This observation leads[31] to the proposal that the principal term in the free energy of hydration of ions should be an ion–dipole term

$$F^\circ_{\text{el}} = Zen_S\mu_S/(r + r_S)^2 \qquad (18)$$

where n_S is the number of solvent molecules of radius r_S in the hydration sphere. Intimations that this equation might apply were put forward by Blandemer and Symons.[32] We have plotted Noyes' revised values[30c] of $\bar{F}^\circ_{\text{el}}$, the electrical contribution to the partial molar free energies of the ions in water at 25°, *vs.* $Z/(r + 0.50)^2$ in Figure 11. We found that setting the distance between charge and solvating dipole to be $r +$ 0.50 A gave separate straight lines for mono-, di- and trivalent cations. We used Pauling's crystal radii as listed by Noyes[30c] for the ionic radii, *r*. The smaller high-charge cations, Be^{2+} and Al^{3+}, lie above the di- and trivalent lines. This could either be real, owing to some degree of covalent bonding between solvent and ion, or an artifact, owing to use of incorrect values for the ionic radii. The slopes, *S*, of the three lines increase linearly with charge type (insert, Figure 11). This might be expected if polarization of the solvent dipoles by the ions is important; it should be important at the small distances involved. We do not wish to carry out an extensive investigation along the lines mentioned above. Our principal purpose is to point out to those investigators who are interested that a more fruitful point of departure in considering hydration of ions in water might be the ion–dipole relation (eq 18) rather than the Born equation.

(31) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953, p 51.

(32) M. J. Blandemer and M. C. R. Symons, *J. Phys. Chem.*, **67**, 1304 (1963).

Octahedral Cobalt(III) Complexes in Dipolar Aprotic Solvents. IX.[1] Solvent Exchange of Some Dimethyl Sulfoxide Containing Bis(ethylenediamine)cobalt(III) Complexes and Solvent-Interchange Reactions of Some *cis*-Chloro(solvent)bis(ethylenediamine)cobalt(III) Ions and the *trans*-Chloroaquobis(ethylenediamine)cobalt(III) Ion in Dimethyl Sulfoxide, N,N-Dimethylformamide, and N,N-Dimethylacetamide

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Abstract: Rate constants for replacement by the solvent of coordinated molecules have been determined for the following systems at a number of temperatures: *cis*-chloro(dimethylacetamide)bis(ethylenediamine)cobalt(III) ion (*cis*-$[CoCl(DMA)(en)_2]^{2+}$) in anhydrous N,N-dimethylformamide (DMF) and *trans*-chloroaquobis(ethylenediamine)cobalt(III) ion (*trans*-$[CoCl(H_2O)(en)_2]^{2+}$) in acidified DMF; *cis*-$[CoCl(DMA)(en)_2]^{2+}$ and *cis*-chloro(dimethylformamide)bis(ethylenediamine)cobalt(III) ion (*cis*-$[CoCl(DMF)(en)_2]^{2+}$) in anhydrous dimethyl sulfoxide (DMSO) and *trans*-$[CoCl(H_2O)(en)_2]^{2+}$ in acidified DMSO; *cis*-$[CoCl(DMF)(en)_2]^{2+}$ and *cis*-$[CoCl(DMSO)(en)_2]^{2+}$ in anhydrous N,N-dimethylacetamide (DMA). Activation parameters have been obtained for most reactions. The steric course of these reactions is interpreted as proceeding by an SN1 mechanism, involving trigonal bipyramidal transition states, to yield *cis*- and *trans*-chloro(solvent)bis(ethylenediamine)cobalt(III) ions. The *trans*-chloro(solvent)bis(ethylenediamine)cobalt(III) isomers formed have not yet been isolated as they are unstable and isomerize to give the *cis* isomer, but the rate of isomerization and the spectra of the two isomers have been obtained. Rate constants for the exchange of DMSO in the following complexes have been determined at 35°: *cis*-chloro(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion and *cis*-$[CoCl(DMSO)(en)_2]^{2+}$ in the presence of bromide ion, *cis*-bromo(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion, *cis*-nitro(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion, and *cis*-bis(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) ion. The strength of the solvents as ligands is shown to be $H_2O \simeq DMA << DMF < DMSO$.

Some recently investigated anation reactions in dipolar aprotic solvents[2–4] have been interpreted as having an SN1 mechanism, and others as having an SN2 mechanism. While data on the rate of solvent exchange in each of these systems would conclusively show the correctness of these assignments, we have only recently developed a method for determining

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(1) Part VI: W. A. Millen and D. W. Watts, *Australian J. Chem.*, **19**, 967 (1966); parts VII, VIII, submitted.

(2) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 2991 (1964).

(3) (a) L. F. Chin, W. A. Millen, and D. W. Watts, *Australian J. Chem.*, **18**, 453 (1965); (b) W. R. Fitzgerald and D. W. Watts, *ibid.*, **19**, 935 (1966).

(4) I. R. Lantzke and D. W. Watts, *ibid.*, **19**, 949 (1966).

Table I. Molar Extinction Coefficients at the Wavelengths Used in the Determination of Rates of Solvent Interchange

	Solvent							
	DMF			DMSO			DMA	
Complex	5200 A	5420 A	5800 A	5280 A	5420 A	5900 A	5280 A	5950 A
cis-$[CoCl(DMF)(en)_2]^{2+}$	118.5	102.5	52				115	36
trans-$[CoCl(DMF)(en)_2]^{2+}$	9	13	52					
cis-$[Co(DMF)_2(en)_2]^{3+}$	150	102.5	37					
cis-$[CoCl(DMSO)(en)_2]^{2+}$				114	107	46.6	117	39
trans-$[CoCl(DMSO)(en)_2]^{2+}$				15	9	46.6		
cis-$[Co(DMSO)_2(en)_2]^{3+}$				127	107	41		
cis-$[CoCl(DMA)(en)_2]^{2+}$	136	133	78	>122			144	61
cis-$[CoCl(H_2O)(en)_2]^{2+}$	101	92	49.5	89	82	37	95	37
trans-$[CoCl(H_2O)(en)_2]^{2+}$	16	22.1	35.8				21	40
cis-$[CoCl_2(en)_2]^+$	90.8	106	87.5					
trans-$[CoCl_2(en)_2]^+$	5.3	7	24					
cis-$[Co(NO_2)(DMSO)(en)_2]^{2+}$				129.5[a]				
cis-$[CoBr(DMSO)(en)_2]^{2+}$						120[b]		
cis-$[Co(DMSO)_2(en)_2]^{2+}$				129.5[a]		120[b]		

[a] At 5180 A. [b] At 5350 A.

these.[5] The work on solvent-interchange reactions was commenced prior to this in the expectation that the replacement of a coordinated solvent molecule by a similar dipolar aprotic solvent would be close to the exchange rate, and that the relative strength of the solvents as ligands could be assessed from equilibrium data.

These expectations have not been completely fulfilled, but the steric course of the solvent replacement to yield both *cis*- and *trans*-chloro(solvent) complexes, the latter unstable, is of interest and supports some recently published work on the aquation[6] of these solvent-containing complexes. Although the *trans*-chloro-(solvent)bis(ethylenediamine)cobalt(III) complexes of DMF, DMSO, and DMA have not yet been isolated, the visible spectra of the first two have been calculated.

In general, the activation parameters of solvent interchange differ from solvent to solvent, but in the absence of exchange data the rate of solvent interchange can be taken as an approximation to the rate of dissociation of the displaced solvent.

Experimental Section

Most of the compounds used in this work were the same batches as used previously.[4,6–8] *cis*-Nitro(dimethyl sulfoxide)bis(ethylenediamine)cobalt(III) perchlorate (*cis*-$[Co(NO_2)(DMSO)(en)_2](ClO_4)_2$) was prepared by heating a mixture consisting of *trans*-chloronitrobis(ethylenediamine)cobalt(III) perchlorate and an equimolar quantity of silver perchlorate in a minimum volume of DMSO. The preparation and heating of this mixture required some caution as it frequently reacted explosively. After maintaining the mixture at 60° for 15 min, silver chloride was filtered. Saturated aqueous lithium nitrate was added to the filtrate. On slow addition of ethanol and then ether, orange crystals of the nitrate perchlorate salt (*cis*-$[Co(NO_2)(DMSO)(en)_2]NO_3ClO_4$) were obtained. These were recrystallized as the perchlorate salt using a DMSO–water mixture (2:1 by volume) at room temperature as solvent, adding solid lithium perchlorate, and cooling on ice. The crystals were filtered, washed with ethanol, then ether, and vacuum dried at 1 mm pressure for 100 hr. Addition of lithium nitrate to the filtrate gave a crop of fine flaky crystals of the nitrate perchlorate salt. *Anal.* Calcd for *cis*-$[Co(NO_2)(DMSO)(en)_2](ClO_4)_2$: Co, 11.7. Found: Co, 11.5.

The *cis* structure of the complex was confirmed by an examination of its pmr spectrum. The nitrogen protons gave rise to four signals which, using our earlier numbering convention[8] with the DMSO considered as ligand X, are assigned as follows (in ppm); δ 5.97 H_5; δ 5.44, H_1, H_3, H_4, and H_2 (high-field shoulder); δ 4.46, H_7 H_6 (doublet); δ 3.73, H_8.

The solvents were purified by the methods previously reported.[9] Special care was needed in the use of DMF and DMA as solvents, as solvolysis reactions conducted in solvent which had been stored for more than a few days were rather erratic. This appears to have been due to attack of the complex by the decomposition products of the DMF. The effect appears to vary from sample to sample as noted by other workers.[10] To overcome this trouble only freshly fractionated solvents were used for all studies.

With one exception the kinetics of the solvent-interchange reactions were determined spectrophotometrically using the equipment and techniques described previously.[3a,4,6] The molar extinction coefficients (ϵ) of the pure complexes in these solvents at the wavelengths used are recorded in Table I.

The rate of exchange of coordinated DMSO, the rate of replacement of coordinated DMF by DMSO, and the confirmation of the steric course of some of the solvent interchange reactions were determined from changes with time of their proton magnetic resonance (pmr) spectra. These were measured on a Varian A-60 analytical nmr spectrometer, using sodium 3-(trimethylsilyl)-1-propanesulfonic acid (NaTMS) as internal standard.

Exchange reactions were determined at 35° by the following method. The sample was prepared in a drybox using 0.6 ml of hexadeuteriodimethyl sulfoxide (d_6-DMSO) and a weighed amount of the complex containing about 10% of NaTMS. This was transferred to a sample tube which was placed in the probe, and spectra and integrals were recorded at convenient times. A sweep time of 250 sec and a sweep width of 250 cps were used to record the spectra. The chemical shifts of DMSO, free and coordinated in these complexes, are recorded in Table II.

Table II. Pmr Signals of Protons of Free and Coordinated DMSO

		Coordinated DMSO			Uncoordinated DMSO	
Complex	Concn, *M*	δ, ppm	Splitting, cps	$W_{1/2}$, cps	δ, ppm	$W_{1/2}$, cps
cis-$[CoCl(DMSO)(en)_2](ClO_4)_2$	0.41	2.77	2.0	8	2.57	1.5
cis-$[CoCl(DMSO)(en)_2]Br_2$	0.07	2.77	Nil	2	2.56	1.5
cis-$[CoBr(DMSO)(en)_2](ClO_4)_2$	0.39	2.75	1.8	3.5	2.57	1
cis-$[Co(NO_2)(DMSO)(en)_2](ClO_4)_2$	0.50	2.74	4.0	25	2.57	1.5
cis-$[Co(DMSO)_2(en)_2](ClO_4)_3$	0.34	2.94	1.4	4	2.57	1

The most consistent rate constants were calculated using the areas under the curves obtained by spectrometer integration. The

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[5] I. R. Lantzke and D. W. Watts, *Australian J. Chem.*, in press.

[6] I. R. Lantzke and D. W. Watts, *ibid.*, in press.

[7] W. R. Fitzgerald and D. W. Watts, *ibid.*, **19**, 1411 (1966).

[8] I. R. Lantzke and D. W. Watts, *ibid.*, in press.

[9] W. A. Millen and D. W. Watts, *ibid.*, **19**, 43 (1966).

[10] H. E. Zaugg and A. D. Schaefer, *Anal. Chem.*, **36**, 2121 (1964).

rate of loss of coordinated DMSO was obtained from the slope of the semilogarithmic graph of ($A - A_\infty$), where A = area under the coordinated DMSO curve at time t and A_∞ = area under the curve at infinite time. In every case A_∞ was zero, corresponding to complete exchange. The rate of appearance of free DMSO in the solution was obtained in a similar manner, but in this case log ($A_\infty - A$) was used, with the value of A_∞ corresponding to the six DMSO protons uncoordinated.

To allow for slow variations with time of the total proton integration, the areas under the DMSO peaks were expressed as fractions of the total number of carbon protons in the complex.

The replacement of coordinated DMF by DMSO was determined by measuring the change in area of the resonances due to the aldehyde proton of DMF which resonates at 7.77 ppm when the solvent is coordinated and at 8.00 ppm when free. Because ordinary DMSO could be used the exchange was conveniently studied at higher temperatures than that of the probe.

Liberated chloride ion was determined by potentiometric titration with standard silver nitrate using silver–silver chloride and mercurous sulfate electrodes. To minimize the loss of chloride ion from the complex, the chilled samples (5 ml) were passed quantitatively through an ice-jacketed column of cation-exchange resin as soon after sampling as possible. The eluent used was 10^{-2} *M* aqueous perchloric acid.

Results

When any compound of the type *cis*- or *trans*-$[CoCl(SOL_1)(en)_2]^{2+}$ is dissolved in a second solvent SOL_2, where SOL_1 and SOL_2 represent any of the potential ligands (H_2O, DMSO, DMF, and DMA), there are two consecutive reactions. Our conclusion is based on observation of (i) *cis* complexes, where SOL_1 is H_2O, DMSO, DMF, and DMA, and (ii) *trans* complexes, where SOL_1 is H_2O and when SOL_2 is any of the ligands DMSO, DMF, or DMA.

By analogy with the aquation[6] of some *cis*-$[CoCl(SOL)(en)_2]^{2+}$ complexes, it seems that the first reaction is

$$cis\text{- or } trans\text{-}[CoCl(SOL_1)(en)_2]^{2+} + SOL_2 \rightleftharpoons cis\text{- and } trans\text{-}[CoCl(SOL_2)(en)_2]^{2+} + SOL_1$$

and that the second reaction is

$$trans\text{-}[CoCl(SOL_2)(en)_2]^{2+} \rightleftharpoons cis\text{-}[CoCl(SOL_2)(en)_2]^{2+}$$

This conclusion is supported by (i) spectrophotometric measurements which indicate a two-stage reaction leading eventually to *cis*-$[CoCl(SOL_2)(en)_2]^{2+}$; (ii) examination of the pmr spectra of these reacting systems which indicate, using the previously recorded criteria,[8] that the product of the initial solvolysis reaction contains *trans* complex which isomerizes slowly to the *cis* complex only; (iii) analysis of the reacting systems for free chloride ion which indicates that the solvolytic removal of chloride is slow compared with the two reactions postulated above and is, in any case, in most of the systems not very important subsequent to these two reactions. Where this reaction is significant it is allowed for.

None of the *trans*-$[CoCl(SOL_2)(en)_2]^{2+}$ species has been isolated, but reasonable visible spectra have been calculated for the cases of $SOL_2 \equiv$ DMF and DMSO, while *trans*-$[CoCl(OH_2)(en)_2]^{2+}$ is produced in acidic solutions of *trans*-$[CoCl(OH)(en)_2]^+$.

1. The Isomerization Reaction: ***trans*-$[CoCl(SOL_2)(en)_2]^{2+} \rightarrow$ *cis*-$[CoCl(SOL_2)(en)_2]^{2+}$.** This reaction could be studied as the second stage in the solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ and *cis*-$[CoCl(OH_2)(en)_2]^{2+}$ in DMF and in the solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ in DMSO, but in this case at only one temperature. The reaction where SOL_2 is H_2O has been studied previously by Baldwin, Chan, and Tobe[11] and by Sargeson.[12] The method of deriving these rate constants is best described in relation to one particular system, in this case following the solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ by DMF.

Spectra recorded at convenient times in this reaction show isosbestic points at 5800 ± 30 and 4900 ± 100 A and increases in the optical density of the solution at wavelengths in between. As chloride ion titrations showed that a side reaction yielding chloride ion was significant (2% free Cl^- at one half-life and 3.7% free Cl^- at two half-lives), rate constants were calculated from the change in extinction at 5420 A, the wavelength of the isosbestic point between the *cis*-$[CoCl(DMF)(en)_2]^{2+}$ and *cis*-$[Co(DMF)_2(en)_2]^{3+}$ spectra. The same initial rate constant was obtained by using the change in extinction at 5200 A and the measured "infinity" extinction.

Rate constants calculated at 5200 A using the measured extinction of *cis*-$[CoCl(DMF)(en)_2]^{2+}$ as the "infinity" spectrum gave the rate of formation of this ion. Rate constants determined for this reaction at several temperatures and wavelengths are listed in Table III.

Table III. Rate Constants for the Reaction *trans*-$[CoCl(DMF)(en)_2]^{2+} \rightarrow$ *cis*-$[CoCl(DMF)(en)_2]^{2+}$ as Subsequent to Solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ in DMF

10^2k, min^{-1}	Temp, °C	λ, A
1.11	27.0	5420
1.12		5200
3.39	35.2	5200
6.16	40.0	5420
6.04		5200
7.1	40.8	5420

These results give an activation energy (E_a) of 24.2 ± 0.5 kcal mole^{-1} and an entropy of activation ($\Delta S^{\ddagger}$) of 3.0 ± 1.6 cal deg^{-1} mole^{-1}. This reaction was very sensitive to impurities in the DMF, and stale DMF gave rate constants from 50 to 100% high, the deviation being greatest at higher temperatures.

The measured "infinity" spectrum corresponded to 90% *cis*-$[CoCl(DMF)(en)_2]^{2+}$ ion and 10% of *cis*-$[Co(DMF)_2(en)_2]^{3+}$ ion. Potentiometric titration showed 9.9% free chloride ion at five half-lives.

When this same reaction is followed as the second stage of the solvolysis of *cis*-$[CoCl(H_2O)(en)_2]^{2+}$ in DMF, the results are similar (Table IV) although complicated more in this system by reactions typical of those associated with solvent decomposition, particularly at higher temperatures.

The isomerization reaction *trans*-$[CoCl(DMSO)(en)_2]^{2+} \rightarrow$ *cis*-$[CoCl(DMSO)Cl]^{2+}$ as the sequence to solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ in DMSO was followed at 5280 A, where at 37.6° k for isomerization was found to be 5.06×10^{-3} min^{-1}. The spectra showed a characteristic isosbestic point at 5900 ± 100 A. Chloride titrations showed the free chloride concentration to be 6% 8 min after the start of the sol-

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[11] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

[12] A. M. Sargeson, *Australian J. Chem.*, **16**, 352 (1963).

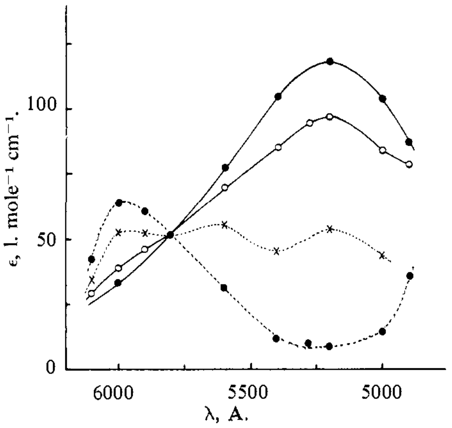

Figure 1. Spectra in N,N-dimethylformamide: —○—, spectrum of the *cis*-$[CoCl(DMF)(en)_2]^{2+}$ ion; -●-, spectrum of the first formed product; --●--, theoretical spectrum of the *trans*-$[CoCl(DMF)(en)_2]^{2+}$ ion assuming the first formed product is an 83:17 mixture of *cis*- and *trans*-$[CoCl(DMF)(en)_2]^{2+}$; --×--, theoretical spectrum of the *trans*-$[CoCl(DMF)(en)_2]^{2+}$ ion assuming the first formed product is a 67:33 mixture of *cis*- and *trans*-$[CoCl(DMF)(en)_2]^{2+}$.

volysis ($t_{1/2}$ = 1.5 min), 5% 19 min after, and 4% 50 min after. This chloride reentry made the study of this isomerization reaction more difficult.

Isomerization reactions cannot be studied as subsequent to the solvolysis of *trans*-$[CoCl(H_2O)(en)_2]^{2+}$ because of the considerable chloride entry to give *trans*-$[CoCl_2(en)_2]^+$. The chloride is necessarily supplied with the source of the complex, *trans*-$[CoCl(OH)(en)_2]Cl \cdot H_2O$. Isomerization of *trans*-$[CoCl(DMA)(en)_2]^{2+}$ as subsequent to solvolysis by DMA is impossible to study because of "bleaching" reactions, most likely a function of solvent decomposition. However, the isosbestic point in the spectra of the isomers at 5950 ± 100 A could be established at early times.

Table IV. Rate Constants for the Reaction *trans*-$[CoCl(DMF)(en)_2]^{2+} \rightarrow$ *cis*-$[CoCl(DMF)(en)_2]^{2+}$ as Subsequent to the Solvolysis of *cis*-$[CoCl(H_2O)(en)_2]^{2+}$ in DMF

Temp, °C	λ, A	ϵ_∞, l. mole⁻¹ cm⁻¹	10^2k, min⁻¹	$t_{1/2}$, min	Cl⁻ release, % (time, min)
23.2	5420	102	0.56		
27.2	5200	118.5	0.92		
	5420	102	1.04	67	4.2 (45) 6.0 (95)
35.4	5420	102	3.8	18	3.9 (12) 8.7 (27) 11.6 (40)
40.8	5420	107	9.4		

2. The Solvent-Interchange Reaction: ***cis*- or *trans*-$[CoCl(SOL_1)(en)_2]^{2+} + SOL_2 \rightarrow$ *cis*- and *trans*- $[CoCl(SOL_2)(en)_2]^{2+} + SOL_1$.** By determining rate constants at the wavelength of the isosbestic point in the spectra of the *cis*- and *trans*-$[CoCl(SOL_2)(en)_2]^{2+}$ ions, the complication of the subsequent isomerization reaction was avoided. It was also possible to calculate rate constants at other wavelengths by using the initial linear portion of the semilogarithmic plots of ($\epsilon - \epsilon_\infty$) against time, where ϵ is the extinction at time t and ϵ_∞ the extinction of the first formed product mixture.

The theoretical spectrum of the first formed product mixture was obtained as previously for the aquation[6] of *cis*-$[CoCl(DMA)(en)_2]^{2+}$. Here ϵ_∞ was chosen as that value which gave the same rate constant as at the isosbestic point.

Rate constants for the solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ by DMF are presented in Table V, while Figure 1 records the spectrum of the first formed products of one run obtained as above. The rate constants give an activation energy of 30.6 ± 0.2 kcal mole⁻¹ and an entropy of activation of 29.5 ± 0.7 eu. The steric course of the reaction was confirmed by the changes in the pmr spectrum of reaction mixtures.

Table V. Rate Constants for the Reaction *cis*-$[CoCl(DMA)(en)_2]^{2+}$ + DMF → *cis*- and *trans*-$[CoCl(DMF)(en)_2]^{2+}$ + DMA

10^3[*cis*-$[CoCl(DMA)(en)_2]^{2+}$], *M*	k, min⁻¹	λ, A	Temp, °C
3.26	6.40×10^{-2}	5800	21.6
3.92	1.17×10^{-1}	5280 (ϵ_∞ 92)	25.1
3.52	1.68×10^{-1}	5800	27.0
4.37	3.27×10^{-1}	5800	31.4
3.59	6.54×10^{-1}	5800	35.2

A low-field resonance at 6.32 ppm due to the *cis*-$[CoCl(DMA)(en)_2]^{2+}$ ion rapidly fades, while a resonance at 6.07 ppm builds up. Within 8 min the low-field resonance consists of one broad peak ($W_{1/2}$ = 25 cps) centered at 6.08 ppm. This resonance then slowly moves to lower field until after 80 min it is at 6.16 ppm ($W_{1/2}$ = 22 cps). An infinite time sample had a low-field resonance at 6.16 ppm ($W_{1/2}$ = 23 cps). The pmr spectrum of the *cis*-$[CoCl(DMF)(en)_2]^{2+}$ ion has a low-field nitrogen proton resonance at 6.19 ppm with a shoulder at 6.02 ppm.

These results are consistent with the product at the end of the first stage of the reaction, consisting of mixed *cis*- and *trans*-$[CoCl(DMF)(en)_2]^{2+}$ isomers, and thus confirm the spectrophotometric results which showed that the solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ had a half-life of ~1 min at 35°, followed by the isomerization reaction of half-life 20 min.

By assuming that the solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ ion by DMF was similar to its aquation and initially gave the theoretical proportion[13] to *trans* isomer, *viz.* 16.6%, it was possible to calculate from the theoretical ϵ_∞ values for the completion of the solvolysis reaction the spectrum of the *trans*-$[CoCl(DMF)(en)_2]^{2+}$ species (±5 l. mole⁻¹ cm⁻¹). This spectrum is recorded in Figure 1. The spectrum, calculated on the assumption that the reaction was an S$_N$2 *trans* attack to give 33.3% *trans* isomer,[13] is also included in Figure 1.

That the *trans*-$[CoCl(DMF)(en)_2]^{2+}$ spectrum calculated on the assumption of 16.6% *trans* product is a distinctly reasonable *trans* spectrum in comparison with a wide range of similar compounds, and that other assumptions lead to impossible solutions (*e.g.*, any figure less than 10% yields negative ϵ values), is compelling evidence for the acceptance of this steric course; the

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[13] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

theoretical steric course for substitution through trigonal bipyramidal intermediates.[18]

The solvolysis of *cis*-$[CoCl(OH_2)(en)_2]^{2+}$ by DMF cannot be studied because of the similarity of the spectrum of this complex (ϵ_{5200} 102, ϵ_{5800} 49.6) to that of the above theoretical product mixture (ϵ_{5200} 97, ϵ_{5800} 52). The constancy of the spectra in the early stages of this reaction is further evidence for accepting this steric course. From the study of the isomerization of the initial products it can be established that the half-life of this solvolysis reaction is *ca.* 2 min at 23.0°.

The results for the solvolysis of *trans*-$[CoCl(H_2O)(en)_2]^{2+}$ by DMF are presented in Table VI. These results are less precise and could not be used for steric course determination because of the interference of the subsequent chloride entry (see above). These results yield an activation energy of 24.0 ± 1 kcal mole^{-1} and $\Delta S^{\ddagger} = 1 \pm 2$ cal deg^{-1} mole^{-1}.

Table VI. Rate Constants for the Reaction *trans*-$[CoCl(H_2O)(en)_2]^{2+}$ + DMF → *cis*- and *trans*-$[CoCl(DMF)(en)_2]^{2+}$ + H_2O

$10^2 k_{5800}$, min^{-1}	Temp, °C
1.3	28.1
3.6	38.0
7.0	43.8

The system which was most amenable to spectrophotometric treatment involved the solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ in DMSO. The results are recorded in Table VII. The activation parameters for this reaction are $E_a = 22.3 \pm 0.6$ kcal mole^{-1} and $\Delta S^{\ddagger} = 1.0 \pm 2.0$ cal deg^{-1} mole^{-1}.

Table VII. Rate Constants and Related Data for the Reaction *cis*-$[CoCl(DMA)(en)_2]^{2+}$ + DMSO → *cis*- and *trans*-$[CoCl(DMSO)(en)_2]^{2+}$ + DMA

10^3[*cis*-[CoCl-(DMA)-$(en)_2]^{2+}$], *M*	10^2k, min^{-1}	Temp, °C	λ, A	ϵ_∞, l. mole^{-1} cm^{-1}	Solvent
4.07	3.1_2	16.6	6000	38	DMSO + 0.4 *M* $NaClO_4$
3.65	4.5_1	19.8	6000	38	DMSO
	4.3_1		5900	46.6	
4.04	4.6_7	20.4	6000	38	DMSO + 0.4 *M* $NaClO_4$
3.96	4.8_5	20.4	6000	38	DMSO
4.04	15.1	29.4	6000	38	DMSO + 0.4 *M* $NaClO_4$
3.98	14.7	29.4	5280	97	DMSO + 0.4 *M* $NaClO_4$
4.98	20.6	32.0	5900	46.6	DMSO
3.43	39.9	37.6	5280	97	DMSO

Figure 2 shows the spectrum of the initial product of solvolysis together with a theoretical *trans*-$[CoCl(DMSO)(en)_2]^{2+}$ spectrum based upon the steric course assumed previously. In this system as before, the existence of *trans*-$[CoCl(DMSO)(en)_2]^{2+}$ as one of the initial products of solvolysis is clearly shown by pmr spectra.

The solvolysis reaction

$$cis\text{-}[CoCl(DMF)(en)_2]^{2+} + DMSO \longrightarrow cis\text{- and } trans\text{-}[CoCl(DMSO)(en)_2]^{2+} + DMF$$

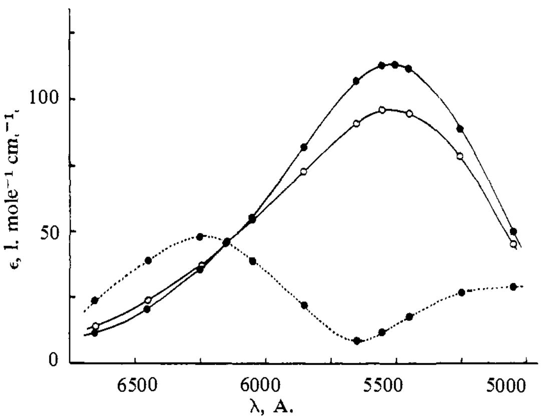

Figure 2. Spectra in dimethyl sulfoxide: —○—, spectrum of the *cis*-$[CoCl(DMSO)(en)_2]^{2+}$ ion; —●—, spectrum of the first formed product; - -○- -, theoretical spectrum of the *trans*-$[CoCl(DMSO)(en)_2]^{2+}$ ion assuming the first formed product is an 83:17 mixture of *cis*- and *trans*-$[CoCl(DMSO)(en)_2]^{2+}$.

is not amenable to spectrophotometric study but has been followed as described previously[5] by studying the decrease in the resonance of the aldehyde proton resonance of the coordinated DMF molecule. The steric course could not be determined, but some *trans* product was again evident before subsequent isomerization. The results which yield activation parameters $E_a = 24.6 \pm 0.5$ kcal mole^{-1} and $\Delta S^{\ddagger} = 0.6 \pm 1.6$ cal deg^{-1} mole^{-1} are recorded in Table VIII.

Table VIII. Rate Constants for the Reaction *cis*-$[CoCl(DMF)(en)_2]^{2+}$ + DMSO → *cis*- and *trans*-$[CoCl(DMSO)(en)_2]^{2+}$ + DMF

[*cis*-[CoCl-(DMF)$(en)_2]^{2+}$], *M*	10^2k, min^{-1}	Temp, C°
0.200	0.94	44.8
0.271	2.76	54.0
0.204	9.0	64.4

The solvolysis reaction

$$trans\text{-}[CoCl(OH_2)(en)_2]^{2+} + DMSO \longrightarrow cis\text{- and } trans\text{-}[CoCl(DMSO)(en)_2]^{2+} + H_2O$$

was more precisely studied than the comparable reaction in DMF because chloride entry was insignificant (<1%) during the first two half-lives of solvolysis. However, chloride entry was significant (>10%) during the first half-life of the isomerization of the *trans*-$[CoCl(DMSO)(en)_2]^{2+}$ ion.

The experimental infinity spectra obtained in this solvolysis reaction agreed to within 1% with the experimental infinity spectra in the solvolysis of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ in DMSO and thus suggested an identical steric course (namely to produce 16.6% *trans* isomer).

The rate constants in Table IX lead to the following activation parameters: $E_a = 26.9 \pm 0.5$ kcal mole^{-1} and $\Delta S^{\ddagger} = 13.3 \pm 1.6$ cal deg^{-1} mole^{-1}.

Solvolysis reactions in DMA were less fruitfully investigated because of an unidentified secondary bleaching reaction which it is assumed, since it was nonreproducible and dependent on solvent age, was associated with solvent decomposition.

Table IX. Rate Constants for the Reaction *trans*-$[CoCl(H_2O)(en)_2]^{2+}$ + DMSO → *cis*- and *trans*-$[CoCl(DMSO)(en)_2]^{2+}$ + H_2O

10^3[*trans*-$[CoCl(H_2O)(en)_2]^{2+}$], *M*	10^3k, min^{-1}	Temp, °C
4.24	8.15	20.5
3.90	39.0	30.8
4.63	71.5	35.0

Table X. Rate Constants for the Replacement of Coordinated Solvent by DMA

Complex	10^3concn, *M*	10^3k, min^{-1}	Temp, °C
cis-$[CoCl(DMF)(en)_2](ClO_4)_2$	5.03	1.61	35.0
	4.29	3.77	41.1
	4.22	8.11	46.4
cis-$[CoCl(DMSO)(en)_2](ClO_4)_2$	5.09	2.54	35.1
	4.15	2.68	35.6
	4.82	6.2	41.8
	4.77	13.4	47.6

Table XI. Rates of Exchange and of Side Reactions of Some DMSO-Containing Complexes at 35°

		10^3k_{ex}, min^{-1}		Side reaction		
Complex	Concn, *M*	From d/d*t* (DMSO-coord)	From d/d*t* (DMSO-free)	Nature	10^4k, min^{-1}	% complex at equil
cis-$[CoCl(DMSO)(en)_2](ClO_4)_2$	0.41	4.1	4.2			
	5.15×10^{-3}			Solvolysis		
cis-$[CoCl(DMSO)(en)_2]Br_2$	0.07	3.9	4.2			>99
	4.04×10^{-3}			Anation	3.45	>93
cis-$[CoBr(DMSO)(en)_2](ClO_4)_2$	0.39	4.6	4.7			
	4.39×10^{-3}			Solvolysis		>99
cis-$[Co(NO_2)(DMSO)(en)_2](ClO_4)_2$	0.50	18.0	18.8			
	4.72×10^{-3}			Solvolysis		99
cis-$[Co(DMSO)_2(en)_2](ClO_4)_3$	0.34	2.65[a]	2.65[a]			

[a] Half the measured rates, to allow for the two identical ligands.

The two reactions

$$cis\text{-}[CoCl(DMF)(en)_2]^{2+} + DMA \longrightarrow cis\text{- and } trans\text{-}[CoCl(DMA)(en)_2]^{2+} + DMF$$

and

$$cis\text{-}[CoCl(DMSO)(en)_2]^{2+} + DMA \longrightarrow cis\text{- and } trans\text{-}[CoCl(DMA)(en)_2]^{2+} + DMSO$$

have been studied and give activation parameters of E_a = 27.4 ± 0.7 kcal $mole^{-1}$ and $\Delta S^{\ddagger}$ = 12.0 ± 2.3 cal deg^{-1} $mole^{-1}$ and E_a = 26.5 ± 0.4 kcal $mole^{-1}$ and $\Delta S^{\ddagger}$ = 9.9 ± 1.3 cal deg^{-1} $mole^{-1}$, respectively. Rate constants are recorded in Table X.

3. Exchange of Coordinated DMSO with d_6-DMSO Solvent. A preliminary publication of some of this work has appeared,[5] but it is reported here in full for comparison in this extended study. In each case the stability of the system to reactions other than solvent exchange has been confirmed by spectrophotometry which by necessity was carried out at lower concentrations. The results are presented in Table XI.

Discussion

Although this work has shown that in general it is not possible to arrive at rates of exchange using apparently similar solvents, two aspects of it are of particular interest. These are the mechanism and steric course of the reactions and the information they provide on the strength of the solvents as ligands. Table XII is a summary of the significant results of this work and of the closely related aquation studies[6] reported previously.

On comparison of the rates and activation parameters of the *cis* complexes it is apparent that for each complex E_a and $\Delta S^{\ddagger}$ are solvent dependent, decreasing in the order DMA > H_2O > DMSO, with these parameters for the reaction of *cis*-$[CoCl(DMA)(en)_2]^{2+}$ in DMF anomalously high. These reactions must all have a similar mechanism, already shown to be SN1 from product analyses of the aquation reactions.[6] Although product analysis has not been possible in these solvent-interchange reactions, it seems that the initial substitution reaction yields 17% *trans* product in most cases and in this is consistent with an SN1 mechanism and a trigonal bipyramidal intermediate. One such intermediate has been demonstrated previously,[14] and these trigonal bipyramidal species have been proposed frequently as intermediates in SN1 reactions of bis(ethylenediamine)cobalt (III) complexes. It is unfortunate that the amount of the unstable *trans* isomer formed is small and prevents its isolation in the systems studied.

Table XII. Summary of the Rate Constants at 35°, Activation Energies, and Entropies of Activation of Some Solvent-Interchange Reactions

Complex	Solvent	*k*, min^{-1} (35°)	E_a, kcal $mole^{-1}$	$\Delta S^{\ddagger}$, cal deg^{-1} $mole^{-1}$
cis-$[CoCl(DMF)(en)_2]^{2+}$	DMSO	2.74×10^{-3}	24.6	0.6
	H_2O	1.71×10^{-3}	25.2	0.5
	DMA	1.61×10^{-3}	27.4	12.0
cis-$[CoCl(DMSO)(en)_2]^{2+}$	DMSO	4.15×10^{-3}		
	H_2O	3.63×10^{-3}	25.2	1.5
	DMA	2.47×10^{-3}	26.5	9.9
cis-$[CoCl(DMA)(en)_2]^{2+}$	DMSO	2.94×10^{-1}	22.3	1.2
	H_2O	2.13×10^{-1}	23.5	4.7
	DMF	6.27×10^{-1}	30.6	29.5
trans-$[CoCl(H_2O)(en)_2]^{2+}$	DMSO	7.15×10^{-2}	26.9	13.3
	DMF	2.46×10^{-2}	23.8	1.1
trans-$[CoCl(DMF)(en)_2]^{2+}$	DMF	3.24×10^{-2}	24.2	3.0
trans-$[CoCl(DMSO)(en)_2]^{2+}$	DMSO	5.06×10^{-3}[a]		
cis-$[CoCl(DMSO)(en)_2]^{2+}$	DMSO + $2Br^-$	4.1×10^{-3}		
cis-$[CoBr(DMSO)(en)_2]^{2+}$	DMSO	4.65×10^{-3}		
cis-$[Co(NO_2)(DMSO)(en)_2]^{2+}$	DMSO			
cis-$[Co(DMSO)_2(en)_2]^{3+}$	DMSO	2.65×10^{-3}		

[a] *k* at 37.6°.

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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 $\Delta S^{\ddagger}$ 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.

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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

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

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,

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