to restricted motional freedom of the R groups in the *trans*-planar form due to their interactions with the 3-*s*Bu substituents. The difference in weighted average $N_t^{298°}$ values for the R-active and R-*meso* sets of isomers (0.16) is much larger than that for Ni(5Me-Amp-sal)$_2$[5] (0.07), consistent with the observably different magnetic moments and electronic spectra for the R-active set of isomers and the total mixture of isomers of Ni(3*s*Bu, 5Me-Amp-sal)$_2$. Differences in these properties of active and racemic Ni(5Me-Amp-sal)$_2$ could not be detected. Finally, confirmatory evidence that the "extra" 5-Me and 4-H signals in the pmr spectrum of Ni(3*s*Bu-5Me-Amp-sal)$_2$ derive from a splitting of these signals in isomer 2 is provided by the virtually identical temperature dependence of ΔF calculated from the two signals (*cf.* Figure 9) using the same coupling constant for both. Because the two signals arise from one molecular species rather than two distinct isomers, the splitting in this case must be attributed to a very small inequivalence in $a_{5\mathrm{Me}}$ and $a_{4\mathrm{H}}$ coupling constants in the two rings.

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Isomerization, Solvolysis, Ion Association, and Solvation of *cis*- and *trans*-Dichlorobis(ethylenediamine)cobalt(III) Cations in Protic and in Dipolar Aprotic Solvents

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Abstract: Solubilities of the chlorides and perchlorates of the *cis*- and *trans*-[CoCl$_2$(en)$_2$]$^+$ cations in the protic solvents water and methanol and in the dipolar aprotic solvents dimethylformamide (DMF), dimethylacetamide (DMA), tetramethylene sulfone (TMS), and dimethyl sulfoxide (DMSO) have been measured. The solvent activity coefficients, for transfer of these isomeric cations from DMA to other solvents, have been calculated in terms of a reasonable extrathermodynamic assumption. It has thus been possible to calculate solvent activity coefficients for ion pairs and for model transition states, which are based on a dissociative mechanism for isomerization and solvolysis. A different model must be used for the transition states for at least some solvolysis reactions. The isomerization equilibrium constants in water and in methanol, in which solvents it cannot be measured directly, have been estimated from the observed value in DMA.

It is now possible to assign solvent activity coefficients to individual anions and cations with some confidence.[3] These are invaluable for the interpretation of solvent effects on rates, equilibria, and mechanism.[4] We now apply them to some reactions of coordination compounds.

The solvent activity coefficients $^0\gamma_i^S$ are defined by eq 1, which expresses the change in the standard chemical potential of the solute, i, in a unimolar solution, hypothetically ideal with respect to Henry's law, on transfer from a reference solvent (superscript 0) to another solvent (superscript S) at a temperature T.

$$\bar{\mu}_i^S = \bar{\mu}_i^0 + RT \ln {}^0\gamma_i^S \qquad (1)$$

In this paper, we consider the effect of solvent transfer on the standard chemical potential of the *cis*- and *trans*-[CoCl$_2$(en)$_2$]$^+$ cations, of their ion pairs with chloride ion, and of possible rate-determining transition states for their isomerization (eq 2) and solvolysis (eq 3 and 4). The significance of (3) and (4) in rate-determining isomerization in solvents other than TMS and MeOH is discussed elsewhere.[5]

$$\textit{cis}\text{-[CoCl}_2\text{(en)}_2]^+ \underset{k_t}{\overset{k_c}{\rightleftharpoons}} \textit{trans}\text{-[CoCl}_2\text{(en)}_2]^+ \qquad (2)$$

$$\textit{cis}\text{-[CoCl}_2\text{(en)}_2]^+ + \text{sol} \longrightarrow \textit{cis}\text{-[CoCl(sol)(en)}_2]^{2+} + \text{Cl}^- \qquad (3)$$

$$\textit{trans}\text{-[CoCl}_2\text{(en)}_2]^+ + \text{sol} \longrightarrow \textit{cis}\text{-[CoCl(sol)(en)}_2]^{2+} + \text{Cl}^- \qquad (4)$$

The equilibrium constant ($K = k_c/k_t$) for isomerization (2) is strongly influenced by ion association and by solvent transfer.[6-10] These strong medium effects have been attributed qualitatively to the dipolar nature of the *cis* isomer,[5-9,11,12] which also appears to be a stronger hydrogen-bond donor than the symmetrical *trans* isomer. The *trans* isomer thus associates with anions and interacts with polar solvents less strongly than the *cis* isomer.[12] The role of hydrogen bonding in accentuating ion association in these cations is comparable to the role of the nitrogen proton

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Table I. Solubilities and Solvent Activity Coefficients of *cis*- and *trans*-$[CoCl_2(en)_2]X$ at 25° (Reference Solvent DMA)

Solvent	$S^h \times 10^3$ M	$K_{ip}{}^f$	$K_s{}^g$	$S^h \times 10^3$ M	$K_{ip}{}^f$	$K_s{}^g$	Log ${}^0\gamma^S{}_{c^+}{}^0\gamma^S{}_{X^-}$	Log ${}^0\gamma^S{}_{t^+}{}^0\gamma^S{}_{X^-}$	Log ${}^D\gamma^S{}_{c^+}$	Log ${}^D\gamma^S{}_{t^+}$
		cis-$[CoCl_2(en)_2]Cl$			*trans*-$[CoCl_2(en)_2]Cl$					
DMA	2.2	20,000[i]	9.6×10^{-8}	0.61	1000[c]	1.8×10^{-7}	0.0	0.0	0.0	0.0
DMF	10.5	8,000[i]	1.2×10^{-6}	1.65	400[c]	1.8×10^{-6}	−1.1	−0.9	+0.2	0.0
DMSO	40.5	400[i]	7.9×10^{-5}	20.0	100[i]	1.0×10^{-4}	−2.9	−2.8	−0.6	−0.5
MeOH	2.71	150[j]	4.0×10^{-6}	31.4	5[c]	7.8×10^{-4}	−1.6	−3.6	+6.2	+4.2
H_2O[b]	140	...	9.0×10^{-3}	1480	...	0.38	−5.0	−6.3	+5.3	+4.0
TMS[a]	5.7	42,000[k]	1.3×10^{-7}	1.00	20[k]	9.5×10^{-7}	−0.1	−0.7	+1.9	+1.3
		cis-$[CoCl_2(en)_2]ClO_4$			*trans*-$[CoCl_2(en)_2]ClO_4$					
MeOH	1.32	...	1.74×10^{-6}	1.55	...	2.55×10^{-6}	0.0[d]	0.0[d]	+6.2[e]	+4.2[e]
H_2O[b]	42.2	...	1.78×10^{-3}	11.3	...	1.33×10^{-4}	−3.0[d]	−1.7[d]	+4.0[e]	+3.3[e]

[a] These results at 30°. [b] Ion association neglected; activity coefficients from the Debye-Hückel limiting law have been used. [c] Values estimated from *K* for similar systems. References 9, 11, and 12. [d] Methanol is reference solvent (see text). [e] DMA is reference solvent (see text). [f] Ion-pair association constant, l. mole^{-1}. [g] Solubility product, mole^2 l.$^{-2}$ corrected for ion association. [h] Solubility, mole l.$^{-1}$. [i] Reference 12. [j] Reference 11. [k] Reference 9.

in the association of partially alkylated ammonium cations with anions.[13,14]

This paper analyzes these observations in more detail, using solvent activity coefficients for transfer to four types of polar solvent:[14] *viz.*, those which are poor hydrogen-bond donors but strong hydrogen-bond acceptors (DMF, DMA, DMSO), those highly structured solvents which are both strong hydrogen-bond acceptors and donors (water), those which are strong hydrogen-bond donors but only moderate acceptors (methanol), and those which are weak hydrogen-bond donors and moderate hydrogen-bond acceptors (TMS).

The isomerization (2) may take place by more than one mechanistic pathway.[5] In DMF and DMSO, and perhaps DMA, a solvent (sol) containing complex, *cis*-$[CoCl(sol)(en)_2]^{2+}$, is an intermediate[7,8,15] (reactions 3 and 4), but no such species has been detected in methanol or TMS.[9-11] In water as solvent, initially only aquation with no isomerization is observed,[16] giving first *cis*- and *trans*-$[CoCl(OH_2)(en)_2]^{2+}$ and later *cis*- and *trans*-$[Co(OH_2)_2(en)_2]^{3+}$. If solvent activity coefficients for the transition states in reactions 2–4 can be estimated, much can be learned about the mechanisms.

The isomerization constant (*K*) for reaction 2, the ion-pair association constants (K_{ip}) for process 5, and the solubility products (K_s) for process 6, as well as the rate constants k_c and k_t for (2) in solvents 0 and S, are related as in eq 7–10.[4] In our notation c^+ represents *cis*-$[CoCl_2(en)_2]^+$, and t^+ represents the *trans* isomer; cip and tip represent the ion pair of the *cis* and *trans* cations, respectively. The expressions for the *cis* isomer are shown, but of course analogous expressions hold for the *trans* isomer. In (10) ${}^0\gamma^S{}_Y$ is the solvent activity coefficient of a reagent, Y, which must be used if reactions are bimolecular. Where Y is a solvent involved in a bimolecular solvolysis, possibly as in (3) and (4), expressions such as (10) cannot be used because Y must be the same in both solvents. In a bimolecular solvolysis, rate data cannot meaningfully be interpreted in terms of solvent activity coefficients.

$$cis\text{-}[CoCl_2(en)_2]^+ + Cl^- \overset{K_{ip}}{\rightleftharpoons} cis\text{-}[CoCl_2(en)_2]^+Cl^- \tag{5}$$

$$cis\text{-}[CoCl_2(en)_2]X(\text{solid}) \overset{K_s}{\rightleftharpoons} cis\text{-}[CoCl_2(en)_2]^+ + X^- \tag{6}$$

$$K^0/K^S = {}^0\gamma^S{}_{t^+}/{}^0\gamma^S{}_{c^+} \tag{7}$$

$$K^0{}_{ip}/K^S{}_{ip} = {}^0\gamma^S{}_{cip}/{}^0\gamma^S{}_{c^+}{}^0\gamma^S{}_{Cl^-} \tag{8}$$

$$K^0{}_s/K^S{}_s = {}^0\gamma^S{}_{c^+}{}^0\gamma^S{}_{Cl^-} \tag{9}$$

$$k^S{}_c/k^0{}_c = ({}^0\gamma^S{}_{c^-}/{}^0\gamma^S{}_{c\ddagger})({}^0\gamma^S{}_Y) \tag{10}$$

Results and Discussion

Estimation of ${}^0\gamma^S{}_{c^+}$ and ${}^0\gamma^S{}_{t^+}$. The solubilities (*S*, mole l.$^{-1}$) of *cis*- and *trans*-$[CoCl_2(en)_2]Cl$ in DMA, DMSO, DMF, TMS, MeOH, and water and of *cis*- and *trans*-$[CoCl_2(en)_2]ClO_4$ in MeOH and water are in Table I. The solubility for *cis*-$[CoCl_2(en)_2]Cl$ in water cannot be used for comparison with solubility in other solvents, because this salt precipitates from aqueous solution as the monohydrate.[12,17] Likewise, the anhydrous perchlorates of both the *cis* and *trans* cations dissolve very readily in dipolar aprotic solvents, but after a short time heavy precipitation of less soluble solvates is found. However, the perchlorates in equilibrium with their saturated methanolic or aqueous solutions were not solvates, and the chlorides in equilibrium with saturated solutions in dipolar aprotic solvents or MeOH are not solvates. Thus the problem of solvate formation, in the estimation of ${}^0\gamma^S{}_{c^+}$ and ${}^0\gamma^S{}_{t^+}$, could be by-passed, as shown below.

The solubilities give the concentration of ions plus ion pairs in equilibrium with solid. The solubility products, for equilibrium 6, have been calculated from (11) using known ion-pair dissociation constants, K_{ip}'s, and are in Table I. The perchlorates are assumed

$$K_s/K_{ip} + K_s{}^{1/2} - S = 0 \tag{11}$$

to be strong electrolytes in all solvents,[18,19] at the concentration of the saturated solutions. In appropriate cases, allowance for long-range coulombic forces has been made using the Debye-Hückel limiting law, as indicated in Table I.

DMA is chosen as the reference solvent for the chlorides, and values of log ${}^D\gamma^S{}_{c^+}{}^D\gamma^S{}_{Cl^-}$ and log ${}^D\gamma^S{}_{t^+}{}^D\gamma^S{}_{Cl^-}$ are calculated from expressions analogous

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Table II. Solvation of Anions, Cations, and Ion Pairs (Reference Solvent DMA, 25°)

Solvent	Log $^{D}\gamma^{S}_{c^+}$	Log $^{D}\gamma^{S}_{t^+}$	Log $^{D}\gamma^{S}_{Cl^-}$[b]	Log $^{D}\gamma^{S}_{Ph_4As^+}$[b]	Log $^{D}\gamma^{S}_{K^+}$[b]	Log $^{D}\gamma^{S}_{Ag^+}$	Log $^{D}\gamma^{S}_{cip}$	Log $^{D}\gamma^{S}_{tip}$
DMA	0.0	0.0	0.0	0.0	...	0.0	0.0	0.0
DMF	+0.2	0.0	−1.3	0.0	0.0[a]	+1.5	−0.7	−0.3
DMSO	−0.6	−0.5	−2.3	0.0	−1.0[a]	−1.6	−1.2	−1.8
MeOH	+6.2	+4.2	−7.8	+2.7	+3.7[a]	+6.6	+0.5	−1.3
H_2O	+4.0	+3.3	−10.3	+6.8	+2.2[a]	+5.8	...	...
TMS	+1.9	+1.3	−2.0	+0.7	...	+4.6	−0.4	+1.0

[a] Reference solvent is DMF; value for DMA is not available. [b] Reference 4.

to (9) for transfer to DMF, DMSO, MeOH, and TMS. Our values[4] of log $^{D}\gamma^{S}_{Cl^-}$ (Table II) give the values shown as log $^{D}\gamma^{S}_{c^+}$ and log $^{D}\gamma^{S}_{t^+}$ in Table I, and as $RT \ln {}^{D}\gamma^{S}_{c^+}$ and $RT \ln {}^{D}\gamma^{S}_{t^+}$ in Figure 1, which arbitrarily has *trans*-[$CoCl_2(en)_2$]$^+$ in DMA as a reference point. Molar free energies of other species in various solvents are relative to this.

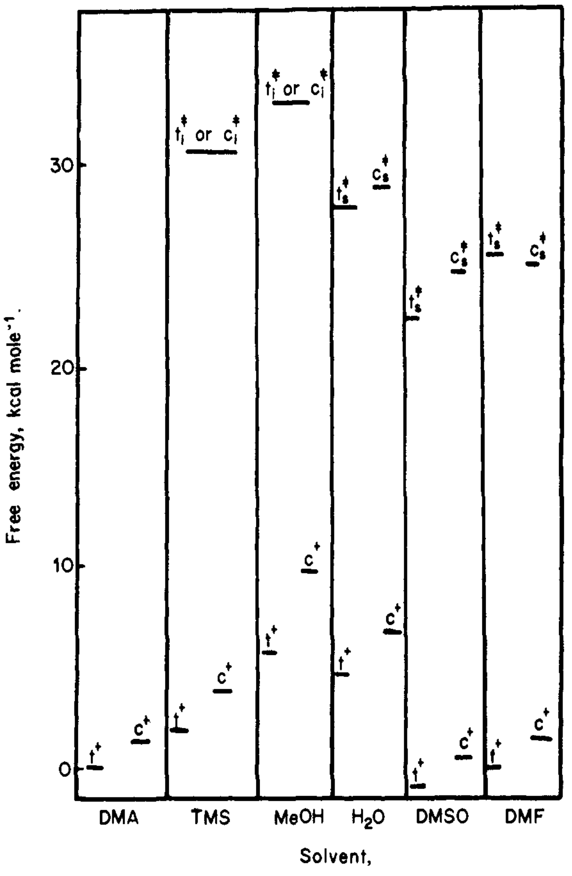

Figure 1. Relative molar free energies of reactants and transition states for an assumed SN1 process of isomerization and solvolysis at 25°. Reference point is molar free energy of *trans*-[$CoCl_2(en)_2$]$^+$ in DMA. Abbreviations: c^+ is *cis*-[$CoCl_2(en)_2$]$^+$; t^+ is *trans*-[$CoCl_2(en)_2$]$^+$; $t_s^{\ddagger}$ and $c_s^{\ddagger}$ are transition states for solvolysis of the *trans* and *cis* cations, respectively; $t_i^{\ddagger}$ and $c_i^{\ddagger}$ are transition states for isomerization.

Methanol is chosen as the reference solvent for the perchlorates, and values of log $^{M}\gamma^{W}_{c^+}$ and log $^{M}\gamma^{W}_{t^+}$ were calculated for transfer from methanol to water, using our value[4] for log $^{M}\gamma^{W}_{ClO_4^-} = -0.8$. The solubilities of the chlorides in methanol and in dipolar aprotic solvents can be compared legitimately, as can the solubilities of perchlorates in methanol and water, as already explained. Thus the two scales can be combined into a single scale for transfer from DMA to water, as in (12). The values are shown in Table I and in Figure 1.

$$\log {}^{D}\gamma^{W}_{c^+} = \log {}^{M}\gamma^{W}_{c^-} + \log {}^{D}\gamma^{M}_{c^+} \qquad (12)$$

Table III. Isomerization Equilibrium Constants (Reference Solvent DMA, 25°)

Solvent	Log $^{D}\gamma^{S}_{t^+}$	Log $^{D}\gamma^{S}_{c^+}$	Log *K* (calcd)	Log *K* (obsd)[b]	Ref
DMA	0.0	0.0	...	0.90	6
DMF	0.0	+0.2	1.1	1.0	8
DMSO	−0.5	−0.6	0.8	0.5	20
MeOH	+4.2	+6.2	2.9	>2[c]	10
H_2O	+3.3	+4.0	1.6	?[d]	..
TMS[a]	+1.3	+1.9	1.5	1.7[e]	9

[a] Values at 30° to avoid solvent solidification. [b] These values have been observed at 60° for DMA, DMF, and DMSO. We have shown that in DMSO *K* is not sensitive to a 30° change in temperature beyond the uncertainty of its determination[20] and assume that there is little change with temperature for DMA and DMF. [c] Reference 10 shows *cis*-[$CoCl_2(en)_2$]$^+$ to be less than 1% of the system at equilibrium in MeOH. [d] Cannot be measured because only aquation is observed. [e] Value extrapolated from $\Delta H°$ and $\Delta S°$.[9]

The behavior of the *cis* and *trans* cations is compared with the behavior of other cations in Table II. The potassium and tetraphenylarsonium cations are typical of cations without specific solvent–solute interactions. The former is of moderate size, whereas the tetraphenylarsonium cation is large and, as a consequence, is poorly solvated by solvents, like water, which have well-developed structure.[4] The silver cation is a Lewis acid and has strong specific interactions with polarizable donor solvents like NH_3, alkenes, CH_3CN, DMSO, and DMA. We do not have data for a model cation (*e.g.*, NEt_3H^+) which is a strong hydrogen-bond donor, like the present cations.

The symmetrical *trans*-[$CoCl_2(en)_2$]$^+$ cation behaves much like the potassium cation on solvent transfer. It does not behave like silver cation in any solvent and in water is not as poorly solvated as the large Ph_4As^+ cation. The more polar *cis*-[$CoCl_2(en)_2$]$^+$ cation, which more strongly donates hydrogen bonds to the solvent, shows a greater "spread" of solvent activity coefficients. In particular, the *cis* cation is very poorly solvated in methanol, relative to behavior in stronger hydrogen-bond acceptors, like DMA, DMF, and DMSO (Figure 1). Both isomers are similarly solvated by DMF, DMA, and DMSO.

Estimation of Isomerization Constants. The equilibrium constant for (2), expressed as a concentration quotient in the solvent DMA, is 8.0. Using this value as K^0 in eq 7, together with the values of log $^{D}\gamma^{S}_{c^+}$ and log $^{D}\gamma^{S}_{t^+}$ from Table I, K_s is calculated for reaction 2 in other solvents. The values are compared in Table

III with observed isomerization constants. The ratio of *trans* to *cis* isomer is strongly dependent on the concentration of the supporting chloride ion in dipolar aprotic solvents, and K is extrapolated to zero chloride ion concentration.[6–9, 20] When the isomerization equilibrium was measured using the perchlorate salt in solvents in which there was virtually no solvolysis (*e.g.*, TMS, MeOH), the value of K was indistinguishable from the value obtained by extrapolation to zero chloride ion of the results for the chloride salt. This confirms our expectation[12] that the perchlorate ion does not associate significantly with the cation. The interesting feature of Table III is that it gives an estimate of the position of the isomerization equilibrium (2) in MeOH and water, solvents in which direct measurement is very difficult: water because of aquation and methanol because the concentration of *cis*-$[CoCl_2(en)_2]^+$ at equilibrium is below detection limits.

The following points are best appreciated by reference to Figure 1. The cations *cis*- and *trans*-$[CoCl_2(en)_2]^+$ are of comparable stability in polar solvents which are strong hydrogen-bond acceptors but weak donors such as DMA, DMF, and DMSO. As already noted, the more polar *cis* cation, which is a good hydrogen-bond donor, is stabilized by such solvents relative to the symmetrical *trans* isomer so that intrinsic stability is leveled. In the less polar methanol, which is a weaker hydrogen-bond acceptor, the greater intrinsic stability (gas phase) of the *trans* cation is less masked by solvation effects.

Estimation of Ion-Pair Solvation. The ion-pair association constants K_{ip} and values of ${}^D\gamma^S{}_{c^+}$ and ${}^D\gamma^S{}_{t^+}$, from Table I, together with ${}^D\gamma^S{}_{Cl^-}$ (Table II) can be manipulated as in eq 8 to give solvent activity coefficients ${}^D\gamma^S{}_{cip}$ and ${}^D\gamma^S{}_{tip}$ of the ion pairs. In Table II, values of ${}^D\gamma^S{}_{c^+}$, ${}^D\gamma^S{}_{t^+}$, ${}^D\gamma^S{}_{Cl^-}$, ${}^D\gamma^S{}_{cip}$, and ${}^D\gamma^S{}_{tip}$ are recorded. It can be seen that the variation of ion association with solvent transfer is due to a combination of anion, cation, and ion-pair solvation changes. Such solvent effects cannot be discussed in terms of the solvation changes of any one of these species; all must be considered. The solvation of the ion pairs does not change as significantly as that of the parent ions, but the ion pairs retain, in a dampened way, some of the features apparent when considering the sum of the solvation effects of the parent cations and chloride ion. The solvent activity coefficient for transfer of the *trans* ion pair from DMA to sulfolane is anomalous in this regard.

Estimation of Transition-State Solvation. A recent evaluation of the kinetics of substitution in Co(III) octahedral complexes[21] suggests that the mechanisms fit within the broad spectrum of "dissociative controlled processes." This assignment has been confirmed for reactions in dipolar aprotic solvent media by our studies of anation reactions,[22] in which a coordinated solvent molecule is replaced by an anion. Anation is not usually a significant reaction in water, where the aquo species are relatively stable.

If the isomerization and solvolysis proceed by dissociative (SN1) mechanisms, then eq 10 simplifies to eq 13,

$$k^S{}_c/k^0{}_c = {}^0\gamma^S{}_{c^+}/{}^0\gamma^S{}_{c\ddagger} \qquad (13)$$

because other species (Y) are not undergoing chemical change in the transition state. If the solvent is specifically involved as in the transition state for a bimolecular isomerization or solvolysis, then neither eq 10 nor 13 can meaningfully be applied to the rate data.[4] In the treatment that follows, we are assuming a dissociative mechanism for both isomerization and solvolysis (*i.e.*, we accept the SN1 mechanism as defined by Basolo and Pearson[23]), in which ionization of a chloride ion from either the *cis*- or *trans*-$[Co(en)Cl_2]^+$ cation is the rate-determining transition state.

Dissociative or SN1 reactions giving high-energy intermediates are not as well suited as associative (SN2) reactions for interpretation in terms of solvent activity coefficients.[4] One cannot be certain that the measured rate constant is for the dissociation step. The dissociation may be complicated by ion-pair return giving an observed rate constant, for isomerization or for solvolysis, which is less than the rate constant for dissociation. When intermediates are involved, one must be concerned about which process is rate determining, formation of the intermediate or its decomposition. Nevertheless, it is instructive to perform calculations on observed rate constants for isomerization and solvolysis in terms of eq 13 to see whether the solvent activity coefficients of *all* the transition states are in accord with a model dissociative transition state like I. In I, a negative charge is developing on chlorine and a doubly positive charge is developing on the cation.

$$[Co(en)_2Cl]^{+\delta+} \cdots {}^{-\delta}Cl$$

I

The molar free energies of transition states for a rate-determining ionization step in solvolysis and isomerization are shown in Figure 1. We consider first the two reactions in which only isomerization (2) is observed (Table IV). We have not included data for reactions in DMA[13] because rates at 25° are not available and the role of solvolysis in isomerization is less certain.[6, 15] Intermediates containing solvent may be involved in isomerization in methanol and sulfolane, but they have not been observed.[5] Our investigation of the forward and backward reaction (2) in sulfolane[9] suggests that such species are at best high-energy intermediates of similar energy to the transition states for dissociation, in this solvent.

Table IV. Rates of Isomerization[d] at 25°
(Reference Solvent MeOH, 25°; k in min^{-1})

$$cis\text{-}[CoCl_2(en)_2]^+ \underset{k_t}{\overset{k_c}{\rightleftharpoons}} trans\text{-}[CoCl_2(en)_2]^+$$

Solvent	Log k_{c^+}	Log k_{t^+}	Log ${}^M\gamma^S{}_{c^+}$	Log ${}^M\gamma^S{}_{t^+}$	Log ${}^M\gamma^S{}_{Cl^-}$	Log ${}^M\gamma^S{}_{c\ddagger}({}_{t\ddagger})$[e]
MeOH	−3.03[a]	−5.9[c]	0.0	0.0	0.0	0.0
TMS	−5.37[b]	−7.0[c]	−4.3	−2.9	+5.8	−1.9

[a] References 10 and 11. [b] Reference 9. [c] Calculated using the values of K recorded in Table III. [d] At zero chloride ion concentration, supporting anion is perchlorate. [e] ‡ denotes transition state.

Table IV has methanol as reference solvent. The transition state must be the same for the forward and backward isomerization (2), so that for a two-step dis-

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[23] Reference 21, pp 124–129.

Table V. Solvation of Transition States for Isomerization and Solvolysis (Reference Solvent DMF at 25° (k, min^{-1}))

Solvent	Reaction	Log k_c	Log k_t	Log $^{D}\gamma^{S}{}_{c^+}$	Log $^{D}\gamma^{S}{}_{t^+}$	Log $^{D}\gamma^{S}{}_{Cl^-}$[i]	Log $^{D}\gamma^{S}{}_{c}\ddagger$	Log $^{D}\gamma^{S}{}_{t}\ddagger$
DMF	Solvolysis[a]	−2.8[c,e]	−4.3[d,e]	0.0	0.0	0.0	0.0	0.0
DMSO	Solvolysis[a]	−3.6[c,g]	−3.8[d,g]	−0.8	−0.5	−1.0	0.0	−1.0
H_2O	Solvolysis[a]	−1.8[c,f]	−2.7[d,h]	+3.8	+3.3	−9.0	+2.8	+1.6
MeOH	Isomerization[b]	−3.0	−5.9	+6.0	+4.2	−6.5	+6.0	
TMS	Isomerization[b]	−5.4	−7.0	+1.9	+1.3	−0.7	+4.2	

[a] Measured at zero chloride ion with ClO_4^- as supporting anion. [b] Data from Table IV, reaction 2 in text. [c] Reaction 3 in text. [d] Reaction 4 in text. [e] Reference 15. [f] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955). [g] Reference 20. [h] R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 2673 (1956); *J. Inorg. Nucl. Chem.*, **1**, 342 (1955). [i] Reference 4.

sociation–association pathway, if the rate-determining step in one direction is dissociation, then the reverse rate-determining step is association.[5,24] Thus we do not know if the transition state for isomerization in methanol and in sulfolane, shown in Figure 1, corresponds to dissociation from the *cis* or from the *trans* cation. This should be remembered when comparison is made in Figure 1 with the two solvolysis transition states, which clearly correspond to dissociation from the *cis* cation and from the *trans* cation, respectively.

The isomerizations are faster in methanol than in the dipolar aprotic sulfolane, so that on these grounds alone, a bimolecular reaction between a cation and chloride ion is unlikely,[4] because chloride ion has a much greater chemical potential in sulfolane than in methanol. The transition-state cation is more solvated by sulfolane than by methanol (Figure 1), as are most cations (Table II), but is much less influenced by solvent transfer than are either of the reactant cations (Table IV and Figure 1). This is not in conflict with a model transition state, I, in which the chloride ion, poorly solvated by sulfolane, has made significant progress toward dissociation from a doubly charged cation. The unfavorable solvation effect of developing chloride ion more than nullifies the favorable solvation of a doubly charged cation in sulfolane relative to methanol. The difference in response to solvent transfer is *not* in accord with a transition state in which there is little charge separation, *e.g.*, an intramolecular rearrangement of the type suggested by Springer and Sievers.[25] We cannot, of course, exclude a bimolecular solvolysis, followed by chloride reentry, on the evidence from the solvent effect on the isomerization rate.

Solvolysis and isomerization rates are interpreted on the basis of a common assumed dissociative rate-determining step in Figure 1. Details are in Table V, with DMF as reference solvent. The transition state for solvolysis of the *cis* cation is similarly solvated by DMF and DMSO; that for solvolysis of the *trans* cation is more solvated by DMSO than by DMF. Neither observation conflicts strongly with the expected behavior of the model transition state, I, because DMSO is slightly more effective than DMF in its ability to solvate most anions and cations.[4]

Solvolysis in water and DMF provides the first anomaly when the free energies of the transition states are compared as in Figure 1. The transition states are *less* solvated by water than by DMF. This suggests that in one or both of these solvents solvolysis does not have a rate-determining transition state which can be modeled by I. A well-dissociated chloride ion is very much more solvated by water than by DMF and, as we saw when isomerizations in methanol and sulfolane were compared, and in line with experience,[4] chloride ion solvation effects between protic and dipolar aprotic solvents outweigh the undoubted advantage which DMF has in solvating the developing doubly charged cation in I. The behavior could fit an SN1 model in which the solvolysis transition states were rather like the reactant cations, *i.e.*, with little charge development on and little separation of chloride. As discussed, we cannot exclude the possibility, *on this evidence*, that the rate constants for either or both of the solvolysis reactions are for an SN2 reaction.

A comparison of the isomerization in sulfolane with the solvolysis in DMF (Table V and Figure 1) suggests that the two processes have rather different rate-determining transition states. The *cis* and *trans* cations are somewhat less solvated by sulfolane than by DMF and the chloride ion is slightly more solvated by sulfolane. The transition state for isomerization (whether it corresponds to dissociation from the *cis* or *trans* cation) is very much less solvated in sulfolane than is the transition state for solvolysis in DMF. This observation is hard to reconcile with a common transition state, I, for isomerization and solvolysis. Although the developing doubly charged cation in I would be more solvated by DMF, this is somewhat nullified by chloride ion solvation, so that we would not expect to see, for a model like I, the difference in transition state solvation, shown in Figure 1.

A comparison of solvolysis in water with isomerization in sulfolane, as in Figure 1, fits nicely within the concept of a common transition state like I. The solvolysis transition state is more solvated by water than is the isomerization transition state by sulfolane. We would expect that a developing doubly charged cation in I would be slightly more solvated by sulfolane (Table II), but this effect is completely swamped by the effect of chloride ion solvation, which is greater in water.

The inconsistencies created by a common model, I, when solvolysis in DMF is compared with solvolysis in water and isomerization in sulfolane, are related to our previous difficulty[26] in assigning a purely dissociative mechanism to reactions in DMF. It would seem from Figure 1 that solvolysis in DMSO creates much the same problem of how a transition state can be well solvated when it contains a very poorly solvated, well-developed chloride ion. The difficulties are removed if solvolysis in DMF and possibly in DMSO proceed through a seven-coordinate intermediate $[CoCl_2(sol)(en)_2]^+$, because Figure 1 is no longer a valid comparison of transition-state solvation. The existence of such an intermediate was suspected[26] but could not be justified with confidence. We can say that the simple SN1

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model, I, is inadequate for solvolysis in DMF and DMSO, if we accept that it is a satisfactory model for isomerization in sulfolane. More tentatively we suggest that one of the possible interpretations of Figure 1 is that solvolysis, at least in DMF and DMSO, is an SN2 process in which solvent entry is well advanced on dissociation.

Although solvolysis of the *cis* and *trans* cations leads to the same product, *cis*-$[CoCl(sol)(en)_2]^{2+}$, except in water (*cf.* eq 3 and 4), Figure 1 shows that the transition state for solvolysis of the *trans* cation is a significantly different species from that for solvolysis of the *cis* cation. This conclusion is the same, whether the mechanism is SN1 or SN2.

Experimental Section

All solubilities were measured on analyzed samples.[8,9,12,15,18-21] The crystalline solids were equilibrated by rapid stirring with thermostated solvent for the longest time possible, consistent with their instability in the solvent. The saturated solutions were analyzed spectrophotometrically and reproducibility was ±2%. Solvates were formed with perchlorate salts in dipolar aprotic solvents. The precipitated solid contained solvent which was detected by infrared measurements and could not be removed by exhaustive washing with dry ether. Solvates could not be detected when perchlorates were recrystallized from methanol or water.

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Geometries and Charge Distributions of Organic Ligands. I. Metal–Carbon π Bonding and the Geometry of Acetylene

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Abstract: The geometrical effects of metal–carbon π bonding on complexed acetylene have been investigated using a model based largely on acetylene intramolecular interactions. The calculations showed that the accumulation of electron density in the π_g orbital through π bonding could lead to either a *cis*- or a *trans*-bent structure, whereas only *cis*-bent structures are observed experimentally. It was found that it was possible to explain this fact in terms of an argument based solely on the symmetry of the metal–acetylene interaction. A similar argument showed that the same forces were also opposed to the *cis* bending of the hydrogen atoms *toward* the metal but had little effect on *cis* bending *away* from the metal.

The nature of the carbon–metal bonding in the transition metal complexes of acetylene has been the subject of considerable speculation. According to the current theory,[1] the carbon–metal bond has two components. The first part comprises of a bond of σ character formed through the overlap between a metal hybrid orbital and the bonding π orbital (π_u) of acetylene, and is assumed to be largely responsible for the bonding. As the π_u orbital is doubly occupied in the free molecule, the formation of this σ bond necessarily leads to transfer of electron density from the acetylene onto the metal. It is assumed that this transfer of charge will be offset by the formation of a π-type bond through the overlap between a filled d_π orbital of the metal and an empty antibonding π orbital (π_g) of acetylene. The net effect of this bonding on acetylene is thus the removal of electron density from the π_u orbital, and a compensating buildup of charge in the π_g orbital.

Although this theory has gained wide acceptance, it has proved very difficult to find any evidence which unambiguously points to the formation of these π bonds. Attempts have been made to remedy this situation by measuring physical constants of the complexed acetylene and then comparing the results with the free-molecule values. For example, a study of the C≡C stretching frequency in a number of acetylene complexes revealed that, in many instances, it is decreased to a value more appropriate for a double, rather than triple, bond.[2,3] This may be interpreted as the result of π bonding, because the addition of electron density to the π_g orbital will reduce the C–C bond order which in turn would, presumably, reduce the vibration frequency. Results of this type are not, however, very conclusive.

Another interesting feature of the acetylene complexes is the change in the acetylene geometry which accompanies their formation.[4,5] Acetylene, which is linear in the free state, usually assumes a *cis*-bent structure in the complex. This change in geometry has been interpreted[6,7] as evidence of metal–carbon π bonding. because such a process would be expected to lead to an electron distribution analogous to that of the ^1A_u excited state of acetylene, which is known to be bent.[8] While being intuitively very attractive, this theory immediately presents two problems which must be resolved before it can be accepted. The first problem is that the analogy with the electron configuration of the

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