

575. *Mechanisms of Octahedral Substitution in Non-Aqueous Solutions. Part II.* Solvolysis and Isomerisation of Dichlorobis(ethylenediamine)cobalt(III) Ions in Anhydrous Dimethyl Sulphoxide.*

By M. L. TOBE and D. W. WATTS.

When *cis*- and *trans*-[Co en₂ Cl₂]ClO₄ are dissolved in anhydrous dimethylsulphoxide (DMSO) containing tetraethylammonium chloride they isomerise and undergo solvolysis. The solvent-complex, [Co en₂ DMSO Cl²⁺]⁺, has been isolated as its nitrate-perchlorate and is probably the *cis*-isomer. At no stage in the reaction could the other isomer be detected. The composition of the solution at equilibrium is dependent upon the concentration of chloride and the change in the ratio of *cis* : *trans* dichloro-complex has been explained in terms of the different ion-association properties of the two isomers. At high chloride concentrations the equilibrium concentration of the solvent-complex becomes independent of [Cl⁻] and this is explained in terms of the formation of the ion-triplet, [Co en₂ DMSO Cl]²⁺ . . . 2Cl⁻. The rates of approach to equilibrium have been studied starting from each of the three complexes and the rate constants for the various reaction steps have been calculated by a series of approximations. The anation of the solvent-complex is virtually independent of the amount of chloride at all but the lowest concentration and gives 55–60% of *cis*-product. The dichloro-complexes undergo solvolysis and direct isomerisation simultaneously, the solvolysis being more important. These results are interpreted in terms of a unimolecular mechanism in which there is competition between the solvent and the chloride ion for the penta-co-ordinated intermediate. The reaction of *cis*- and *trans*-[Co en₂ Cl₂]⁺ in a variety of solvents are discussed in terms of this competition.

In Part I of this series, the isomerisation of *cis*- and *trans*-[Co en₂ Cl₂]⁺ ions in dimethylformamide and dimethylacetamide solutions was reported. It was observed that the position of equilibrium and the rate at which it was reached was dependent upon the concentration of the free chloride ions and this was explained in terms of the different abilities of the *cis*- and *trans*-dichloro-cations to associate with chloride ions. At no stage in the reaction was there any evidence for the presence of solvent containing complexes, although [Co en₂ DMF Cl]²⁺ has since been prepared and characterised.¹ Preliminary observations made on solutions of both *cis*- and *trans*-[Co en₂ Cl₂]⁺ salts in dimethyl sulphoxide indicated that a third species was present in solution and in this paper we describe the characterisation of this species and the study of the equilibria and the kinetics of the system.

(1) *Equilibria*.—When solutions of *cis*(violet)- or *trans*(green)-[Co en₂ Cl₂]ClO₄ in anhydrous dimethyl sulphoxide are warmed, the colour slowly changes to reddish violet. Prolonged heating or exposure to sunlight causes a further change to bright emerald green, and studies of the changes in the visible absorption spectra indicate that two processes are involved, the second of which leads to a reduction of the cobalt(III) to form tetrahedral Co(II) species. This is similar to the behaviour in dimethylformamide except that, provided light is excluded, the second step is too slow to interfere with any study of the first.

The initial changes in the spectra could not be accounted for by a simple *cis* ⇌ *trans* isomerisation and it was obvious by inspection that at least one more light-absorbing species was being formed in solution, probably a solvolysis product. The isolation of a solvent containing complex from the reaction mixture was achieved by heating the *cis*-[Co en₂ Cl₂]ClO₄ with slightly less than an equimolar amount of silver perchlorate in anhydrous dimethyl sulphoxide. When lithium nitrate was added to the filtrate, a

* The Paper by Tobe and Watts, *J.*, 1962, 4614, is considered to be Part I.

¹ Watts, unpublished work.

crystalline complex $[\text{Co en}_2 \text{Me}_2\text{SO Cl}]\text{NO}_3 \text{ClO}_4$ was obtained. The spectrum of this complex, together with those of the *cis*- and *trans*-dichloro-complexes, in dimethyl sulphoxide is given in Fig. 1. It was possible to construct all the spectra measured in the first stage of the reaction by a suitable combination of these three spectra and it was concluded therefore that only one of the isomeric forms of the chloro(dimethyl sulphoxide)-complex was present in the mixture in any significant quantity. The definite assignment of a configuration to this isomer is not possible at this stage. The visible absorption spectrum suggests that it is the *cis*-isomer if one reasons by analogy with the corresponding *cis*-

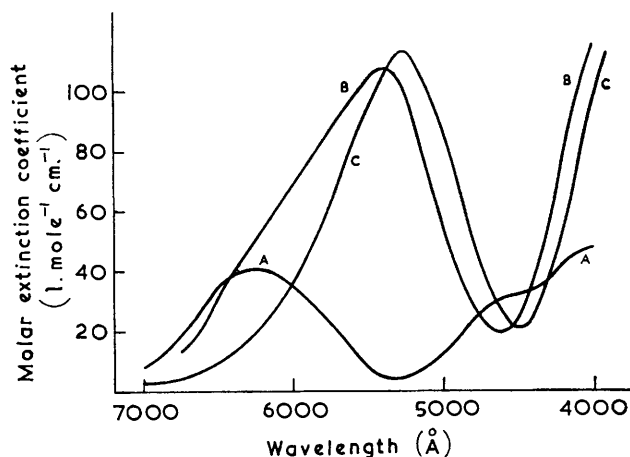
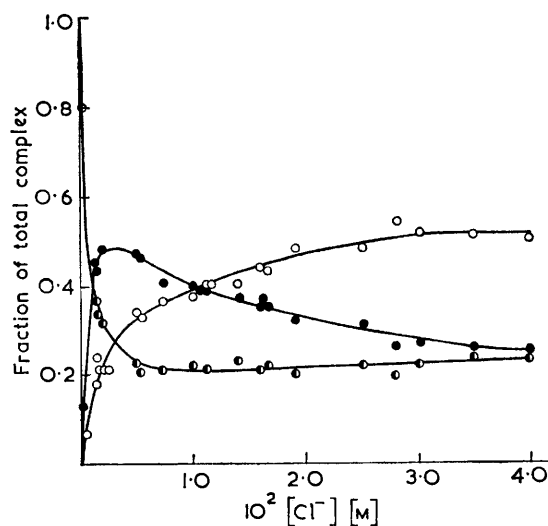


FIG. 1. Visible absorption spectra of

A, *trans*- $[\text{Co en}_2 \text{Cl}_2]\text{ClO}_4$
 B, *cis*- $[\text{Co en}_2 \text{Cl}_2]\text{ClO}_4$.
 C, *cis*- $[\text{Co en}_2 \text{DMSO Cl}]\text{ClO}_4 \text{NO}_3$
 in dimethyl sulphoxide.

FIG. 2. Equilibrium composition of solutions in dimethyl sulphoxide as a function of added $[\text{Et}_4\text{N}]\text{Cl}$ at 60° .

○, *cis*- $[\text{Co en}_2 \text{Cl}_2]^+$.
 ●, *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$.
 ⊙, *cis*- $[\text{Co en}_2 \text{DMSO Cl}]^{2+}$.



and *trans*-chloroaquo-,² and chloro-methanolo-complexes,³ where the *trans*-isomers have a spectrum similar in shape to that of *trans*-dichloro-complex but shifted a little towards shorter wavelengths. Provided that the dimethyl sulphoxide is linked by the oxygen atom and its ligand-field strength does not differ greatly from that of the other oxygen ligands, we might expect a similar relation.⁴ It has not yet been possible to resolve this complex and so the assignment of a *cis*-configuration can be regarded only as tentative.

² Baldwin, Chan, and Tobe, *J.*, 1961, 4637.

³ Bosnich and Tobe, unpublished work.

⁴ Cotton and Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.

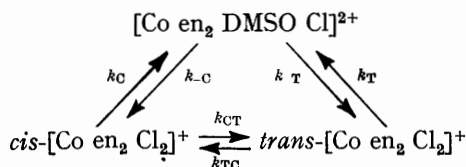
The compositions of the solutions at equilibrium and approaching equilibrium were determined spectrophotometrically from the light absorption data given in Table I.

TABLE I.

Absorption data used for the spectrophotometric analysis: molar extinction coefficients expressed as $l. \text{ mole}^{-1} \text{ cm}^{-1}$.

Wavelength (Å)	6450	6000	5437	5250
<i>cis</i> -[Co en ₂ Cl ₂] ⁺	36.8	68.5	107	98.4
<i>trans</i> -[Co en ₂ Cl ₂] ⁺	36.8	33.8	5.5	4.3
[Co en ₂ DMSO Cl] ²⁺	10.6	33.8	100	112

The compositions of the equilibrium mixtures are given in Fig. 2 as a function of the final chloride concentration. It will be seen in this Figure that the isomeric ratio of the dichloro-complexes is dependent upon the concentration of chloride and also that the amount of chloro(dimethyl sulphoxide) complex does not decrease to zero as the chloride concentration increases, but reaches a minimum and thereafter appears to increase slightly. For a particular chloride concentration, the equilibrium compositions are reproducible whichever of the three complexes is supplied initially.



(2) *Kinetics*.—The rates of approach to equilibrium were studied by the same spectrophotometric technique as was used in the study of the equilibria. A solution was prepared containing known amounts of the complex and tetraethylammonium chloride, samples

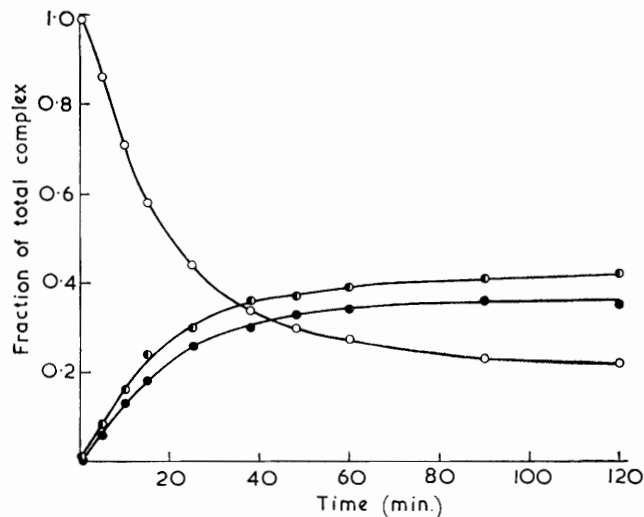


FIG. 3. Change, with time, of the composition of a solution of *cis*-[Co en₂ DMSO Cl]NO₃ ClO₄ ($4.15 \times 10^{-3} \text{ M}$) + [Et₄N]Cl ($1.97 \times 10^{-2} \text{ M}$) in dimethyl sulphoxide at 60°.

- , *cis*-[Co en₂ Cl₂]⁺.
- , *trans*-[Co en₂ Cl₂]⁺.
- , *cis*-[Co en₂ DMSO Cl]²⁺.

were brought to the reaction temperature and then withdrawn at known times and analysed spectrophotometrically. The approach to equilibrium was studied starting from each of the three complexes and the changes of composition with time for three typical experiments are shown in Figs. 3–5. Although the rate laws for such a cyclic process can be completely integrated,⁵ the reactions studied here are not completely of first order and the accuracy of the data from the spectrophotometric analyses is not adequate to fit

⁵ Frost and Pearson, "Kinetics and Mechanism," John Wiley and Sons Inc., New York, 1953, p. 160.

into the equations to obtain the rate constants. It has, however, been possible to obtain some of the rate constants by three approximate treatments. Preliminary observations based on initial slopes indicated that the rates were not markedly dependent upon chloride concentration, furthermore in most of the cases, the chloride-ion concentration was in sufficient excess to produce pseudo-first-order conditions.

(a) The most precise treatment makes use of the observation that, when the starting material was $[\text{Co en}_2 \text{DMSO Cl}]^{2+}$, the ratio of *cis* : *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$ produced during the reaction remains constant at all times during the reaction. If we ignore the direct isomerisation of the dichloro-complexes, *i.e.*, assume that k_{CT} and k_{TC} are zero, the reaction scheme

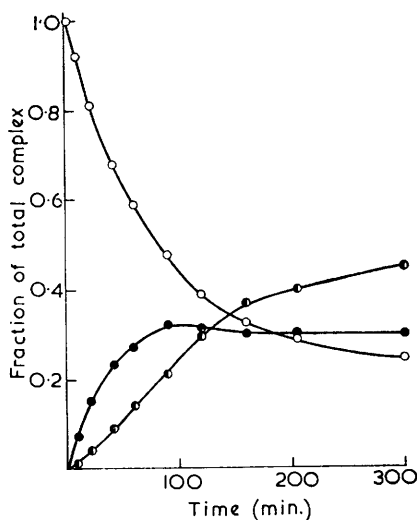


FIG. 4. Change, with time, of the composition of a solution of *cis*- $[\text{Co en}_2 \text{Cl}_2]\text{ClO}_4$ ($4.58 \times 10^{-3}\text{M}$) + $[\text{Et}_4\text{N}]\text{Cl}$ ($1.60 \times 10^{-3}\text{M}$, initially) in dimethyl sulphoxide at 60° .

- , *cis*- $[\text{Co en}_2 \text{Cl}_2]^+$.
- , *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$.
- , *cis*- $[\text{Co en}_2 \text{DMSO Cl}]^{2+}$.

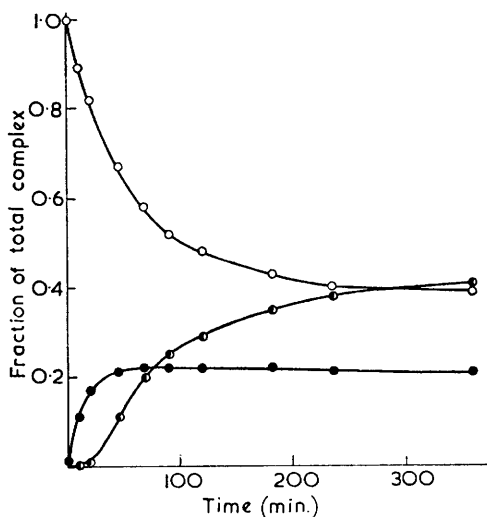


FIG. 5. Change, with time, of the composition of a solution of *trans*- $[\text{Co en}_2 \text{Cl}_2]\text{ClO}_4$ ($4.63 \times 10^{-3}\text{M}$) + $[\text{Et}_4\text{N}]\text{Cl}$ ($1.02 \times 10^{-3}\text{M}$) in dimethyl sulphoxide at 60° .

- , *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$.
- , *cis*- $[\text{Co en}_2 \text{Cl}_2]^+$.
- , *cis*- $[\text{Co en}_2 \text{DMSO Cl}]^{2+}$.

simplifies considerably. It will be shown below that the relative rates are such that this approximation is valid. First-order kinetics being assumed, it is possible to show (see Appendix), that if $\log_{10}(x_\infty - x)$ is plotted against time, t , where $x_\infty = [\textit{cis} + \textit{trans} \text{ dichloro-complex}]$ at equilibrium and x is the concentration at time t , a straight line will be obtained, slope = $-\frac{(k_{-C} + k_{-T})}{2.303} \frac{a}{x_\infty}$ (where $a = \text{initial concentration of complex}$).

The experimental plots curved somewhat towards the end of the reaction, mainly because of the dependence of the rate constant upon $[\text{Cl}^-]$, but this was only serious for the experiment where $[\text{Cl}^-] < [\text{complex}]$ and even there it was not difficult to measure the initial slope. The constants $(k_{-C} + k_{-T})$ are plotted as a function of $[\text{Cl}^-]_{\text{initial}}$ in Fig. 6.

(b) In the experiments starting from pure *cis*- or *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$, k_C and k_T , respectively, were determined from the initial slope of the curve of the concentration of starting dichloro-isomer against time. As the graphical determination of the tangent at $t = 0$ was extremely inaccurate, the following procedure was adopted. The quantity, $k^* = 2.303 \log_{10}(a/x)$ (where all symbols have the same meaning as before) was calculated for each of the points measured up to $t = 120$ mins., and then, by plotting k^* against t ,

the value for k^* at $t = 0$ could be obtained by extrapolation. This is equal to the first-order rate constant for the consumption of the *cis*- or *trans*-dichloro-complex, $k_C + k_{CT}$, and $k_T + k_{TC}$, depending upon which isomer was being studied. These constants are given in Fig. 6 as a function of chloride concentration.

(c) The third approach is, by far, the least accurate of the three and is intended to serve only as an indication of the magnitude of the constants k_{CT} and k_{TC} . The initial rate constant for the formation of $[\text{Co en}_2 \text{ DMSO Cl}]^{2+}$ was computed from the variation of concentration of solvento-complex with time by the method outlined in (b). The extrapolation is considerably more difficult because the values of k^* change very rapidly with time and, in

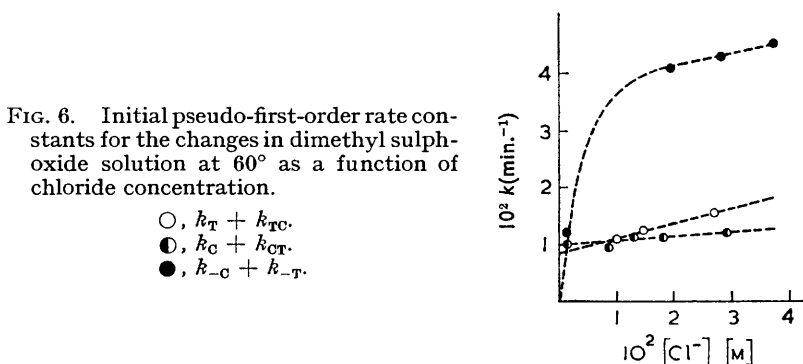


FIG. 6. Initial pseudo-first-order rate constants for the changes in dimethyl sulphoxide solution at 60° as a function of chloride concentration.

○, $k_T + k_{TC}$.
◐, $k_C + k_{CT}$.
●, $k_{-C} + k_{-T}$.

most cases, the amount of solvent-complex formed is never very large. In every case, the constant determined by this method was smaller than that determined from the rate of disappearance of the dichloro-complex in the same run. The constants are compared in Table 2, and the difference is taken to be the rate constant for the direct interconversion

TABLE 2.

Derived rate constants for the solvolysis and isomerisation of *cis*- and *trans*- $[\text{Co en}_2 \text{ Cl}_2]^+$ in dimethyl sulphoxide at 60° .

(a) <i>cis</i> - $[\text{Co en}_2 \text{ Cl}_2]^+$			
$[\text{Cl}^-]_{\text{initial}}$ (mmoles/l.)	$k_C + k_{CT}$ ($\text{min.}^{-1}; \times 10^2$)	k_C ($\text{min.}^{-1}; \times 10^2$)	k_{CT}^* ($\text{min.}^{-1}; \times 10^3$)
1.60	1.01	0.83	2
13.0	1.14	0.8—0.9	2—3
18.2	1.12	0.85	3
29.4	1.25	1.03	2
(b) <i>trans</i> - $[\text{Co en}_2 \text{ Cl}_2]^+$			
$[\text{Cl}^-]_{\text{initial}}$ (mmoles/l.)	$k_T + k_{TC}$ ($\text{min.}^{-1}; \times 10^{-2}$)	k_T ($\text{min.}^{-1}; \times 10^2$)	k_{TC}^* ($\text{min.}^{-1}; \times 10^3$)
10.2	1.17	1.18	—
14.8	1.24	1.01	2
27.3	1.54	1.09	4

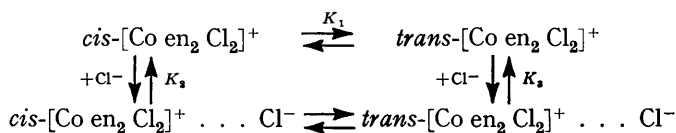
* By difference.

of the dichloro-isomers. This direct interconversion appears, therefore, to make a significant contribution to the overall process studied. The results of this derivation are far too inaccurate for it to be possible to discuss any significant relationship between the rate constant and the concentration of chloride but it does appear that some 20—30% of the reactions of the *cis*-complex go *via* direct isomerisation, whereas the amount of *trans*-complex that undergoes direct isomerisation increases with increasing chloride concentration. It would be of interest to confirm this by a very careful examination of the rate of chloride release.

DISCUSSION

In Part I, the equilibrium, $cis-[Co en_2 Cl_2]^+ \rightleftharpoons trans-[Co en_2 Cl_2]^+$, in dimethylformamide and dimethylacetamide was shown to be dependent upon the chloride-ion concentration. This was explained in terms of ion association and the relevant constants evaluated. The same system in dimethyl sulphoxide is more difficult to evaluate because of the appearance of the solvent containing species. Nevertheless, it is possible to consider this system in two parts, the first involving the $cis \rightleftharpoons trans$ equilibria of the dichloro-complexes and the second involving the solvolytic equilibria. The $cis \rightleftharpoons trans$ equilibrium can be treated as if no solvent-complex was present. The accuracy of the derivation will be less, especially at the low chloride concentrations because, (i) the dichloro-complex forms only a part of the total complex, (ii) the analysis of a three-component system is less accurate than that of one of two components, and (iii) a significant amount of chloride can be "tied up" in ion association with the DMSO complex.

The $cis \rightleftharpoons trans$ equilibrium was split into the following components.

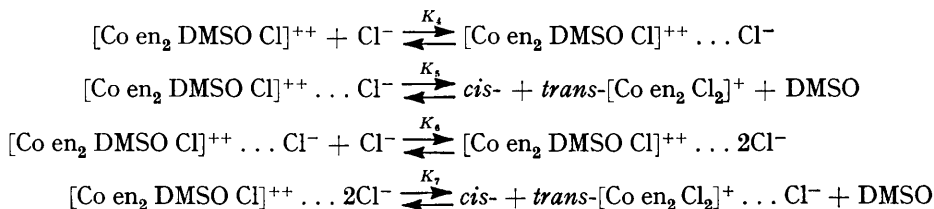


Assuming that $[Cl^-]_{free} \gg [Cl^-]_{associated}$ and using a modified form of the expression derived previously, we obtain

$$\frac{[cis\text{-dichloro-complex}]_{total}}{[trans\text{-dichloro-complex}]_{total}} = X = \frac{1}{K_1} \left\{ \frac{1 + K_2[Cl^-]}{1 + K_3[Cl^-]} \right\}.$$

X , at equilibrium, was plotted against the chloride-ion concentration and the best curve to fit these data was calculated by using the above equation (Fig. 7). The values of the constants are given in Table 3, where they are compared with values for the ion association constants determined in other solvents.

The complete treatment of the solvolytic equilibria is beyond the scope of the available data, since most of the change in the concentration of the dimethyl sulphoxide complex occurs in the region of very low chloride-ion concentration. The complete system can be represented by the three equilibria already given, together with the following:



These seven equilibria are more than adequate to characterise the whole system but it is convenient to make use of them all. If we examine the situation where the ion-triplet of the solvent-complex is unimportant, *i.e.*, K_6 and K_7 are ignored, it is easy to obtain the expression:

$$\frac{[total\ dichloro-complex]_{equil.}}{[total\ DMSO\ complex]_{equil.}} = K_4 K_5 [Cl^-] \left\{ \frac{1 + (K_2 + K_1 K_3)[Cl^-]/(1 + K_1)}{1 + K_4 [Cl^-]} \right\}$$

This function will increase indefinitely with increase in the chloride-ion concentration and is therefore not in accordance with the experimental observations that this ratio reaches a

maximum finite value. If, however, we include K_6 and K_7 in our calculations, it is possible to show, without introducing K_1 , K_2 , and K_3 , that

$$\frac{[\text{total dichloro-complex}]_{\text{equil.}}}{[\text{total DMSO complex}]_{\text{equil.}}} = K_4 K_5 [\text{Cl}^-] \left\{ \frac{1 + (K_6 K_7 / K_5) [\text{Cl}^-]}{1 + K_4 [\text{Cl}^-] + K_4 K_6 [\text{Cl}^-]^2} \right\}$$

This is a function that has a limit, when $[\text{Cl}^-]$ is large, $=K_7$. This result can be deduced by inspection since, at the highest concentrations of chloride, all the complex species will be fully associated with chloride and so the equilibrium will be entirely controlled by K_7 . It can be seen in Fig. 2 that the fraction of total complex in the form of the solvent-complex remains constant over a range of chloride concentration where the *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$ cation is certainly not completely ion-paired and so it is necessary to conclude

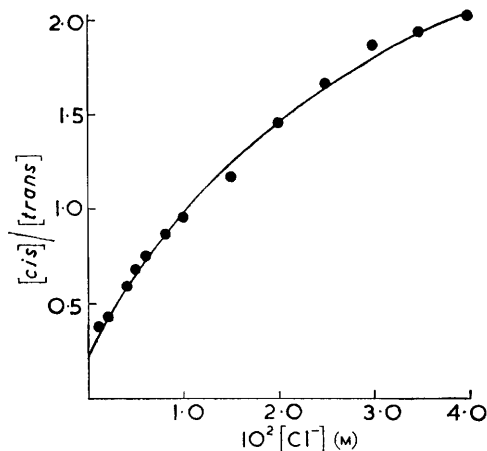


FIG. 7. Variation of the equilibrium ratios of the isomers of $[\text{Co en}_2 \text{Cl}_2]^+$ with chloride concentration in dimethyl sulphoxide at 60° . The curve is calculated by using the derived formula with $K_1 = 4.0$, $K_2 = 400$ l./mole and $K_3 = 27$ l./mole.

that K_5 and K_7 are nearly equal, ~ 4 . Thus, the free-energy changes for the rearrangements of the ion-pair and the ion-triplet of the solvent-species in dimethyl sulphoxide at 60° is not very large, approx. 1 kcal./mole. To use Taube's nomenclature,⁶ the inner sphere complex has a very similar free energy to its outer sphere "isomer," *i.e.*, the one in which the chloride is in the outer sphere and the co-ordination position is occupied by a solvent molecule. These observations are very similar to those of Posey and Taube on the $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} \text{SO}_4^{2-}$ system in aqueous solution.⁶

TABLE 3.

Ion-association constants for *cis*- and *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$ cations with chloride ions.

Solvent	T°	K_1	K_2 (l./mole)	K_3 (l./mole)	Dielectric constant at 25°
Dimethyl sulphoxide.....	60	4.0	400	27	46
Dimethylformamide	60	7	1800	30	37.6 Part I
Dimethylacetamide	60	8	1700	Not measured	38.9 ,, I
Methanol.....	25	$>40^7$	150 * ⁸	Not detectable	33.6

* This constant was determined spectrophotometrically. Unpublished results of Bosnich⁹ indicate a value of 300 for the constant determined from kinetic data and a considerably higher value determined spectrophotometrically.

The kinetic aspects of this investigation are of considerable interest. The lack of a definite first-order dependence upon the concentration of chloride enables us to rule out a classic bimolecular mechanism. The sections where a marked dependence of the rate upon the concentration of chloride is observed can be explained in terms of a pre-equilibrium ion association. The dependence of the rate of anation upon the concentration of

⁶ Taube and Posey, *J. Amer. Chem. Soc.*, 1953, **75**, 1463.

⁷ Brown and Nyholm, *J.*, 1953, 2696.

⁸ Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379.

⁹ Bosnich and Tobe, unpublished work.

chloride when $[Cl^-] < [complex]$ is fully in keeping with the concept of competition between chloride and the solvent for the quinque-co-ordinated intermediate. Since this is also the region where the concentration of the chloride-ion pair of the solvent-complex is very sensitive to the concentration of chloride, it is likely that the chloride ion can only compete effectively with the solvent when it is preassociated with the complex ion. Although the accuracy of the constants k_C and k_T is not sufficient to make it possible to discuss the dependence of rate constant upon chloride-ion concentration, it can be stated that this dependence, if there is any, is not large, but, since, over the range of chloride concentrations studied, most of the *cis*-complex is in the form of the ion-pair, this is not surprising. However, the amount of the *trans*-complex in the form of the ion-pair changes quite considerably over this range of chloride concentration and so the small variation of rate with $[Cl^-]$ indicates that the solvolytic lability of the free ion and the ion pair are similar.

The observation of a path of direct isomerisation is possibly the most important aspect of this work. The accuracy of k_{CT} and k_{TC} is insufficient for them to be used for a detailed discussion of their dependence on $[Cl^-]$, but one might expect, by analogy with the corresponding reaction in dimethylformamide, that k_{CT} is independent of $[Cl^-]$ whereas k_{TC} has an almost linear dependence.

A few deductions can be made concerning the steric course of some of these reactions. The non-appearance of the *trans*- $[Co en_2 DMSO Cl]^{2+}$ isomer may possibly be due to its lability, *i.e.*, it might rearrange rapidly to the *cis*-isomer. Until this *trans*-isomer can be prepared and studied separately it will not be possible to say whether or not solvolysis of the dichloro-complexes yields 100% of *cis*-product. Certainly, in the case of the analogous *trans*- $[Co en_2 H_2O Cl]^{2+}$ and *trans*- $[Co en_2 CH_3OH Cl]^{2+}$ cations, such an isomerisation is known and is sufficiently fast. The steric course of the anation can be determined approximately from the relations: $k_{-C} = k_C [cis\text{-dichloro-complex}]_{\text{equil.}} / [DMSO Cl]_{\text{equil.}}$ and $k_{-T} = k_T [trans\text{-dichloro-complex}]_{\text{equil.}} / [DMSO Cl]_{\text{equil.}}$. Summation of k_{-C} and k_{-T} determined in this way gives values that agree within 15% of those directly determined in the anation. Considering the errors in the determination of k_C and k_T , such an agreement is reasonable. The steric course, expressed as % of *cis*-dichloro-complex produced, $= 100k_{-C} / (k_{-C} + k_{-T})$ and is found to vary from 55 to 60% over the range $1.9 \times 10^{-2} M < [Cl^-] < 3.8 \times 10^{-2} M$.

Finally, it is of interest to compare the behaviour of the dichlorobis(ethylenediamine)-cobalt(III) cations in the range of solvents that have now been studied. These observations are summarised in Table 5.

TABLE 4.

The behaviour of *cis*- and *trans*- $[Co en_2 Cl_2]^+$ ions in the presence of chloride ions.

Solvent	Solvolytic behaviour	Isomerisation behaviour
Liquid ammonia	Very rapid and irreversible solvolysis	None observed. ¹⁰
Water	Solvolysis predominates. Reversible	Isomerisation is observed in concentrated solution. All takes place <i>via</i> a solvolysis-anation process. ¹¹
Dimethyl sulphoxide	Reversible solvolysis is observed	Isomerisation takes place both by direct S_N1 chloride exchange and by solvolysis-anation combination.
Methanol	Only observed at very low $[Cl^-]$ ¹²	Takes place almost entirely by S_N1 chloride exchange.
Dimethylformamide	Not observed	Takes place by S_N1 chloride exchange.
Dimethylacetamide	Not observed	Takes place by S_N1 chloride exchange.

The mechanism of the reaction in liquid ammonia is by no means clear. The reaction is very rapid, even at low temperatures and it is not unlikely that the mechanism differs from that in the other solvents.¹⁰ (Whether it is a bimolecular process or a redox-catalysed

¹⁰ Archer and Bailar, *J. Amer. Chem. Soc.*, 1961, **83**, 812; Werner, *Annalen*, 1912, **386**, 201.

¹¹ Eittle and Johnson, *J.*, 1939, 1490.

¹² Watts and Tobe, unpublished work.

substitution is not yet clear.) All the other reactions reported in Table 4 undoubtedly go by a unimolecular mechanism. The change in the role of the solvent from water to dimethylacetamide arises from its decreasing ability to compete for the quinque-co-ordinated intermediate, $\text{Co en}_2 \text{Cl}^{2+}$. The factors that determine the competitive ability of the solvent are not yet clear. Certainly solvation and ion-association do not provide the complete answer and the donor capacity of the solvent and the orientation of individual molecules around the complex must be taken into account.

EXPERIMENTAL

Preparations.—*trans*-Dichlorobis(ethylenediamine)cobalt(III) perchlorate was prepared by adding dilute perchloric acid to a dilute solution of pure *trans*- $[\text{Co en}_2 \text{Cl}_2]\text{Cl}$ in water. The perchlorate is insoluble in dilute perchloric acid. The green crystals were washed with water, alcohol, and ether, and dried at 110° (Found: co-ordinated Cl, 20.4. $\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Cl}_2\text{ClO}_4$ requires Cl, 20.3%).

cis-Dichlorobis(ethylenediamine)cobalt(III) perchlorate was prepared by the addition of lithium perchlorate to a cold saturated aqueous solution of pure *cis*- $[\text{Co en}_2 \text{Cl}_2]\text{Cl}$. This perchlorate is much more soluble than that of the *trans*-isomer and also aquates more rapidly. The complex was recrystallised from water in the presence of lithium perchlorate, washed with alcohol and ether, and dried at 110° (Found: co-ordinated Cl, 20.4. $\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Cl}_2\text{ClO}_4$ requires Cl, 20.3%).

cis-Chloro(dimethyl sulphoxide)bis(ethylenediamine)cobalt(III) nitrate perchlorate was prepared by dissolving *cis*- $[\text{Co en}_2 \text{Cl}_2]\text{ClO}_4$ (4 g.) and dried silver perchlorate (2.3 g.) in the minimum amount of anhydrous dimethyl sulphoxide. The mixture was heated to 60° for 15 min., cooled, and filtered from the precipitated silver chloride. The filtrate was added to an equal volume of a saturated aqueous solution of lithium nitrate and on scratching the walls of the vessel, purple-red crystals of the complex separated. These were recrystallised by dissolving them in the minimum amount of anhydrous dimethyl sulphoxide and adding the solution to an equal volume of saturated aqueous lithium nitrate. In spite of this treatment, the complex still separated as the nitrate perchlorate. The identity of the mixed salt was confirmed, both by analysis and by its infrared spectrum, which possessed the characteristic bands of NO_3^- and ClO_4^- (Found: C, 16.1; Cl, 7.9; S, 6.9. $\text{C}_6\text{H}_{22}\text{N}_4\text{SOClCo}\cdot\text{NO}_3\cdot\text{ClO}_4$ requires C, 15.9; Cl, 7.8; S, 7.05%).

Dimethyl sulphoxide was dried by fractional distillation at low pressure from anhydrous magnesium perchlorate following an initial azeotropic distillation with benzene.

Tetraethylammonium chloride was recrystallised from the minimum amount of warm water by adding ethanol and ether.

Kinetics and Equilibria.—All complexes, salts, and solvent samples were stored, after being dried, in desiccators and handled in a dry-box. Solutions, prepared in the absence of moisture, were divided into portions and sealed into Pyrex-glass ampoules. These were placed in an oil thermostat, withdrawn at known times and cooled rapidly in ice. The solutions for the equilibrium studies were treated in a similar way and allowed to remain in the thermostat for a period of time sufficient for the attainment of equilibrium. No attempt was made to maintain a constant ionic strength. The region studied was well outside the area within which the Debye-Hückel law was obeyed and the major salt effect that was in operation arose from the process of ion association.

The spectra were measured with a Unicam S.P. 500 spectrophotometer, silica cells being used.

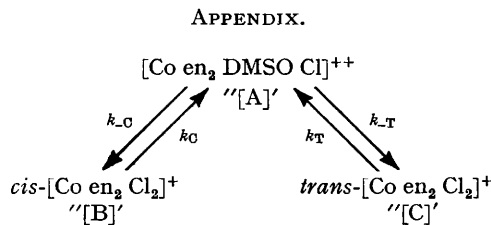
Light was excluded as a routine precaution.

One of us (D. W. W.) acknowledges the award of a D.S.I.R. fellowship.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET, LONDON W.C.1.

[Present address (D. W. W.): UNIVERSITY OF WESTERN AUSTRALIA, NEDLANDS,
WESTERN AUSTRALIA.]

[Received, September 16th, 1963.]

3000 *Octahedral Substitution in Non-Aqueous Solutions. Part II.*

Assuming that the rates are independent of $[\text{Cl}^-]$ we may write,

$$-d[\text{A}]/dt = (k_{-C} + k_{-T})[\text{A}] - k_C[\text{B}] - k_T[\text{C}] \quad (1)$$

At time $t = 0$, $[\text{A}] = a$, $[\text{B}] = [\text{C}] = 0$

At time $t = t$ $[\text{A}] = a - x$, $[\text{B}] + [\text{C}] = x$.

It is observed experimentally that $[\text{B}]/[\text{C}] = \text{constant} = \beta$ at all times during the reaction.

$$[\text{B}] = \beta[\text{C}]$$

and

$$[\text{B}] + [\text{C}] = [\text{C}](1 + \beta) = x;$$

therefore

$$[\text{C}] = x/(1 + \beta) \quad (2)$$

and

$$[\text{B}] = \beta x/(1 + \beta). \quad (3)$$

Substituting equations (2) and (3) into equation (1) we obtain

$$-d(a - x)/dt = (k_{-C} + k_{-T})(a - x) - [k_C\beta/(1 + \beta) + k_T/(1 + \beta)]x. \quad (4)$$

At equilibrium;

$$[\text{A}]_\infty/[\text{B}]_\infty = k_C/k_{-C} \text{ and } [\text{A}]_\infty/[\text{C}]_\infty = k_T/k_{-T} \text{ and } [\text{B}]_\infty/[\text{C}]_\infty = \beta \quad (5)$$

Substituting (5) into (4) we obtain

$$-d(a - x)/dt = (k_{-C} + k_{-T})(a - x) - (k_{-C} + k_{-T}) \frac{[\text{A}]_\infty}{[\text{B}]_\infty + [\text{C}]_\infty},$$

which rearranges to give

$$-d(a - x)/dt = (k_{-C} + k_{-T})(a - ax/x_\infty) \quad (6)$$

Integration gives

$$\log \frac{x_\infty}{x_\infty - x} = (k_{-C} + k_{-T}) at/x_\infty.$$