The spectra calculated for the *trans*-chloro(solvent) complexes assuming 17% *trans* product compare favorably with the spectra of *trans* complexes with ligands of similar strength. Spectra calculated on product ratios greatly different from this yield unreasonable spectra for the *trans* complex.

It seems unlikely that the reaction of *cis*-[CoCl(DMA)(en)$_2$]$^{2+}$ in DMF, which gives anomalous activation parameters, has an SN2 mechanism as this would involve a large decrease in entropy in the formation of the transition state, and thus $\Delta S^{\ne}$ would be negative. We feel sure it has a similar mechanism to the other reactions, but we cannot explain the parameters.

By comparing parameters for the reactions of a series of similar complexes in one solvent, as was done in the discussion of the activation parameters for the aquation of the *cis*-solvent complexes, it is established that the strengths of the metal–ligand bond are in the order DMSO > DMF > DMA. Since activation parameters could not be determined for the reaction of the *cis*-chloroaquo complexes, the position of H_2O in this series could not be established.

Little can be gained from a comparison of the few results obtained for *trans* complexes, as these have nothing in common. The results for substitution into *trans*-[CoCl(H$_2$O)(en)$_2$]$^{2+}$ are complicated by chloride entry in all solvents except DMSO.

In view of the weakness of water as a ligand,[6] coupled with the high rate of exchange of *cis*-[Co(NO$_2$)(DMSO)(en)$_2$]$^{2+}$ (see below), it seems possible that solvent interchange may also be significant in some recently published anation reactions[15] where direct anation has been considered as the sole mechanism of reaction in solvents quite likely to coordinate.

A comparison of the rates of exchange of DMSO as a function of the other monodentate ligand and the comparison of these results with those on aquation of the monochloro complexes of the type [CoClA(en)$_2$]$^+$ is rewarding.[16] It can be seen that for Cl$^-$, Br$^-$, or DMSO as the unreplaced ligand (A) the rate of DMSO exchange is not greatly different, but with NO$_2^-$ the rate of DMSO exchange increases more than tenfold. This is interpreted[5] as a result of a change in mechanism, the electron-withdrawing nitro group facilitating an SN2 mechanism and inhibiting an SN1 mechanism.

The rate of exchange of DMSO by the *cis*-[CoCl(DMSO)(en)$_2$]$^{2+}$ ion appears to be uninfluenced by ion association, as indicated by using the bromide salt.

[15] M. N. Hughes and M. L. Tobe, *J. Chem. Soc.*, 1204 (1965).
[16] S. Asperger and C. R. Ingold, *ibid.*, 2862 (1956).

Octahedral Cobalt(III) Complexes in Dipolar Aprotic Solvents. X. The Isomerization of *cis*- and *trans*-Dichlorobis(ethylenediamine)cobalt(III) Ions, [CoCl$_2$(en)$_2$]$^+$, in Anhydrous Sulfolane

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Abstract: The isomerization of *cis*- and *trans*-[CoCl$_2$(en)$_2$]$^+$ ions has been studied in sulfolane (tetramethylene sulfone). No evidence has been found for solvent-containing complexes. The mechanism of isomerization for both species is interpreted as SN1, the rates being influenced by ion pairing. Activation parameters have been obtained for the isomerization reactions commencing from both *cis* and *trans* isomers, and in addition the equilibrium constants and the standard-state enthalpy and entropy changes for this isomerization and for the formation of the ion pair of the *cis*-[CoCl$_2$(en)$_2$]$^+$ ion with chloride ion have been measured. An energy-profile diagram for the system is presented, and correlation of the thermodynamic and kinetic results is discussed.

This work is a continuation of the work of this group[1-9] and Tobe and Watts[10,11] on reactions of octahedral cobalt(III) complexes in dipolar aprotic solvents.

Previous studies of equilibria of the type

$$cis\text{-}[CoX_2(en)_2]^+ = trans\text{-}[CoX_2(en)_2]^+$$

where "en" represents ethylenediamine and "X," a halide ion, in various solvents have been complicated by a number of factors. In dimethyl sulfoxide[11] and dimethylformamide[4,5] the solvent (SOL) containing species [CoX(SOL)(en)$_2$]$^{2+}$ is an appreciable part of the equilibrium mixture. In the case of the [CoCl$_2$(en)$_2$]$^+$ species in dimethylacetamide,[12] where no significant amounts of solvent-containing species are formed,

[1] L. F. Chin, W. A. Millen, and D. W. Watts, *Australian J. Chem.*, **18**, 453 (1965).
[2] W. A. Millen and D. W. Watts, *ibid.*, **19**, 43 (1966).
[3] W. A. Millen and D. W. Watts, *ibid.*, **19**, 51 (1966).
[4] W. R. Fitzgerald and D. W. Watts, *ibid.*, **19**, 935 (1966).
[5] I. R. Lantzke and D. W. Watts, *ibid.*, **19**, 949 (1966).
[6] I. R. Lantzke and D. W. Watts, *ibid.*, **19**, 969 (1966).
[7] W. R. Fitzgerald and D. W. Watts, *ibid.*, **19**, 1411 (1966).
[8] I. R. Lantzke and D. W. Watts, submitted for publication.
[9] I. R. Lantzke and D. W. Watts, submitted for publication.
[10] M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 4616 (1962).
[11] M. L. Tobe and D. W. Watts, *ibid.*, 2991 (1964).
[12] I. R. Lantzke, unpublished results.

subsequent reduction reactions make equilibrium measurements inaccurate.[10,12]

Equilibria involving the $[\mathrm{CoCl_2(en)_2}]^+$ species in methanol[13] are not complicated by the presence of methanol-containing complexes. However, in methanol, the *cis*-$[\mathrm{CoCl_2(en)_2}]^+$ is not a significant part of the system at equilibrium, and thus equilibrium studies are not practicable. In dipolar aprotic solvents, the *cis* ion is stabilized by ion-pair formation and by solvation of the dipolar *cis* isomer by the dipolar solvent.[11] In the protic solvent methanol, anions are more strongly solvated owing to hydrogen bonding,[14] so that ion pairing is less. [*E.g.*, the ion association constant for the *cis*-$[\mathrm{CoCl_2(en)_2}]^+\cdots\mathrm{Cl}^-$ ion pair in methanol (dielectric constant = 33.2[14]) is 135[13] at 25° and in dimethylformamide (dielectric constant = 37.6[14]) is 5500 at 25°.[2] The present results in sulfolane (dielectric constant = 44[14]) extrapolate to a value of 53,000 at 25°.]

In the $[\mathrm{CoCl_2(en)_2}]^+$ system in sulfolane, no detectable amounts of solvent-containing complex are formed, and the ratio in concentration of the *cis* and *trans* ions is always measurable and varies considerably with chloride ion concentration. There is no evidence of subsequent reactions, such as reduction, in the time required to establish the isomerization equilibrium. For these reasons this system is an ideal model for the study of isomerization kinetics and equilibria.

Experimental Section

(a) **Preparation of Compounds and Purification of Solvents.** The *cis*- and *trans*-$[\mathrm{CoCl_2(en)_2}]\mathrm{Cl}$ were from batches used previously[5] and were recrystallized as the perchlorates.

Anal. Calcd for *cis*-$[\mathrm{CoCl_2(en)_2}]\mathrm{ClO_4}$: complexed Cl, 20.29. Found: complexed Cl, 20.23. Calcd for *trans*-$[\mathrm{CoCl_2(en)_2}]\mathrm{ClO_4}$: complexed Cl, 20.29. Found: complexed Cl, 20.31.

Tetraethylammonium chloride was recrystallized from hot dimethylacetamide, washed with acetone and ether, and dried under vacuum for 6 hr at room temperature.

Sulfolane was purified and dried by shaking with 4-A molecular sieves and allowing the mixture to stand with the sieves overnight at 30°. The solvent was then distilled under reduced pressure through a fractionating column, the middle 70% being collected. With very impure batches a second distillation was required.

Several attempts were made to prepare sulfolane-containing complexes by methods previously used for the preparation of the analogous compounds containing dipolar aprotic solvents,[1,4,5,7-9] but as yet no compounds have been isolated.

(b) **Kinetic Technique.** The rates of isomerization were studied using the wavelength 5420 A. At this wavelength, the molar extinction coefficient of the *cis*-$[\mathrm{CoCl_2(en)_2}]^+$ ion is 102.5 and of the *trans*-$[\mathrm{CoCl_2(en)_2}]^+$ ion is 7.3. To check if a third component was present at any stage, measurements were also made at the isosbestic point in the spectra of the *cis*- and the *trans*-$[\mathrm{CoCl_2(en)_2}]^+$ ions at 4700 A at which the extinction coefficient is 29.0.

For runs starting with *cis*-$[\mathrm{CoCl_2(en)_2}]^+$, samples were withdrawn at known times, frozen rapidly, and, when convenient, thawed: their spectra were measured on an Optica 220 double-beam automatic spectrophotometer thermostated at 30°. During sampling, the reaction vessel was flushed with solvent-saturated dry nitrogen in order to exclude moisture.

With reactions of *trans*-$[\mathrm{CoCl_2(en)_2}]^+$ the complex precipitated as the chloride salt when samples were cooled. Thus these reactions were studied in an absorption cell thermostated in the spectrophotometer. Even at 80°, the temperature fluctuation was no more than ±0.1°.

(c) **Technique for Obtaining Ion-Pair Association Constants.** The method used was similar to that described by Millen and Watts.[2] However, as sulfolane cannot be accurately dispensed volumetrically at room temperature, the stock solutions of anion and complex were added by weight. The density of sulfolane (1.2623[15]) was then used to find volume concentrations.

Spectrophotometric measurements were made using a Unicam SP 500 spectrophotometer fitted with a thermostated cell compartment. Measurements were made at 3150 and 3400 A. The *cis*-$[\mathrm{CoCl_2(en)_2}]^+$ ion is convenient for this study in sulfolane because the spectra of the *cis*-$[\mathrm{CoCl_2(en)_2}]^+$ ion and the *cis*-$[\mathrm{CoCl_2(en)_2}]^+\cdots\mathrm{Cl}^-$ ion pair have an isosbestic point at 3400 A, and the spectrum of the *cis*-$[\mathrm{CoCl_2(en)_2}]^+$ ion is flat around 3150 A. The extinction coefficients of the free ion and the ion pair at 3150 and 3400 A at the three temperatures used (30.2, 40.2, and 49.8°) are recorded in Table I.

Table I. Ion-Pair Association Constants for the *cis*-$[\mathrm{CoCl_2(en)_2}]^+$ Ion and Chloride Ion in Sulfolane

Temp, °C	ϵ_{CIP} (315 mμ)	ϵ_{c} (315 mμ)	$\epsilon_{\mathrm{CIP}} = \epsilon_{\mathrm{c}}$ (340 mμ)	K_2, l. mole^{-1}
30.2	1282	787	616	42,000 ± 800
40.2	1316	795	623	29,000 ± 600
49.8	1348	804	628	21,000 ± 400

Results and Discussion

Reproducible equilibria are found in the reactions of both *cis*- and *trans*-$[\mathrm{CoCl_2(en)_2}]^+$ in sulfolane, the positions of equilibrium being independent of the starting material. Because the *trans* isomer was studied over a greater range of chloride ion concentration, the equilibrium results presented are those using *trans*-$[\mathrm{CoCl_2(en)_2}]^+$ as starting material.

Figure 1 shows the variation with chloride ion concentration of the position of this equilibrium at 70°. The results are similar to those obtained for other systems,[4,5,10,11] the *cis* isomer being stabilized by ion-pair formation.

The system can be represented as previously[10] by the following equations

$$\begin{tikzcd}[row sep=large, column sep=large]
\begin{array}{c}\textit{cis}\text{-}[\mathrm{CoCl_2(en)_2}]^+ \\ + \\ \mathrm{Cl}^-\end{array} \arrow[r, shift left=1.5, "k_c"] \arrow[r, phantom, "(1)"] \arrow[d, shift left, "K_2"] & \begin{array}{c}\textit{trans}\text{-}[\mathrm{CoCl_2(en)_2}]^+ \\ + \\ \mathrm{Cl}^-\end{array} \arrow[l, shift left=1.5, "k_t"] \arrow[d, shift left, "K_3"] \\
\textit{cis}\text{-}[\mathrm{CoCl_2(en)_2}]^+\cdots\mathrm{Cl}^- \arrow[u, shift left, "(2)"] \arrow[r, shift left] & \textit{trans}\text{-}[\mathrm{CoCl_2(en)_2}]^+\cdots\mathrm{Cl}^- \arrow[l, shift left] \arrow[u, shift left, "(3)"]
\end{tikzcd}$$

where K_1, K_2, and K_3 are equilibrium constants for reactions 1, 2, and 3, and k_c and k_t are initial first-order rate constants for the removal of *cis*-$[\mathrm{CoCl_2(en)_2}]^+$ and *trans*-$[\mathrm{CoCl_2(en)_2}]^+$, respectively ($K_1 = k_c/k_t$). Under conditions of chloride ion concentration in which the *cis* isomer exists almost exclusively as the ion pair *cis*-$[\mathrm{CoCl_2(en)_2}]^+\cdots\mathrm{Cl}^-$, the forward rate constant is symbolized k_{CIP}. These subscripts are maintained throughout the discussion and apply to all relevant thermodynamic and activation parameters. (*e.g.*, ΔH°_2 is the standard enthalpy of the ion-pair reaction 2 and $\Delta H^\circ{}_{\mathrm{CIP}}{}^{\mp}$ the standard enthalpy of activation for the removal of the *cis* isomer under conditions of chloride concentration in which formation of the ion pair is complete).

Values of K_1, K_2, and K_3 have been calculated as previously[10] from a consideration of the *cis* and *trans* equilibrium results and their chloride concentration dependence and are 36 ± 5, 4800 ± 700 l. mole^{-1}, and 4 ± 1 l. mole^{-1} at 70°.

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[13] R. G. Pearson, P. M. Henry, and F. Basolo, *J. Am. Chem. Soc.*, **79**, 5382 (1957).

[14] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

[15] R. Férnandez-Prini and J. E. Prue, *Trans. Faraday Soc.*, **62**, 1257 (1966).

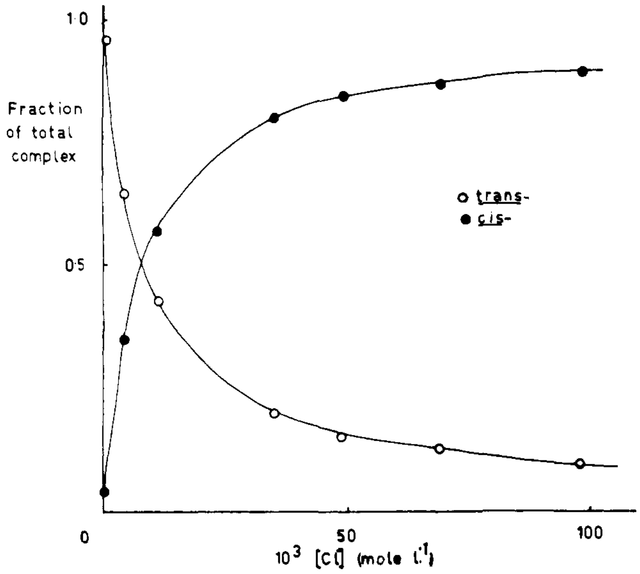

Figure 1. Equilibria of *cis*- and *trans*-$[CoCl_2(en)_2]^+$ in sulfolane at 70°: total complex concentration ~5×10^{-3} *M*; ●, fraction of *cis*-$[CoCl_2(en)_2]^+$; ○, fraction of *trans*-$[CoCl_2(en)_2]^+$.

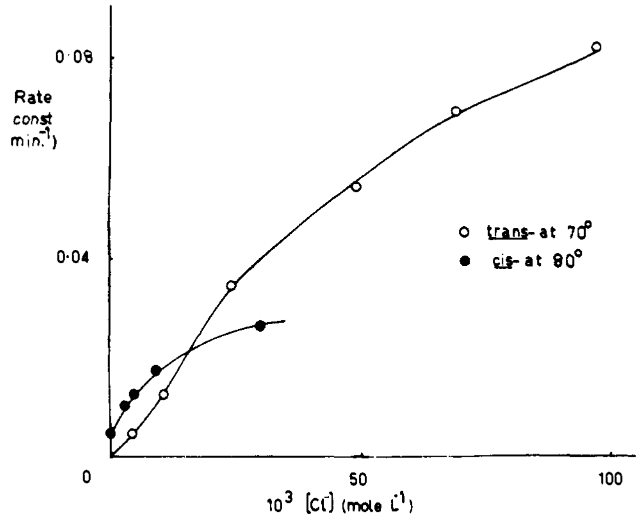

Figure 2. Dependence of k_c and k_t on chloride concentration: total complex concentration ~5×10^{-3} *M*; ●, k_c at 80°; ○, k_t at 70°.

The value of K_3 is almost certainly too low because of difficulties associated with the ion pairing of chloride with the tetraethylammonium cation. However, it is clear as in other systems,[2,4,5,10,11] that the *cis* ion is appreciably more ion paired than the *trans* ion.

No account is taken of the activity coefficients of the various species in the evaluation of K_2. For the ion pair which has no net charge, the activity coefficient will be close to unity. However, for the *cis*-$[CoCl_2(en)_2]^+$ and the Cl^- ions, the activity coefficients will be about 0.75 at the ionic strengths used (15×10^{-3} *M*) according to the Debye–Hückel limiting law. (This value of 0.75 has been obtained using the dielectric constant for sulfolane at 30°.) Therefore, the value of the ion-pair constant (K_2) expressed in the form

$$K_2 = \frac{[\text{ion pair}]}{[\text{free ion}][Cl^-]f_1f_2}$$

where f_1 and f_2 are the activity coefficients for the free complex ion and the chloride ion, will be approximately 9000 l. mole^{-1} at 70°. This value based on the displacement of the isomerization equilibrium agrees reasonably well with the more precise value obtained from direct measurements on the ion-pair equilibrium discussed below. From this a value of 11,000 ± 300 was obtained for K_2 at 70°.

The initial rates of isomerization of the *cis* and the *trans* isomers (k_c and k_t) at various chloride concentrations are shown in Figure 2. The rates show first-order characteristics and are affected by ion-pair formation. It is expected that the rate of isomerization of the *trans* isomer would eventually flatten off as does the *cis* rate if the chloride concentration could be raised sufficiently to bring about complete ion pairing.

A feature of the reactions studied in sulfolane is that they are very much slower than the corresponding reactions in other solvents, particularly hydroxylic solvents. This correlates with expected poorer solvation of the dissociating anion by sulfolane in the formation of a trigonal bipyramidal intermediate. For example, the half-life for isomerization of *cis*-$[CoCl_2(en)_2]^+$ at zero chloride concentration in methanol[16] is 8.3 min and in dimethylacetamide[12] is 350 min at 60°, compared with 1310 min for the present work in sulfolane.

Table II shows activation parameters for isomerization of both the *trans* and the *cis* isomers at various chloride ion concentrations. It can be seen that the activation energy for isomerization of the *cis*-$[CoCl_2(en)_2]^+$ ion is unaffected by ion-pair formation. The amount of isomerization of the *trans*-$[CoCl_2(en)_2]^+$ ion at zero chloride concentration is too small to enable a rate constant to be obtained, and it is thus not possible to obtain an activation energy under these conditions.

The values of $\Delta G°_1$ for the isomerization of *cis*-$[CoCl_2(en)_2]^+$ at zero chloride concentration at various temperatures are listed in Table III. These values of $\Delta G°_1$ were calculated from spectrophotometric measurements on equilibrium mixtures obtained from the reaction of *cis*-$[CoCl_2(en)_2]^+$ at various temperatures. No significant variation of $\Delta G°_1$ with temperature is observed so that $\Delta G°_1 = \Delta H°_1 = -2.5 \pm 0.1$ kcal mole^{-1} and $\Delta S°_1 = 0 \pm 0.5$ cal deg^{-1} mole^{-1}.

The energy-profile diagram for the isomerization at zero chloride concentration is shown in Figure 3. From the values $\Delta H°_c{}^{\ddagger} = 25.0 \pm 0.2$ kcal mole^{-1} and $\Delta H°_1 = -2.5 \pm 0.1$ kcal mole^{-1} for *cis*-$[CoCl_2(en)_2]^+$ isomerization at zero chloride concentration, the value $\Delta H°_t{}^{\ddagger} = 27.5 \pm 0.3$ kcal mole^{-1} is obtained for *trans*-$[CoCl_2(en)_2]^+$ isomerization at zero chloride. The activation energy for *trans*-$[CoCl_2(en)_2]^+$ measured at 4.3×10^{-3} *M* chloride is $\Delta H°_t{}^{\ddagger} = 20.3 \pm 0.2$ kcal mole^{-1}. This discrepancy can be explained only by stabilization of the transition state by ion association.

The values of K_2 at various temperatures are listed in Table I. These values were obtained from spectrophotometric results as previously described[2] and yield $\Delta H°_2 = -7.1 \pm 0.1$ kcal mole^{-1} and $\Delta S°_2 = -2.5 \pm 0.3$ cal deg^{-1} mole^{-1}.

That the activation energy for *cis* isomerization is not affected by ion-pair formation means the transition state is stabilized in ion association by the same energy as the reacting *cis*-$[CoCl_2(en)_2]^+$ ion. Thus the energy of the transition state is lowered by 7.1 kcal mole^{-1}

(16) D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, 2696 (1953).

Table II. Measured Activation Parameters in Sulfolane

10^3[Cl$^-$],	$\Delta H^{\circ\ddagger}$, kcal mole^{-1}			$\Delta S^{\circ\ddagger}$, cal deg^{-1} mole^{-1}		
M	$\Delta H^{\circ}{}_{c}{}^{\ddagger}$	$\Delta H^{\circ}{}_{CIP}{}^{\ddagger}$	$\Delta H^{\circ}{}_{t}{}^{\ddagger}$	$\Delta S^{\circ}{}_{c}{}^{\ddagger}$	$\Delta S^{\circ}{}_{CIP}{}^{\ddagger}$	$\Delta S^{\circ}{}_{t}{}^{\ddagger}$
0	25.0 ± 0.2			-6.4 ± 0.5		
4.3		25.0 ± 0.2	20.2 ± 0.2		-4.7 ± 0.5	-18.4 ± 0.5
30.0		25.0 ± 0.2			-3.1 ± 0.5	

Table III. Values of $\Delta G^{\circ}{}_1$ at Various Temperatures for the Isomerization of *cis*-[$CoCl_2(en)_2$]$^+$ at [Cl$^-$] = 0 in Sulfolane

	70°	80°	90°	100°	116°
ΔG°, kcal mole^{-1}	-2.4 ± 0.1	-2.5 ± 0.1	-2.4 ± 0.1	-2.5 ± 0.1	-2.6 ± 0.1

when it is associated with chloride ion. At fairly low concentrations of tetraethylammonium chloride ($\sim 5 \times 10^{-3}$ M), the ion pairing of the *trans* isomer will be small (<5%) so that its energy can be considered to be unchanged. The energy of activation of the *trans*-[$CoCl_2(en)_2$]$^+$ ion in the presence of chloride ion will therefore be the activation energy of *trans*-[$CoCl_2(en)_2$]$^+$ in the absence of chloride less the stabilization energy of the transition state. The value so calculated is 20.4 ± 0.4 kcal mole^{-1} (Figure 3), which compares well with the measured value.

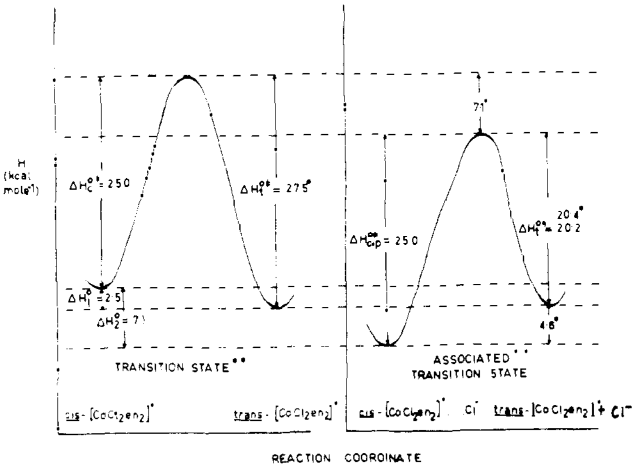

Figure 3. Reaction profile for the reactions (a) *cis*-[$CoCl_2(en)_2$]$^+$ = *trans*-[$CoCl_2(en)_2$]$^+$ and (b) *cis*-[$CoCl_2(en)_2$]$^+\cdots Cl^-$ = *trans*-[$CoCl_2(en)_2$]$^+$ + Cl^-. * These values have been calculated from the other energies which have been measured independently in this investigation. ** In the region of these transition states there must exist at least one intermediate and one other transition state. For an SN1 mechanism the intermediate is a trigonal bipyramid and the transition states are intermediate between this geometry and that of the two octahedral isomers.

It must be emphasized that some approximations have been made in the above discussion. At 4.3×10^{-3} M chloride, the *cis*-[$CoCl_2(en)_2$]$^+$ ion is only 80% ion paired and thus to allow the full 7.1 kcal mole^{-1} (the value of $\Delta H^{\circ}{}_2$, the difference between the free energy of the ion pair and the free ions in the standard state) is excessive. Further approximation is made in making no allowance for ion pairing of the *trans*-[$CoCl_2(en)_2$]$^+$ ion. However, under the prevailing conditions where it is inevitable that no allowance can be made for the variation of the transition state from the standard-state conditions, further refinement in respect to the reactant and product free energies must be unrewarding. In addition no present theory could allow for activity coefficient variation in such a system.

The approximations, however, do not detract from the results which yield the first appreciably correct reaction profile for reactions of this type. (Recently we have published[17] an appreciably similar treatment of a reversible SN2 reaction involving trimethylsulfonium bromide.) Clearly ion association which stabilizes the *cis* isomer relative to the *trans* isomer produces a remarkably similar stabilization of the transition state and thus lowers the energy requirement for the conversion of *trans*-[$CoCl_2(en)_2$]$^+$ into *cis*-[$CoCl_2(en)_2$]$^+$.

The present work contributes no more to recent publications[7,9,13,16,18] with regard to the assignment of detailed mechanisms of these reactions as SN1, involving a trigonal bipyramidal intermediate, or SN2 solvolytic,[18] involving a very unstable solvent-containing species. We feel that the slow rates in sulfolane could correlate with the low solvation of a dissociating anion in this solvent, and thus, as in the recent work on solvent exchange in these complexes,[9] we prefer the assignment of an SN1 mechanism.

Acknowledgment. We wish to acknowledge Dr. A. J. Parker whose ideas[14] and constant discussion have strongly influenced the thinking of this group.

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(17) Y. C. Mac, W. A. Millen, A. J. Parker, and D. W. Watts, *J. Chem. Soc.*, in press.

(18) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 141–152.