753. *Mechanism of Octahedral Substitution Reactions in Non-aqueous Solutions. Part IV.** *The Kinetics and Steric Course of Chloride Exchange in the* cis-*Dichlorobis(ethylenediamine)cobalt*(III) *Cation in Methanol*

By B. Bosnich, Sir Christopher Ingold, and M. L. Tobe

The kinetics of racemisation, of *cis*- ⟶ *trans*-isomerisation, and of chloride exchange of $(+)_D$-*cis*-$[Co_5en_2Cl_2]^+$ have been studied in methanol at 35·0°. The rates are dependent upon $[Cl^-]$ at low concentrations, but a limiting rate is approached at higher concentrations, and each of the three processes follows the same rate law. The form is consistent with the pre-equilibrium formation of an ion-pair of the type, *cis*-$[Co\,en_2Cl_2]^+ \ldots Cl^-$ with an association constant of 250 l. mole^{-1}. The ion-pair reacts in all three measured processes some 90—110% faster than the free ion does, but the steric course of entry of chloride into the ion-pair and into the free ion is fairly similar. The free ion exchanges its chloride with about 70% conversion to the *trans*-form, and the *cis*-product contains both *dextro* and *lævo* forms. The accuracy of the label transfer experiments is not sufficient for us to say whether the enantiomeric forms are produced in equal amounts or whether there is a slight preponderence of inversion. The ion-pair exchanges its chlorine with about 85% conversion into the *trans*-form and the *cis*-part of the product is in the form of the racemate. A unimolecular mechanism is proposed in which the five-co-ordinate intermediate has a lifetime almost sufficient for it to come to equilibrium with its environment.

Some years ago, studies of the substitution reactions of *cis*-$[Co\,en_2Cl_2]^+$ in methanol

$$X^- + cis\text{-}[Co\,en_2Cl_2]^+ \longrightarrow [Co\,en_2ClX]^+ + Cl^-$$

indicated two types of behaviour depending upon the nature of the entering group.[1] Reagents such as Cl^-, Br^-, SCN^-, and NO_3^- entered at a common rate that was independent of their concentration, whereas CH_3O^-, N_3^-, and NO_2^- reacted more rapidly at rates that were dependent upon their concentration. It was later shown [2] that the behaviour of N_3^- and NO_2^- was due to the formation of methoxide ions from the solvolysis of these basic reagents, *e.g.*,

$$N_3^- + CH_3OH = HN_3 + CH_3O^-$$

and once this solvolytic disturbance was removed by the addition of a small amount of acid, all the reagents, methoxide excepted, behaved in the same way. The lyate ions, hydroxide in water and methoxide in methanol, are very reactive towards these complexes and the mechanisms of these reactions is still discussed.[3] Although the reactions of this complex appeared to be unimolecular in methanol, it had been observed in the reaction with azide [2] that, even when the solvolytic disturbance was removed, the rate depended on $[N_3^-]$ when this concentration was small.

During studies of competition between azide and chloride ions for substitution in the *cis*-$[Co\,en_2Cl_2]^+$ ion in methanol, Watts [4] observed that the rate of the *cis* ⟶ *trans* reaction was very sensitive to chloride ion concentration within the region $0 < [Cl^-] < 10^{-2}$M. The rate profile was similar to that reported by Basolo, Henry, and Pearson for

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* Part III, M. N. Hughes and M. L. Tobe, *J.*, 1965, 1204.

[1] (*a*) D. D. Brown and C. K. Ingold, *J.*, 1953, 2680; (*b*) D. D. Brown and R. S. Nyholm, *J.*, 1953, 2696.

[2] R. G. Pearson, P. M. Henry, and F. Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5382.

[3] (*a*) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958, p. 129; (*b*) M. L. Tobe, *Sci. Progress*, 1960, **48**, 483; S. C. Chan and M. L. Tobe, *J.*, 1962, 4533.

[4] D. W. Watts, unpublished results.

the reaction with azide [2] where a pre-equilibrium ion-association was invoked to explain the results. Because of experimental difficulties, they were not able to examine this postulated association by non-kinetic methods, but they pointed out that there was spectrophotometric evidence for association between the *cis*-dichloro-cation and chloride ions.

Our purpose was to study the dependence of the rate of entry of chloride ion into *cis*-$[\mathrm{Co\ en_2Cl_2}]^+$ on chloride concentration, in order to ascertain whether it arose from ion-association and to determine any stereochemical consequences of ion-association.

(1) *Conversion of* cis-*Dichlorobis(ethylenediamine)cobalt*(III) *Tetraphenylborate into the* trans-*Isomer in Methanol at* 35·0°.—Brown and Nyholm studied this reaction where the concentration of chloride was much greater than of the complex.[1b] There was a small increase in rate with increasing concentration, but this was explained in terms of a secondary salt effect. We used the tetraphenylborate of the complex, which was readily and rapidly soluble in methanol, so that it was possible to study the reaction in its very early stages and also where $[\mathrm{Cl}^-] < [\text{complex}]$.

The isomerisation was followed spectrophotometrically by measuring the change in optical density at 540 mμ where the *cis*-complex has a much stronger absorption than the *trans*. The first-order rate constants were calculated from the slope of the plot of $\log_{10}(D_t - D_\infty)$ against time, where D_t and D_∞ are the optical densities of the reaction mixture at time t and after ten half-lives, respectively. The results are plotted as a function of added LiCl concentration in Figure 1. These data refer only to a constant initial concentration of complex of 10^{-3}M. If this is increased to 8×10^{-3}M, the observed rate constant in the absence of added LiCl increases from $3{\cdot}2 \times 10^{-3}$ min.$^{-1}$ to $3{\cdot}9 \times 10^{-3}$ min.$^{-1}$.

(2) *Racemisation of* $(+)_{\mathrm{D}}$-cis-*Dichlorobis(ethylenediamine)cobalt*(III) *Perchlorate* † *in Methanol at* 35·0°.—The racemisation studies used the $(+)_{\mathrm{D}}$-*cis*-$[\mathrm{Co\ en_2Cl_2}]\mathrm{ClO_4}$, and the first-order rate constants were determined from the slope of the plot of $\log_{10}\alpha_{\mathrm{D}}$ against time, α_{D} being the measured rotation of the solution at time t. The constants are plotted against added [LiCl] in Figure 1. The initial concentration of the complex was held constant at 10^{-3}M.

(3) *The Kinetics of Exchange of Isotopically Labelled Chloride.*—Calculation of the rate constant k for the reaction

$$cis\text{-}[\mathrm{Co\ en_2Cl_2}]^+ + \mathrm{Cl}^{*-} \longrightarrow cis\text{- and } trans\text{-}[\mathrm{Co\ en_2Cl\ Cl^*}]^+ + \mathrm{Cl}^-$$

from the rates of transfer of a radioactive label among the various species is complicated by the fact that the system cannot be studied at equilibrium, since at that point all the dichloro-complex is in the form of the *trans*-isomer. The exchange studies, therefore, had to be made under conditions in which some acts of substitution involve some enantiomeric change, $[(+)_{\mathrm{D}}\text{-}cis \longrightarrow (-)_{\mathrm{D}}\text{-}cis]$, some non-enantiomeric chemical change ($cis \longrightarrow trans$), and some not otherwise observable chemical change, $[(+)_{\mathrm{D}}\text{-}cis \longrightarrow (+)_{\mathrm{D}}\text{-}cis]$. This problem was solved in the original work [1] by calculating rate constants on the assumption that only one chloride was being exchanged, and then extrapolating the rate constants back to $t = 0$, where this assumption was valid. In those experiments, moreover, the amount of chloride present as Cl^- was always much greater than the amount co-ordinated to the metal and so there was no need to take any account of isotopic dilution. In this work, however, we are interested in the region where the concentration of ionic chloride does not differ greatly from that of the co-ordinated chloride, and so isotopic dilution is of utmost importance. In order not to rely on an extrapolation to zero time, where the data are least accurate, we attempted to calculate an accurate expression for the relationship between the rate of appearance of radioactivity in the complex and the pertinent rate constants. We did not solve the complete problem, which should include the contribution made by exchange of the *trans*-product. But the rate constant of that reaction

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† This form was designated as *l-cis* by Werner, since it is lævorotatory at the red hydrogen-c line.

is 1×10^{-3} min.$^{-1}$, without any important ion-pairing variation, presumably because the *trans*-ion has no dipole moment. This comes from Pearson, Henry, and Basolo's data,[5] with an approximate allowance for the small temperature differences, and is substantially smaller than the rate constant for the exchange of the *cis*-isomer, 5—8 $\times 10^{-3}$ min.$^{-1}$ (depending upon concentration, because of ion-pairing; see Table 1). Therefore we felt justified in ignoring the reaction of the *trans*-isomer in the early stages of the observed reaction of the *cis*, when the amount of *trans*-isomer present is smaller than the amount of *cis*. Under these circumstances, the rate equation (see Appendix) is

$$\frac{\mathrm{d}X}{\mathrm{d}t} = ka \exp\left[-\frac{k+\kappa}{2}t - \frac{ka}{\kappa b}(1 - \exp\{-\kappa t\})\right]$$

where X = the amount of label transfer (and is proportional in any run to the number of counts per unit time measured for a constant amount of isolated complex cation), a and b are the initial concentrations of *cis*-complex and chloride, respectively, κ is the separately measured rate constant for the *cis*- ⟶ *trans*-isomerisation, and k is the required rate constant for chloride substitution in the *cis*-complex. It was not possible to integrate this expression in a closed form and so the approximation was made of assuming that $\exp(-\kappa t) \approx 1 - \kappa t$. In this region, where $b \approx a$ and the second term in the exponent of the rate equation is important, κ is of the order of 5×10^{-3} min.$^{-1}$, and the error introduced by this aproximation is 0·5% after 20 min., 3·7% after 50 min., and 20% after 100 min. Since the main weight was given to data collected in the first 60 min. of the reaction, the approximation was thought to be justified.

As a result of this approximation, the rate equation reduces to

$$\frac{\mathrm{d}X}{\mathrm{d}t} = ka \exp\left(-\frac{k+\kappa}{2} - \frac{ka}{\kappa b}\right)t$$

which integrates to a reaction progress equation of simple logarithmic form. We could not, however, semilogarithmically plot our data, because we could not calculate X_∞ without a prior knowledge of k, and we could not obtain X_∞ experimentally because our rate equation is valid only over the earlier part of the reaction. An iteration method of obtaining k was not readily convergent, and Guggenheim's method [6] of treating a first-order reaction without a knowledge of X_∞ was unsuitable because we had been following only the first half-life of exchange, for the reason explained in the preceding paragraph. The rate constant, k, was finally computed directly from the rate equation, by plotting the counts per minute against time, and measuring rates as slopes, $\theta = \alpha\, \mathrm{d}X/\mathrm{d}t$, where α is the constant relating counts per minute to the fraction of activity transferred, X. Then,

$$\log_{10}\theta = \log_{10}\alpha + \log_{10}ka - \frac{1}{2{\cdot}303}\left(\frac{k+\kappa}{2} + \frac{ka}{b}\right)t$$

and the plot of $\log_{10}\theta$ against time should be linear, within the validity of the approximation, with slope $= -\dfrac{1}{2{\cdot}303}\left(\dfrac{k+\kappa}{2} + \dfrac{ka}{b}\right)$.

Since the exchange studies had to be carried out at a higher concentration of complex than was used in the spectrophotometric determination of κ, it was necessary to take account of the fact that κ was a function of the initial concentration of complex, as well as that of chloride. As will be seen in section 4, this variation of κ arises from the distribution of the substrate between the free ion and the ion-pair, so that it is possible to calculate κ from the known total concentration of complex and added chloride using an

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[5] R. G. Pearson, P. M. Henry, and F. Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379.
[6] E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

ion-association constant of 250 l. mole^{-1}. Inserting the appropriate values of κ it was possible, as described above, to calculate k. The values are collected in Table 1.

TABLE 1

First-order rate constants for the reaction

cis-$[\text{Co en}_2\text{Cl}_2]^+ + \text{Cl}^{*-} \longrightarrow$ *cis* + *trans*-$[\text{Co en}_2\text{ClCl}^*]^+ + \text{Cl}^-$ in methanol at 35·0°

Initial [Complex] (mmole/l.)	[LiCl] (mmole/l.)	% in form of ion-pair	10^3k (min.$^{-1}$)	Initial [Complex] (mmole/l.)	[LiCl] (mmole/l.)	% in form of ion-pair	10^3k (min.$^{-1}$)
2·0	1·0	15	4·7	2·0	20·0	82	7·0
2·0	2·0	27	4·7	2·0	30·0	88	7·9
2·0	5·0	50	6·2	1·0	40·0	91	8·4
2·0	10·0	68	6·3	1·0	60·0	94	8·0
2·0	15·0	77	6·7				

(4) *Ion-association Equilibria.*—The dependence of the rates of isomerisation and racemisation upon total chloride ion concentration, as shown in Figure 1, is of a similar form to that observed in the replacement of chloride by azide.[2] In calculating ion-association constants, Basolo *et al.* used the Debye–Hückel expression to correct for ionic strength effects, but the data were obtained in a region of ionic strength that is too high for this approximation to be valid It was not possible to provide a source of constant ionic strength that did not interfere, either by precipitating the complex or by participating in the reaction, and so, as a first approximation, we have treated the data for isomerisation on the assumption that the ion-association constant is not significantly affected by changes in ionic strength, within our range.

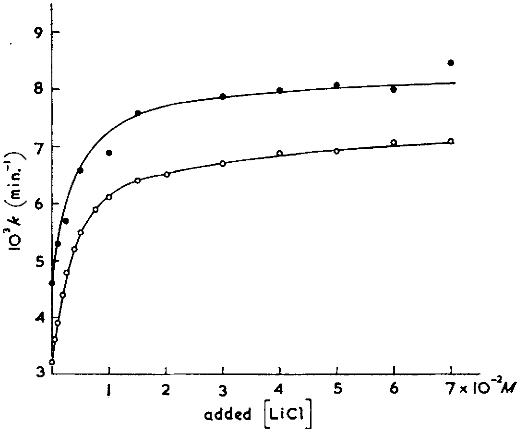

FIGURE 1. First-order rate constants for *cis*- $\longrightarrow$ *trans*-isomerisation, ○, and racemisation, ●, of $(+)_D$ -*cis*-$[\text{Co en}_2\text{Cl}_2]^+$ in methanol at 35·0° as a function of the concentration of added lithium chloride

For an equilibrium of the type

$$\begin{tikzcd}
\underset{\text{"free ion"}}{cis\text{-}[\text{Co en}_2\text{Cl}_2]^+ + \text{Cl}^-} \arrow[r, shift left, "K"] \arrow[d, "\kappa_a"] & \underset{\text{"ion-pair"}}{cis\text{-}[\text{Co en}_2\text{Cl}_2]^+\ldots\text{Cl}^-} \arrow[l, shift left] \arrow[d, "\kappa_b"] \\
trans\text{-}[\text{Co en}_2\text{Cl}_2]^+ + \text{Cl}^- & trans\text{-}[\text{Co en}_2\text{Cl}_2]^+\ldots\text{Cl}^-
\end{tikzcd}$$

we can say that,

$$d[trans]/dt = \kappa_a[\text{free ion}] + \kappa_b[\text{ion-pair}] \qquad (1)$$

and that,

$$\frac{[\text{ion-pair}]}{[\text{free ion}][\text{Cl}^-]} = K \qquad (2)$$

Also we have,

$$[cis\text{-complex}] = [\text{free ion}] + [\text{ion-pair}] \qquad (3)$$
$$= [\text{free ion}] + K\,[\text{free ion}][\text{Cl}^-]$$

Wherefore,

$$[\text{free ion}] = [cis\text{-complex}]/(1 + K[\text{Cl}^-]) \qquad (4)$$

Assuming that sufficient chloride is present to allow the approximation $[\text{Cl}^-] \approx [\text{LiCl}]$, then,

$$\mathrm{d}[trans]/\mathrm{d}t = \kappa_a \frac{[cis\text{-complex}]}{1 + K\,[\text{LiCl}]} + \kappa_b \frac{K\,[cis\text{-complex}][\text{LiCl}]}{1 + K\,[\text{LiCl}]} \qquad (5)$$

Since for any experiment, [LiCl] remains constant, this expression becomes,

$$\mathrm{d}[trans]/\mathrm{d}t = \kappa_{\text{obs}}[cis\text{-complex}]$$

where

$$\kappa_{\text{obs}} = \frac{\kappa_a + K\kappa_b[\text{LiCl}]}{1 + K[\text{LiCl}]} \qquad (6)$$

which can be rearranged to give,

$$\frac{1}{\kappa_{\text{obs}} - \kappa_a} = \frac{1}{(\kappa_b - \kappa_a)K[\text{LiCl}]} - \frac{1}{(\kappa_b - \kappa_a)} \qquad (7)$$

Now κ_a is the value of κ_{obs} extrapolated to [LiCl] = 0, and, on plotting $1/(\kappa_{\text{obs}} - \kappa_a)$ against $1/[\text{LiCl}]$, a straight line should be obtained of slope $1/(\kappa_b - \kappa_a)K$ and intercept $-1/(\kappa_b - \kappa_a)$. The points at low [LiCl] were omitted from this plot because the approximation that $[\text{Cl}^-] = [\text{LiCl}]$ is not valid in this region. The slope and intercept gave the value $K = 270\text{M}^{-1}$, and $\kappa_b - \kappa_a = 4{\cdot}0 \times 10^{-3}$ min.$^{-1}$; and, since $\kappa_a = 3{\cdot}2 \times 10^{-3}$ min.$^{-1}$, it follows that $\kappa_b = 7{\cdot}2 \times 10^{-3}$ min.$^{-1}$. On feeding these rate constants into a point-by-point treatment, which takes into account that part of the chloride of the added lithium chloride held in the complex ion-pair, by using, for the definition of K,

$$K = \frac{\alpha[cis\text{-complex}]}{(1 - \alpha)[cis\text{-complex}]([\text{LiCl}] - \alpha[cis\text{-complex}])} \qquad (8)$$

where

$$\alpha = \frac{\kappa_{\text{obs}} - \kappa_a}{\kappa_b - \kappa_a}$$

it was found that $K = 250 \pm 24\text{M}^{-1}$. This figure was used in all further calculation (cf. section 3).

It is desirable to examine alternative, non-kinetic, evidence for this ion-association, and to compare the values of the association constant. Basolo *et al.*[2] utilised the change in the light absorption at 300 and 310 mμ resulting from ion-association, and obtained a value of 135M^{-1} for K at 25°, for an ionic strength of about 0·02M. The changes in optical density are small compared with the total optical density and the published data admit, without correction for ionic strength effects, values up to 400M^{-1}. In this system, spectrophotometry does not provide sufficient accuracy.

DISCUSSION

The rate constants for geometric isomerisation, racemisation, and chloride exchange are plotted in Figure 2 as a function of the fraction of the *cis*-complex in the form of the ion-pair, assuming an ion-association constant of 250M^{-1}, and ignoring any salt effects. The linear relationship for the relatively accurate isomerisation and racemisation data is in full agreement with the concept of the free ion and the ion-pair having different rate constants for these processes. The rate constants for the chloride exchange fit the same type of behaviour even though the experimental scatter is here much larger. The work of Brown, Ingold, and Nyholm,[1] carried out at high chloride concentration, indicated that the rate constants for racemisation and exchange were identical. It is not possible to claim identity from the data presented in Figure 2, but it is certain that the constants do not differ greatly.

By using the relationships, % *trans*-product = $100\,\kappa/k$, and % *cis*-enantiomer = $50(k_i - \kappa)k$, where k_i is the polarimetric rate constant, it is possible to calculate that the steric course of the chloride substitution in the free ion and the ion-pair lies between the limits shown in Table 2.

TABLE 2

Steric course of chloride exchange in the free ion and the ion-pair of the *cis*-dichlorobis(ethylenediamine)cobalt(III) ion in methanol at 35·0°

Factor	*trans* (%)	$(+)_D$-*cis* (%)	$(-)_D$-*cis* (%)
$[(+)_D\text{-}cis]^+ + Cl^-$	Limits { 84 72	0 14	16 14
$[(+)_D\text{-}cis]^+ \ldots Cl^-$	84	8	8

The difference in the steric course of the free ion and the ion-pair is just outside the limits of experimental error; however, the important observation is, not that the steric courses differ, but that they should be so similar.

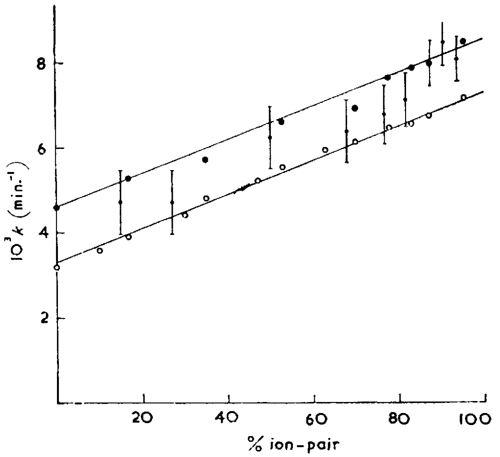

FIGURE 2. First-order rate constants for *cis*- ⟶ *trans*-isomerisation, ○, racemisation, ●, and chloride exchange, I, of $(+)_D$-*cis*-$[Co\ en_2Cl_2]^+$ in methanol at 35·0° as a function of the percentage of the *cis* substrate in the form of the ion-pair. The vertical lines associated with the exchange rate constants represent the limits of experimental error

There is little doubt now that the mechanism of the reaction is unimolecular, *i.e.*, that there is no bonding between the cobalt and the entering chloride in the transition state of the rate-determining step. It is therefore necessary to explain why, if the mechanism is unimolecular in this sense, the observed rate constants for the reaction of the free ion and the ion-pair are different, whereas the steric course of substitution does not alter greatly on going from the free ion to the ion-pair. For this purpose one must distinguish the transition state, where the Co–Cl bond is stretched but not broken, from the five-co-ordinated intermediate, which is the product of this stage of the substitution process. The transition state determines the rate of the reaction and, insofar as it affects the geometry of the intermediate, plays a part in determining the steric course. The intermediate has no effect on rate, but it controls product composition, and therefore the steric course of substitution. It must be realised also that all reactants are to be considered in their immediate environments, *i.e.*, their solvation shells.

The free ion can be looked upon as the octahedral entity with an inner solvation shell containing only solvent molecules, whereas, in the ion-aggregate, the octahedral complex is in association with a chloride ion that presumably occupies a specific position in the inner solvation shell. The difference in the rates of the slow step in the free ion and the ion-pair is, therefore, probably a medium effect, whereby the bond-fission process is affected by the change in the environment. This has been observed in cases of ion-pair assisted solvolytic reactions, where a molecule of solvent, and not the anion, enters the co-ordination shell of the metal.[7] The greater rates given by the ion-pair than by the free complex cation present no obvious problem because it is to be expected that the counter-ion of the

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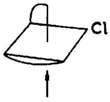
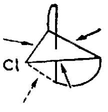
[7] A. W. Adamson and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1954, **76**, 3379.

ion-pair will selectively stabilise the very strongly dipolar transition state of cobalt–chlorine heterolysis.

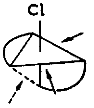
The steric course of the reaction can give us some indication of the lifetime and configuration of the five-co-ordinate intermediate. A square-pyramidal intermediate (I) derived in the simplest way from the octahedron by chloride loss, would have that octahedral position open for recombination, so inviting reagents to enter without steric change; but stero-change predominates; and therefore we conclude that the trigonal-bipyramidal configuration probably is adopted. It is possible to derive two forms from the *cis* isomer, one with the remaining chlorine in the equatorial plane (II), and the other with the chlorine in an axial position (III). Allowing for edge displacement on re-entry (as indicated by the broken arrow) in addition to entry at the edges of the trigonal plane, the entry of chloride into (II) could lead to (+)-*cis*-, (—)-*cis*-, and *trans*-products in unrelated proportions, whilst its entry into (III) should give (+)-*cis*- and (—)-*cis*-products in equivalence, plus an unrelated proportion of *trans*-product. The fact that, in conditions in which, as pointed out below, we believe the intermediate to have had time to settle to its equilibrium configuration, (+)-*cis*- and (—)-*cis*-products do arise in a proportion undetectably different from equivalence, favours the idea of intermediate (III), which requires that result in principle, though it does not exclude intermediate (II), which could give the same result coincidentally to within the experimental uncertainty.*

I


should give (+)-*cis* only.

II


should give (+)-*cis*, plus (—)-*cis*, plus *trans*, all three in unrelated proportions.

III


should give (+)-*cis* equivalent * to (—)-*cis*, plus an unrelated proportion of *trans*.

* Equivalent if there is no memory.

FIGURE 3

It has been suggested that such trigonal-bipyramidal intermediates would always lead to a mixture of *trans*-, (+)-*cis*-, and (—)-*cis*-products, but always under the condition that *cis*- (retained) $\geqslant$ *cis*- (enantiomer).[9] The results in Table 2 indicate that, in the reaction of the free ion, there is possibly an excess of the enantiomer formed. These data can be understood if we take into account the positions most favoured by the counter-ions in the solvation shell of the cation and the extent to which the intermediate has lost the "memory" of its origin.

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* The steric course of aquation of this, and similar *cis*-complexes, where the absence of any racemisation appears to rule out the formation of intermediate (III), has been explained in terms of intermediate (II).[8] The equatorial location of the chlorine was favoured presumably because the interaction between the ligands and the six non-bonding electrons is thereby minimised, one possibility being that four of these electrons are placed in orbitals derived from the d_{xz} and d_{yz} atomic orbitals and the other pair enter one of the two orbitals derived from the d_{xy} and $d_{x^2-y^2}$ pair, the remaining orbital being used for the π bond. However, if this repulsion is ignored, the chlorine can make a more effective π bond when it is in an axial position. In all probability the two forms have similar energies and are both possible.

[8] S. C. Chan and M. L. Tobe, *J.*, 1963, 5700.

[9] Ref. 3*a*, p. 217.

We should expect the intermediate from the ion-pair to lose memory of its origin relatively rapidly. It is formed within a solvation shell containing one counter-ion in mobile equilibrium with a high concentration of ambient counter-ions. A second counter-ion, ejected from the octahedral complex into this solvation shell, will be lost therefrom to the surrounding medium very rapidly. On the other hand, the free octahedral ion ejects a counter-ion into a solvation shell otherwise free from counter-ions, and the newly arrived counter-ion has to come into distribution equilibrium with a much lower concentration of ambient ions. Its loss from the solvation shell will be a substantially irreversible and relatively slow process, because it has to surmount a double sized coulombic energy barrier, before the improved solvation at higher ionic separations takes over control of the energy variation.

While such separation is not more than a few atomic diameters one expects some shielding by the departing counter-ion, that is, we expect the effects described as " memory." In this situation, not only has the solvent shell not fully reached equilibrium composition, but also the interior five-co-ordinate complex has not yet fully settled down to its equilibrium configuration. An excess of attacking chloride will now come in from the remote side of the complex cation. The product of such an attack on intermediate (II) will contain a large excess of *trans*-isomer, particularly since the co-ordinated chloride, bearing an appreciable negative charge, reinforces the repulsion of the departing counter-ion. Similarly, the product of such an attack on intermediate (III) will contain an excess of the *cis* enantiomer. (Note that the substitution is still unimolecular, because the transition state will have been traversed at an earlier degree of separation of the departing chloride ion.) But in the " settled " situation, when " memory " has been lost, and the original counter-ion is far away, attack by chloride is not affected by the departing ion so that intermediate (III) will form racemic *cis*-product.

Thus our results are consistent with the view that, in our solvent, the five-co-ordinate intermediate of the unimolecular mechanism lives long enough to settle down to an equilibrium state of configuration and solvation, when the adjustment of solvation is expected to be fast, and even lives nearly long enough to do so, when the adjustment of solvation is thought to be as slow as we could make it.

EXPERIMENTAL

cis-*Dichlorobis*(*ethylenediamine*)*cobalt*(III) *Tetraphenylborate*.—Prepared by adding sodium tetraphenylborate (4 g.) in water (100 ml.) to *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride (3 g.) in water (300 ml.), the insoluble, fine, pink crystals were induced to grow by adding acetone (5 ml.) drop by drop to the stirred suspension. After standing for ½ hr. the crystals were filtered off, washed with a little water, and dried by suction. The *compound* was twice recrystallised by adding ether to its solution in acetone (yield 5 g.) (Found: C, 58·4; H, 7·3; N, 9·8. $C_{28}H_{36}BCl_2CoN_4$ requires C, 59·1; H, 6·4; N, 9·8%). The visible absorption spectrum of a methanol solution of this complex is identical to that of an analytically pure specimen of the chloride.

$(+)_D$-*cis*-Dichlorobis(ethylenediamine)cobalt(III) perchlorate was prepared from $(+)_D$-*cis*-dichlorobis(ethylenediamine)cobalt(III) (+)-α-bromocamphor-π-sulphonate [10] by adding perchloric acid.

Anhydrous lithium chloride was recrystallised from acetone.

Lithium (^{36}Cl)chloride was prepared by adding (^{36}Cl)hydrochloric acid (17·8 ml. of 2·5N) to a suspension of lithium carbonate (1·65 g.) in water (10 ml.). The solution was evaporated to dryness and the resulting anhydrous salt stored over phosphoric oxide.

AnalaR methanol was dried by refluxing over magnesium methoxide, distilled through a 20 cm. fractionating column, and stored and handled in a dry-box.

Kinetics.—(*a*) *Spectrophotometric*. The required amount of *cis*-dichlorobis(ethylenediamine)cobalt(III) tetraphenylborate was dissolved in methanol together with the required amount of anhydrous lithium chloride. The solutions were made up to the required volume,

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[10] J. C. Bailar and C. L. Rollinson, *Inorg. Synth.*, 1946, **2**, 224.

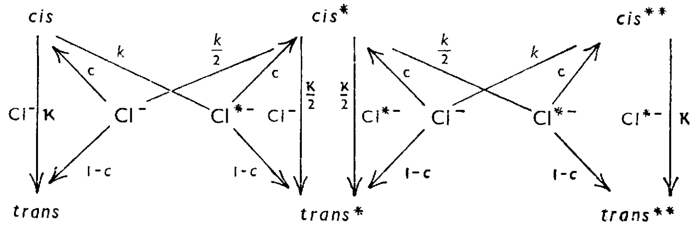
and transferred to a darkened vessel in the thermostat. Samples were withdrawn at appropriate times, and cooled rapidly in acetone–solid CO_2 to stop the reaction. The solutions were then rapidly warmed to room temperature, and the optical densities measured with a Unicam S.P. 500 spectrophotometer.

(*b*) *Polarimetric.* The solutions were prepared as for spectrophotometry, but the complex was provided as the $(+)_D$-*cis*-dichlorobis(ethylenediamine)cobalt(III) perchlorate. The optical rotation of the solutions were measured with an ETL–NPL Automatic Polarimeter, type 143A, using a Na_D filter.

(*c*) *Radiochloride exchange.* The solutions were prepared as for spectrophotometry. Aliquot samples (15·0 ml.) were withdrawn at appropriate times, and the reaction was stopped by cooling. Water (10 ml.) was added to each portion, and the mixture immediately passed down a column of anion exchange resin (Amberlite IRA 400) in the chloride form, contained in a 20 × 2 cm. diameter ice-cooled tube. It was found, in trial samples, that this procedure completely exchanged the radioctive chloride ions with unlabelled chloride from the resin and the activity in the effluent came solely from active chloride within the complex. The effluent and washings were collected to a volume of 50·0 ml. A 10·0 ml. sample of this was transferred to a liquid counter and the activity measured with an EKCO Scalar type N 529 counter.

APPENDIX

The general reaction network for two steps of chloride exchange with concurrent *cis*-→ *trans*-isomerisation of the *cis*-dichlorobis(ethylenediamine)cobalt(III) cation can be represented as follows:



In this network we have ignored the subsequent exchange of the *trans*-isomer, assuming that it is formed irreversibly. This approximation does not affect the data gathered in the earlier stages of the reaction, but it precludes the use of an experimentally determined " infinity " value in any subsequent calculation. The first-order rate constant k for the replacement of co-ordinated chloride by chloride ion is the quantity we wish to calculate, but the rate constant κ for the *cis*- → *trans*-isomerisation is obtained from separate spectrophotometric studies. The proper fraction c is the proportion in which a *cis*-isomer, once substituted, gives a *cis*-isomer; so that the proportion of concurrently formed *trans*-isomer is $1 - c$. The isomerisation rate constant κ is then related to the substitution rate constant by the expression

$$\kappa = k(1 - c) \qquad (1)$$

When the two combined chlorine atoms are non-identical isotopically, the rate constants will involve a statistical factor of $\frac{1}{2}$, as shown. Single and double asterisks represent the transfer of one and two labels of radioactivity, respectively. The two direct conversions *cis** → *trans** are different; one goes by replacement of Cl by Cl, the other by replacement of Cl* by Cl*.

At time $t = 0$, let $[cis] = a$ and $[Cl^{-*}] = b$, and let all other concentrations be zero. At time $t = t$, let $[cis] = u$, $[cis^*] = u^*$, $[cis^{**}] = u^{**}$, $[trans] = v$, $[trans^*] = v^*$, and $[trans^{**}] = v^{**}$. Then

$$u + u^* + u^{**} + v + v^* + v^{**} = a \qquad (2)$$

and taking into account the first-order *cis*- ⟶ *trans*-conversion

$$u + u^* + u^{**} = a\exp(-\kappa t) \tag{3}$$

The extent of label transfer, X, is a function of the above concentrations as follows:

$$u^* + v^* + 2u^{**} + 2v^{**} = X \tag{4}$$

As a result of the assumption that the *trans*-complex is formed irreversibly and is non-exchanging, the only concentrations needed for the equation for dX/dt are u, u^*, and u^{**}, because the starting materials for all the acts of label transfer are all forms of the *cis* isomer. There are therefore four unknown concentrations, u, u^*, u^{**}, and X, and only one relationship between them alone (*viz.* 3), so that, beside the equation in dX/dt itself, two other equations are needed. It is convenient to use equations for du^*/dt and du^{**}/dt.

The equation for the rate of label transfer is

$$\mathrm{d}X/\mathrm{d}t = ku\frac{b-X}{b} + \frac{ku^*}{2}\frac{b-X}{b} - \frac{ku^*}{2}\frac{X}{b} - \mathrm{k}u^{**}\frac{X}{b} \tag{5}$$

which, combined with equation (3), gives,

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{k}{b}\left[a(b-X)\exp(-\kappa t) - \frac{bu^*}{2} - bu^{**}\right] \tag{6}$$

The equation for du^*/dt in terms of the same concentration variables is,

$$\frac{\mathrm{d}u^*}{\mathrm{d}t} = ku\frac{b-X}{b}c + ku^{**}\frac{X}{b}c - \frac{ku^*}{2}\frac{X}{b} - \frac{ku^*}{2}\frac{b-X}{b} - \frac{ku^*}{2}(1-c) \tag{7}$$

which, combined with equation 3 and simplified, becomes,

$$\frac{\mathrm{d}u^*}{\mathrm{d}t} = \frac{k}{b}\left\{ac(b-X)\exp(-\kappa t) - u^*\left[\left(1+\frac{c}{2}\right)b - cX\right] - u^{**}c(b-2X)\right\} \tag{8}$$

The corresponding equation for du^{**}/dt is

$$\begin{aligned}\frac{\mathrm{d}u^{**}}{\mathrm{d}t} &= \frac{ku^*}{2}\frac{b-X}{b}c - ku^{**}\frac{X}{b} - ku^{**}\frac{b-X}{b}(1-c)\\ &= \frac{k}{b}\left\{u^*\frac{c}{2}(b-X) - u^{**}[X + (1-c)(b-X)]\right\}\end{aligned} \tag{9}$$

Let us combine u^* and u^{**} in

$$y = u^* + 2u^{**} \tag{10}$$

where y represents the amount of label acquired by the *cis*-isomer. Equation 6 can immediately be rewritten as

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k\left[a\left(1-\frac{X}{b}\right)\exp(-\kappa t) - \frac{y}{2}\right] \tag{11}$$

and, since $\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{\mathrm{d}u^*}{\mathrm{d}t} + 2\frac{\mathrm{d}u^{**}}{\mathrm{d}t}$, equations (8) and (9) give

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k\left[ac\left(1-\frac{X}{b}\right)\exp(-\kappa t) - \left(1-\frac{c}{2}\right)y\right] \tag{12}$$

The elimination of y between (11) and (12) can be done in the following way: Substituting for y in the last term of (12) by means of (11), we obtain,

$$\frac{\mathrm{d}y}{\mathrm{d}t} = kac\left(1-\frac{X}{b}\right)\exp(-\kappa t) + 2\left(1-\frac{c}{2}\right)\left[\frac{\mathrm{d}X}{\mathrm{d}t} - ka\left(1-\frac{X}{b}\right)\exp(-\kappa t)\right]$$

$$= 2\left(1-\frac{c}{2}\right)\frac{\mathrm{d}X}{\mathrm{d}t} - 2(1-c)ka\left(1-\frac{X}{b}\right)\exp(-\kappa t) \qquad (13)$$

Differentiating (11) and replacing coefficient κ by $(1-c)k$, as in (1), we find,

$$\frac{\mathrm{d}^2X}{\mathrm{d}t^2} = -\frac{ka}{b}\exp(-\kappa t)\frac{\mathrm{d}X}{\mathrm{d}t} - ak^2(1-c)\left(1-\frac{X}{b}\right)\exp(-\kappa t) - \frac{k}{2}\frac{\mathrm{d}y}{\mathrm{d}t} \qquad (14)$$

and replacing $\mathrm{d}y/\mathrm{d}t$ by means of (13) we obtain,

$$\frac{\mathrm{d}^2X}{\mathrm{d}t^2} = -\frac{ka}{b}\exp(-\kappa t)\frac{\mathrm{d}X}{\mathrm{d}t} - ak^2(1-c)\left(1-\frac{X}{b}\right)\exp(-\kappa t) - k\left(1-\frac{c}{2}\right)\frac{\mathrm{d}X}{\mathrm{d}t}$$

$$+ (1-c)k^2a\left(1-\frac{X}{b}\right)\exp(-\kappa t)$$

$$= k\left[-\left(1-\frac{c}{2}\right) - \frac{a}{b}\exp(-\kappa t)\right]\frac{\mathrm{d}X}{\mathrm{d}t} \qquad (15)$$

which is independent of y. This can be integrated by writing $p = \frac{\mathrm{d}X}{\mathrm{d}t}$, so that it becomes

$$\frac{\mathrm{d}p}{\mathrm{d}t} = kp\left[-\left(1-\frac{c}{2}\right) - \frac{a}{b}\exp(-\kappa t)\right] \qquad (16)$$

the integral of which is

$$\ln p = -k\left(1-\frac{c}{2}\right)t + \frac{ka}{\kappa b}\exp(-\kappa t) + \alpha \qquad (17)$$

When $t = 0$ there has been no dilution of the isotopic label, and so the only reactions are with Cl^{*-}, and these lead to label transfer; and consequently at $t = 0$, $p \equiv \frac{\mathrm{d}X}{\mathrm{d}t} = ka$, so that

$$\alpha = \ln ka - \frac{ka}{\kappa b}$$

Inserting this value, and replacing c in accordance with (1), we obtain,

$$p \equiv \frac{\mathrm{d}X}{\mathrm{d}t} = ka\exp\left[-\frac{k+\kappa}{2}t - \frac{ka}{b}(1-\exp\{-\kappa t\})\right] \qquad (18)$$

Further integration in closed form is not possible.

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