than chloride for the pentacoordinated $[\text{Co diars}_2 \text{Cl}]^{++}$ and $[\text{Co diars}_2 \text{NCS}]^{++}$ species, an observation in direct contrast to the properties of $[\text{Co en}_2 \text{Cl}]^{++}$, where chloride is approximately some seven times more effective than thiocyanate.¹²

EXPERIMENTAL

Preparations.—*trans*- $[\text{Co diars}_2 \text{Cl}_2] \text{ClO}_4$ was prepared by Nyholm's method.⁶ *cis*- $[\text{Co diars}_2 \text{Cl}_2] \text{ClO}_4$ was prepared by a modification of the method of Dunn, Nyholm, and Yamada.⁷ $[\text{Co diars}_2 \text{I}_2] \text{I}$, prepared by the action of KI on a solution of the *trans*-dichloro-chloride, was suspended in 80% ethanol : 20% water (1 g. in 40 c.c.s) and an excess of silver acetate added. The mixture was left overnight, filtered, and treated with concentrated hydrochloric acid (5 c.c.) and concentrated perchloric acid (10 c.c.), the solution being kept cold. Some *trans*-dichloro-perchlorate precipitated immediately and was filtered off and a second batch that settled out more slowly was filtered off before the filtrate was passed into 1M-aqueous perchloric acid (400 ml.). A reddish-brown flaky precipitate formed immediately and was filtered off, dissolved in methanol and reprecipitated in the same way. After two such reprecipitations the *complex* was analytically pure but not suitable for kinetic purposes. The complex was dissolved in acetone and reprecipitated by adding HCl, HClO_4 , and water, and the process repeated until the rate of reaction of the sample was not further affected. The rate of isomerisation after seven reprecipitations was the same as that measured after thirteen reprecipitations. In the final reprecipitation it was convenient to use ethanol instead of acetone. The rates were reproducible with different preparations that had been subject to this purification procedure (Found: C, 29.8; H, 4.1; Cl (co-ordinated) 8.7; Co, 7.2%. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{CoCl}_2\text{ClO}_4$ requires C, 30.0; H, 4.0; Cl (co-ordinated) 8.8; Co, 7.35%). Even after the complete purification process the yield was 50% based upon the amount of $[\text{Co diars}_2 \text{I}_2] \text{I}$ taken. $[\text{Co diars}_2 (\text{SCN})_2] \text{SCN}$ was prepared by Nyholm's method⁶ and also by treating the *trans*- or the *cis*- $[\text{Co diars}_2 \text{Cl}_2] \text{ClO}_4$ with thiocyanate. All three samples were identical.

Lithium chloride and potassium thiocyanate were AnalaR reagents that had been recrystallised and dried. An analytically pure sample of phenyltrimethylammonium thiocyanate was kindly provided by Dr. M. N. Hughes.

Methanol. Only the AnalaR solvent would give reproducible results. This was dried by refluxing over magnesium methoxide and used as soon as possible. Solutions were prepared in a dry box and placed in small flasks, painted black to exclude the light. These were placed in a thermostat and withdrawn at the appropriate times and cooled. Some experiments were carried out by taking samples from solutions in larger flasks but the results were no different.

¹² Watts and Tobe, unpublished results.

Addition of 2% water to the methanol did not have any significant effect upon the rates of the reactions.

Spectra were measured with a Perkin-Elmer model 137 spectrophotometer and spectrophotometric analyses were carried out using a Unicam S.P. 500 Quartz spectrophotometer. The solutions were contained in 4 cm., 1 cm., and 2 mm. silica cells.

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