889. *Isomerisation of Dichlorobisethylenediaminecobalt*(III) *Ions in Anhydrous Dimethylformamide and Dimethylacetamide.*

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The behaviour of solutions of *cis*- and *trans*-[Co en_2Cl_2]ClO_4 in anhydrous dimethylformamide and dimethylacetamide has been studied spectrophotometrically. An equilibrium is established between the two isomers, the position of which depends upon the concentration of free chloride ions in solution. The amount of *cis*-isomer at equilibrium increases with chloride concentration in a way that is consistent with the formation of a strong ion-pair between chloride and the *cis*- and a weak one with the *trans*-isomer. The rates of approach to equilibrium have been measured and some preliminary chloride-exchange rates are recorded.

THE isomerisation of the *cis*-[Co en_2Cl_2]$^+$ cation in methanol solution has been studied in considerable detail.[1] That information has been augmented by chloride-exchange studies on this [2] and the *trans*-isomer [3] and the studies have been extended to ethanol,[4] propanol,[4] and 2-methoxyethanol [5] solutions. In all cases there was no detectable amount of the *cis*-isomer present at equilibrium, and the rates of isomerisation were similar. In an attempt to improve our understanding of the processes involved, and also to find a solvent of considerably lower acidity than methanol in order to study other replacement reactions, the studies were extended to dimethylformamide, dimethylacetamide, and dimethyl sulphoxide solutions. The results obtained in the first two solvents are reported in this paper and the behaviour in the last solvent will be reported later.

Equilibria.—When a solution of *cis*- or *trans*-[Co en_2Cl_2]Cl in dimethylformamide is heated, the colour soon changes from violet or green to greyish-violet and then, at much later times, to a much deeper blue-green. A study of the absorption spectra in the wavelength range 7500—4000 Å and the way in which they change with time indicated that two separate processes were involved, the first being an equilibration, in which the spectra corresponded to mixtures of the *cis*- and *trans*-dichloro-complexes, and the second the appearance of a band at 6700 Å, which increased in intensity and was responsible for the final green colour of the solution. At this stage the spectra corresponded very closely to those obtained by Buffagni and Dunn [6] in their study of the complexes of cobalt(II) and chloride ion in dimethylformamide solution. It is therefore assumed that the second step involves a reduction to cobalt(II) and complete decomposition of the original complex,

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[1] Brown and Nyholm, *J.*, 1953, 2696.
[2] Brown and Ingold, *J.*, 1953, 2680.
[3] Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379.
[4] Brasted and Hirayama, *J. Amer. Chem. Soc.*, 1958, **80**, 788.
[5] Trimble, *J. Amer. Chem. Soc.*, 1954, **76**, 6321.
[6] Buffagni and Dunn, *J.*, 1961, 5105.

but since this interfered with the equilibrium studies only at the lowest chloride concentrations, and then only because of the very high extinction coefficients of the tetrahedral cobalt(II) species at the wavelengths used for the measurements, the process was not investigated further.

The position of equilibrium at any one chloride concentration was obtained from duplicate experiments starting from both pure *cis*- and pure *trans*-isomer. When the chloride concentration was high, the spectra of the solutions at equilibrium could be measured directly and were, for a given concentration of complex and chloride, independent of the side from which equilibrium was approached. At low chloride concentrations, where the subsequent reduction interfered with direct determination of the position of isomeric equilibrium, the approach was studied from both sides until the reduction became noticeable and the position of equilibrium was obtained by interpolation. The accuracy of the determinations at the lowest chloride concentrations studied was therefore not as good as at the higher concentrations. A second criterion of a good estimation of the position of equilibrium was a linear semilogarithmic plot when this value was used as the " infinity " in the kinetic treatment (see below). The results for the equilibria in anhydrous dimethylformamide at 60° are presented in Fig. 1.

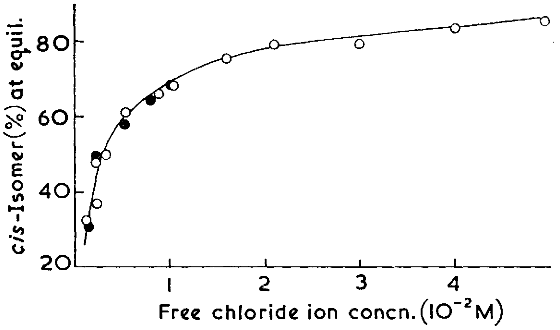


FIG. 1. Isomeric compositions of solutions of $[Co\ en_2Cl_2]^+$ in dimethylformamide at equilibrium at 60° as a function of free chloride ion concentration.

○ Starting from the *trans*-isomer.
● Starting from the *cis*-isomer.

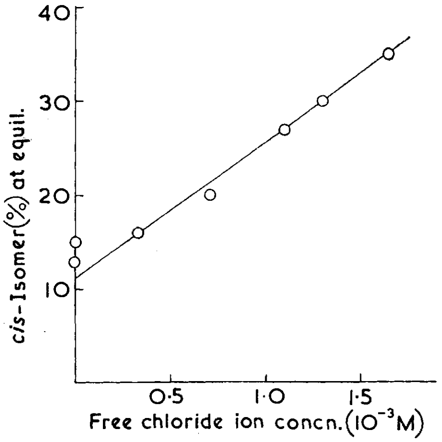


FIG. 2. Isomeric compositions of solutions of $[Co\ en_2Cl_2]^+$ in dimethylacetamide at equilibrium at 60° as a function of free chloride ion concentration.

The studies in dimethylacetamide were complicated by the small solubilities of the chlorides in this solvent. Although it was possible to dissolve considerable quantities of *cis*-$[Co\ en_2Cl_2]Cl$, prepared by dehydrating the monohydrate, in this solvent, most of it crystallised again after a short time. No attempt was made to shed more light on this curious phenomenon. By preparing solutions of the *cis*- and *trans*-dichloro-perchlorates in dimethylacetamide and then adding solutions of a quaternary ammonium chloride, it was possible to study the reactions at low ionic chloride concentration. In spite of the fact that many of these values are obtained from supersaturated solutions, it was not possible to study chloride concentrations greater than 2×10^{-3}M (only one-twentieth of the range covered in dimethylformamide). It was fortunate, however, that the reduction that forms the tetrahedral cobalt(II) complexes is too slow to interfere even when no chloride was present: it is demonstrable, however, when the solutions are kept for a long time at a high temperature or in sunlight. The dependence of the position of equilibrium on the chloride concentration in dimethylacetamide at 60° is shown in Fig. 2.

Kinetics.—Solutions containing the appropriate amount of complex and tetraethylammonium chloride were mixed and allowed to react at 60°, samples were withdrawn at convenient times and chilled, and the spectra were measured over the range 7500—4000 Å. In all cases, until reduction intervened, the spectra were identical with those of solutions containing *cis*- and *trans*-dichloro-complexes as the only light-absorbing species. At no stage, even at the lowest concentrations of added chloride, was there evidence for another species that could be produced by solvolytic replacement of the co-ordinated chlorine. The rate of approach to equilibrium, determined spectrophotometrically at 5375 Å, where the molar extinction coefficients of the pure *cis*- and *trans*-isomers are 104 and 6·0 mole^{-1} cm.$^{-1}$, respectively, was of the first order with respect to complex, and linear semilogarithmic plots were obtained over a minimum of three half-lives. When the position of equilibrium could not be determined directly with accuracy, an acceptable value was chosen such that the semilogarithmic plot was linear and had the same slope irrespective of which isomer was being studied. The constant, k_1, determined from the slope of the plot of $\log_{10}(D_\infty - D_t)$ against time, was equal to the sum of the forward and the backward rate constant for the process,

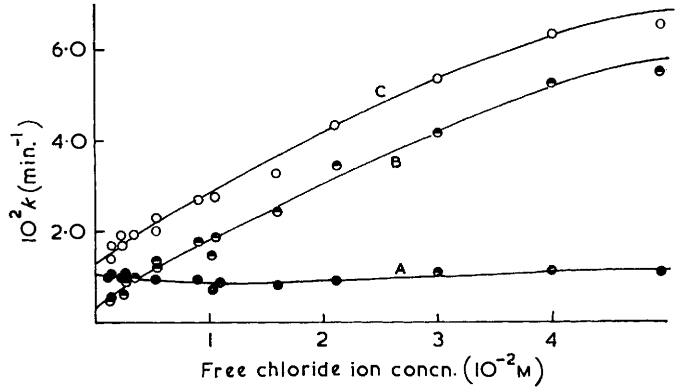


FIG. 3. First-order rate constants for isomerisation of $[Co\ en_2Cl_2]^+$ in dimethylformamide at 60° as a function of free chloride ion concentration.

(A) k_c (*cis* $\longrightarrow$ *trans*).
(B) k_t (*trans* $\longrightarrow$ *cis*).
(C) $k_c + k_t$.

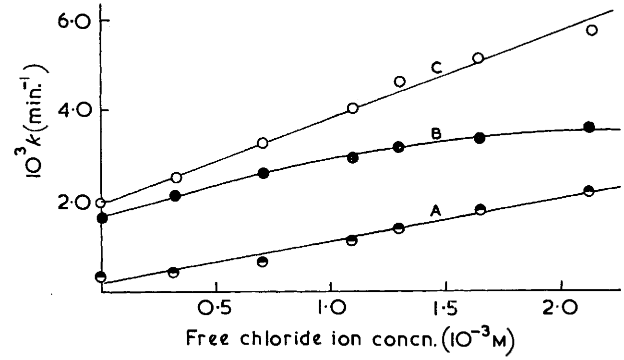


FIG. 4. First-order rate constants for isomerisation of $[Co\ en_2Cl_2]^+$ in dimethylacetamide at 60° as a function of free chloride ion concentration.

(A) k_c (*cis* $\longrightarrow$ *trans*).
(B) k_t (*trans* $\longrightarrow$ *cis*).
(C) $k_c + k_t$.

$$cis\text{-}[Co\ en_2Cl_2]^+ \underset{k_t}{\overset{k_c}{\rightleftharpoons}} trans\text{-}[Co\ en_2Cl_2]^+$$

i.e., $k_1 = k_c + k_t$, and since the rate constants are also related by the expression $k_c/k_t = [trans]/[cis]$ (at equilibrium), both partial constants could be evaluated. (D_∞ and D_t are the optical densities of the solution at equilibrium and time, t, respectively.)

The dependence of the constants k_1, k_c, and k_t on the free chloride-ion concentrations are shown in Fig. 3 for dimethylformamide and in Fig. 4 for dimethylacetamide. Again, the results for the latter cover the low chloride region which could not be studied accurately with the former, but do not cover the higher chloride region because of low solubility.

Exchange Studies with Labelled Chloride.—An isomerisation is generally the result of a chemical process that has caused a change in the configuration of the complex. Although it is easy to measure rates of isomerisation, it is dangerous to interpret them without some idea of the chemical processes that cause them. From analogy with the methanol system it seemed likely that the isomerisation was the result of chloride exchange and some exchange experiments were carried out to test this. The tracer was supplied as $Et_4N^+\,{}^{36}Cl^-$, and the appearance of the radioactivity in the complex cation was measured. Measurements were made on solutions originally containing pure *cis*- and pure *trans*-isomer severally but the calculation of rate constants is complicated by the presence of two equivalent chlorine atoms and the simultaneous isomerisation. An attempt was made to determine the exchange rate for the pure isomers by extrapolating the observed rate constants to zero time. The results are collected in the Table.

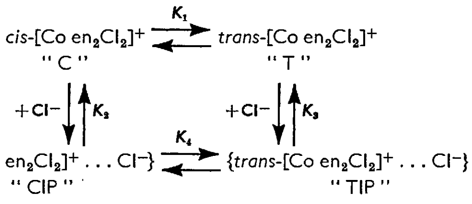
TABLE

Rate constants for chloride exchange in *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) ions in dimethylformamide at 60°.

	[Complex]	[Et_4NCl]	*cis* (%) at equil.	k_{ex} (min.$^{-1}$)	k_c/k_{ex}	k_t/k_{ex}
cis	$2{\cdot}30 \times 10^{-3}$	$5{\cdot}61 \times 10^{-3}$	60	0·0127	0·70	—
trans	$2{\cdot}30 \times 10^{-3}$	$5{\cdot}91 \times 10^{-3}$	61	0·0129	—	1·0

Discussion.—The observation that an increase in the concentration of chloride leads to a stabilisation of *cis*-$[Co\,en_2Cl_2]^+$ with respect to the *trans*-isomer can readily be explained in terms of ion association. Pearson, Henry, and Basolo [7] demonstrated such an association between the *cis*-dichloro-complex and chloride ions in methanol and calculated the association constant. They were unable to show any association between the *trans*-isomer and chloride ions.

The equilibria present in the studied solutions can be represented as:



Of the four equilibria represented, any three are independent and determine the properties of the fourth.

By using the abbreviated forms for the concentrations of the various species as detailed above the following expressions can be written:

$$[T]/[C] = K_1; \tag{1}$$

$$[CIP]/[C][Cl^-] = K_2; \tag{2}$$

$$[TIP]/[T][Cl^-] = K_3; \tag{3}$$

$$[T] + [C] + [TIP] + [CIP] = [\text{Total complex}]. \tag{4}$$

Substitution of (1), (2), and (3) in (4) gives

$$[T] + [T]/K_1 + K_3[T][Cl^-] + K_2[T][Cl^-]/K_1 = [\text{Total complex}]. \tag{5}$$

Then

$$[T] = \frac{[\text{Total complex}]}{1 + 1/K_1 + K_3[Cl^-] + K_2[Cl^-]/K_1}. \tag{6}$$

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[7] Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5382.

$$\text{Total } trans \text{ species} = [\text{T}] + [\text{TIP}] = \frac{[\text{Total complex}](1 + K_3[\text{Cl}^-])}{1 + 1/K_1 + K_3[\text{Cl}^-] + K_2[\text{Cl}^-]/K_1}; \tag{7}$$

or, on simplification,

$$\frac{[\text{Total complex}]}{[\text{Total } trans\text{-complex}]} = \frac{1}{x} = 1 + \frac{1}{K_1}\left\{\frac{1 + K_2[\text{Cl}^-]}{1 + K_3[\text{Cl}^-]}\right\}. \tag{8}$$

In the spectrophotometric analyses it was not possible to distinguish between the free ion and the ion-pair, since they have identical spectra in the range studied. By plotting the reciprocal of the fraction ($1/x$) of the complex in the *trans*-form against chloride concentration (Fig. 5) it is possible to evaluate K_1, K_2, and K_3, as follows. Since the intercept for $[\text{Cl}^-] = 0$ is equal to $1 + 1/K_1$ and does not appear to be very much greater than 1, and since the extrapolation is not very reliable, it is only possible to set limits for K_1, namely, $1 < (1 + 1/K_1) < 1{\cdot}15$, *i.e.*, $K_1 > 7$. By taking a tangent to the curve at zero chloride concentration it is possible to estimate a value for K_2 since the slope is equal to K_2/K_1 and is found to be 251 moles/l. However, K_2 cannot be determined with any greater accuracy than K_1. Also, K_3 can be obtained readily from expression (8) by substituting values for K_1 and K_2. If this is done at fairly high chloride concentrations the value is not greatly affected by inaccuracies in the value for K_1, as can be seeen if equation (8) is rewritten in the form:

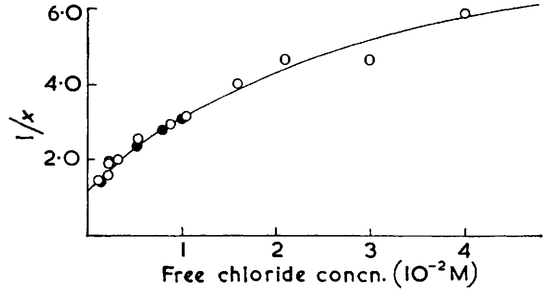


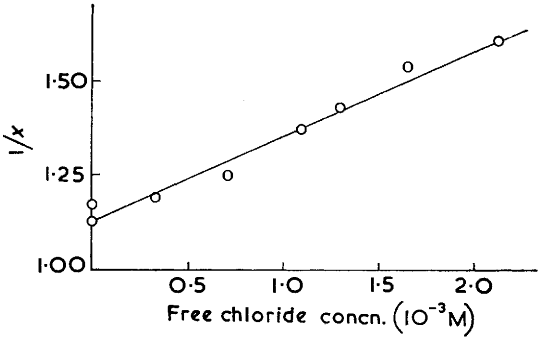
FIG. 5. Equilibria of *cis*- and *trans*-$[\text{Co en}_2\text{Cl}_2]^+$ in dimethylformamide at 60°.

$1/x$ plotted as a function of chloride concentration. The curve is calculated for $K_1 = 7$, $K_2 = 1{\cdot}8 \times 10^3$ mole^{-1}, $K_3 = 30$ mole^{-1}.

○ Starting from the *trans*-isomer.
● Starting from the *cis*-isomer.

FIG. 6. Equilibria of *cis*- and *trans*-$[\text{Co en}_2\text{Cl}_2]^+$ in dimethylacetamide at 60°.

$1/x$ plotted as a function of chloride concentration. The line indicates that $K_1 = 8$ and $K_2 = 1{\cdot}7 \times 10^3$ mole^{-1}.



$$K_3 = \frac{1}{K_1\left(\frac{1}{x} - 1\right)[\text{Cl}^-]} + \frac{1}{\frac{K_2}{K_1}\left(\frac{1}{x} - 1\right)} - \frac{1}{[\text{Cl}^-]}.$$

At high $[\text{Cl}^-]$ the first term, which is the only one involving K_1 alone, is small. By using K_2/K_1, $[\text{Cl}^-]$, and x as measured quantities it is possible to show, at relatively low chloride concentrations that $K_1 < 10$. The best fit to the experimental data is given by the values, $K_1 = 7$, $K_2 = 1{\cdot}8 \times 10^3$ mole^{-1}, and $K_3 = 30$ mole^{-1}, and the curve in Fig. 5 is calculated from these values.

The results obtained in dimethylacetamide solutions do not present these problems. $1/x$ is plotted against [Cl$^-$] in Fig. 6 and the extrapolation is easy. It was not possible, however, to obtain results at chloride concentrations high enough for the departure from linearity, which was a measure of K_3, to be significant. It was only possible to draw a straight line through the points, from which it could be calculated that $K_1 = 8$ and $K_2 = 1{\cdot}7 \times 10^3$ mole^{-1}.

The rate constants for the isomerisation could also be treated in terms of ion association. The analysis of the specific rate constants for approach to equilibrium in Fig. 3 indicates that the constant for the *cis* ⟶ *trans* change, k_c, hardly changes over the whole range of chloride concentration whereas that for the *trans* ⟶ *cis* change, k_t, is very sensitive to chloride concentration. This is not surprising, since, even at the lowest concentration studied ($1{\cdot}5 \times 10^{-3}$M), 70% of the *cis*-complex is in the form of the ion-pair, at 5×10^{-3}M this increases to 90%, and at 10^{-2}M-[Cl$^-$] the figure is 94%. Nevertheless, the observations at low chloride concentration indicate that the rate of exchange of the free *cis*-ion does not differ greatly from that of the ion-pair, for which it is estimated that $k_c \approx 8 \times 10^{-3}$ min.$^{-1}$. In dimethylacetamide it is found that k_c for the free *cis*-ion is $1{\cdot}7 \times 10^{-3}$ min.$^{-1}$, and for the ion-pair it is $4{\cdot}1 \times 10^{-3}$ min.$^{-1}$. In the case of the *trans*-isomer in dimethylformamide, the dependence of the rate constant, k_t, on chloride concentration completely parallels the formation of the ion-pair and it can be estimated that k_t for the free *trans*-ion is 3×10^{-3} min.$^{-1}$, whereas that for the ion-pair is $9{\cdot}3 \times 10^{-2}$ min.$^{-1}$.

We are therefore left with the observation that, whereas the isomerisation rate constant of the *cis*-[Co en$_2$Cl$_2$]$^+$ cation does not change much when it is converted into the chloride ion-pair, the *trans*-ion-pair isomerises some 30 times faster than the free ion. The exchange experiments, although preliminary and confined to a single chloride concentration, tell us that the difference for the *trans*-isomer is due to a considerable increase in the lability of the co-ordinated chlorine when the ion-pair is formed and not to a change in the steric course. At the pertinent chloride concentration ($5{\cdot}9 \times 10^{-3}$M) only 15% of the *trans*-isomer is in the form of the ion-pair. The rate constant for chloride exchange is, nevertheless, equal to the isomerisation rate constant, indicating that nearly every exchange produces steric change. Since an explanation of the different isomerisation rates in terms of different steric course for the free ion and the ion-pair would require that the former exchanged its chlorine with almost complete retention of configuration while the latter exchanged with considerable steric change, it can be ruled out, and one is forced to conclude that the act of ion-pairing increases considerably the lability of the co-ordinated chlorine in *trans*-[Co en$_2$Cl$_2$]$^+$. It is not yet clear why this is not also so in the case of the *cis*-isomer and it is hoped that further work will shed more light on this intriguing problem.

EXPERIMENTAL

cis- and *trans*-Dichlorobisethylenediaminecobalt(III) chloride were prepared and purified by standard methods.[8] [Found for *trans*-isomer: Co, 20·7; Cl, 37·4. For *cis*-isomer: Co, 20·6; Cl, 37·2. Calc. for $Co(C_2H_8N_2)_2Cl_3$: Co, 20·6; Cl, 37·2%].

The perchlorates were prepared by adding lithium perchlorate to solutions of the chlorides. The *trans*-isomer {Found: Cl, 20·4. Calc. for $[Co(C_2H_8N_2)Cl_2]ClO_4$: Cl, 20·2%} is almost insoluble in water. The *cis*-isomer is much more soluble and it is necessary to add a large quantity of solid lithium perchlorate to a saturated solution of the chloride. In order to obtain a pure sample, it was necessary to repeat this precipitation twice more (Found: *cis*-isomer, Cl, 20·4%).

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

Dimethylformamide and dimethylacetamide were purified by the method outlined by Buffagni and Dunn.[6]

Kinetics.—Solutions containing appropriate amounts of the dichloro-perchlorate (or

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[8] Bailar and Rollinson, *Inorg. Synth.*, 1946, **2**, 222.

chloride) and tetraethylammonium chloride were mixed and aliquot portions sealed into Pyrex tubes in the absence of moisture. The tubes were placed in a thermostat-bath at 60° and withdrawn and chilled at the required times. For the isomerisation and equilibrium studies, the contents of the tubes were emptied into a silica spectrophotometer cell and examined in a Unicam S.P. 500 quartz spectrophotometer. For the radiochloride exchange experiments, the unlabelled complex was provided as the perchlorate and the tetraethylammonium chloride was labelled with ^{36}Cl. The reactions were initiated and stopped in the same way as before. The contents of the tube were diluted with an equal amount of water and passed down an ice-jacketed Amberlite IRA-400 anion-exchange column in the chloride form. In this way the labelled anionic chloride exchanged completely with the great excess of unlabelled chloride on the resin, and the resulting dilution was such that all the activity present in the effluent came from the chloride within the complex cation. This technique was found to be far more efficient than that involving replacement of the chloride by another anion, *e.g.*, perchlorate, but the radiochloride could not be recovered for further use. The activity was measured with a liquid counter, and the rate of exchange was calculated from the rate of appearance of chloride in the complex cation. The data were treated by Harris's method [9] for more than one type of exchanging species in solution.

All reactions were carried out in the absence of light as a routine precaution.

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

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[*Received, May 4th,* 1962.]

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[9] Harris, *Trans. Faraday Soc.*, 1951, **47**, 716.