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Substitution Reactions of Metallic Complexes of β,β',β''-Triaminotriethylamine. 13. Kinetics of Solvolysis of the Dichloro(β,β',β''-triaminotriethylamine)cobalt(III) and -chromium(III) Cations in Nonaqueous Media and Synthesis and Characterization of Some Cobalt(III) and Chromium(III) Halo–tren Complexes Containing Coordinated Neutral Nonaqueous Ligands[1]

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The kinetics of solvolysis of $[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$ and $[Cr(tren)Cl_2]Cl$ have been measured in dimethyl sulfoxide (Me_2SO), *N*,*N*-dimethylformamide (DMF), *N*-methylformamide (NMF), and formamide (form). These reactions occur via dissociative mechanisms. For the general reaction $M(tren)Cl_2^+ + Y = M(tren)ClY^{2+} + Cl^-$, values for M = Co or Cr and Y = Me_2SO, DMF, NMF, or form of 10^4k (25 °C)/s^{-1}, $\Delta H^\ddagger$/kcal mol^{-1}, and $\Delta S^\ddagger$/cal mol^{-1} K^{-1} are as follows: (Co, Me_2SO) 0.224 ± 0.006, 21.2 ± 1.7, −7.0 ± 2.0; (Co, DMF) 0.118 ± 0.005, 24.6 ± 1.0, 4.0 ± 2.0; (Co, NMF) 56.9 ± 0.5, 17.1 ± 1.0, −11.2 ± 2.0; (Co, form) 8.27 ± 0.01, 20.1 ± 0.9, −4.9 ± 2.0; (Cr, Me_2SO) 0.501 ± 0.003, 17.7 ± 0.9, −18.5 ± 1.7; (Cr, DMF) 0.162 ± 0.004, 22.0 ± 0.9, −6.2 ± 1.5; (Cr, NMF) 601 ± 11, 10.4 ± 1.1, −29.1 ± 2.0; (Cr, form) 48.6 ± 0.5, 14.9 ± 1.0, −18.9 ± 2.0. These results yield the following values of $\Delta(\Delta S^\ddagger_{Cr-Co})$/cal mol^{-1} K^{-1}: Me_2SO, −11.5 ± 3.7; DMF, −10.2 ± 3.5; NMF, −17.9 ± 4.0; form, −14.0 ± 4.0. Equilibria exist for both complexes in Me_2SO and DMF, and the concentration of added chloride ion affects both the position of these equilibria and the rates of solvolysis. The ion-pairing constants (K_{IP}) have been determined in Me_2SO and DMF for both complexes. The chloride anation of $[Co(tren)Cl(Me_2SO)]^{2+}$ has been studied and found to occur by means of an $(S_N1)_{IP}$ mechanism. A number of the solvolysis products have been isolated and characterized. The dissociative character of reaction of these Cr(III) complexes is in contrast to the type of reaction of a number of simple chromium(III) ammines. It may imply that tren sterically blocks nucleophilic attack.

Introduction

In recent years, many studies of the solvolysis reaction of cobalt(III) and chromium(III) tetraamines have been undertaken.[2-12] In most cases, the reactions are complicated by the presence of cis–trans equlibria. The β,β',β''-triaminotriethylamine (tren) ligand, however, forms metal complexes in which isomerization cannot occur, due to the tripodal nature of the amine. We were convinced, therefore, that it would be instructive to study the kinetics of solvolysis of $[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$ and $[Cr(tren)Cl_2]Cl$ in various nonaqueous solvents. These tren complexes offer a unique opportunity to gather a significant amount of information about the mechanisms of such solvolysis reactions in the absence of the complicating isomerizations. We report here the kinetics of solvolysis of these two complexes in dimethyl sulfoxide (Me_2SO), *N*,*N*-dimethylformamide (DMF), *N*-methylformamide (NMF), and formamide (form) and the synthesis and characterization of some of these solvolysis products. In addition, the chloride anation of one of these products, $[Co(tren)Cl(Me_2SO)]^{2+}$, of the mechanism of the solvolysis reactions.

Experimental Section

(A) Materials. Me_2SO and DMF were Fisher certified reagents. NMF and formamide were purchased from Aldrich Chemical Co. All solvents were stored over molecular sieves and used without further purification. The salts $Mg(ClO_4)_2$, NaCl, and $AgClO_4$ were anhydrous reagent grade quality.

(B) Preparation of Compounds. (1) Dichloro(triaminotriethylamine)cobalt(III) Chloride Hemihydrate, $[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$. Dichloro(triaminotriethylamine)chromium(III) chloride, $[Cr(tren)Cl_2]Cl$, and dibromo(triaminotriethylamine)cobalt(III) bromide, $[Co(tren)Br_2]Br$, were synthesized by published methods.[13-15]

(2) Chloro(solvo)(triaminotriethylamine)metal(III) Diperchlorate (solvo = Me_2SO, DMF, NMF, form; metal = Co, Cr), $[M(tren)Cl(solvo)](ClO_4)_2$. The appropriate dichloro complex was dissolved in 10–20 mL of solvent, and 2 equiv of $AgClO_4$ was added. After the reaction was complete, the AgCl was removed by filtration, and the filtrate as poured into 100 mL of absolute ether. An oil appeared immediately, and after decantation of the ether, the oil was washed with 100–400 mL of 1:1 ethanol–ether. The ethanol–ether was decanted, and the oil was treated with 10 mL of ice-cold H_2O. After 5 min, 5 mL of a saturated aqueous $NaClO_4$ solution was added, and the mixture was cooled in ice for 2 h. The resulting crystals were filtered, washed with ethanol and ether, and air-dried. The corresponding bromo complexes of cobalt(III) were prepared in a similar manner.[16]

(C) Infrared Spectra. Infrared spectra were obtained with a Perkin-Elmer Model 457 recording spectrophotometer. Solid samples in Nujol mulls were examined between potassium bromide plates from 4000 to 600 cm^{-1}. Measurements in the 600–250-cm^{-1} region were performed with cesium bromide plates.

(D) Electronic Absorption Spectra. The visible spectra were obtained with a Beckman Acta MIV recording spectrophotometer. Approximately millimolar solutions were scanned in matched cells of 1-cm path length.

(E) Analyses. Carbon, hydrogen, and nitrogen analyses were performed by Strauss, Oxford, England. Perchlorate was analyzed by precipitation with Nitron.[17] Chromium was determined by spectrophotometric analysis of chromate at 372 nm after decomposition of the complexes and oxidation of chromium(III) with alkaline peroxide.[18]

(F) Kinetic Measurements. The basic kinetic techniques, i.e., thermostating of cells and calculation of pseudo-first-order rate

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(1) Work done by M.J.S. in partial fulfillment of the requirements for the Ph.D. degree at SUNY—Binghamton, 1980. Part of this work was presented by D.W. at the American Chemical Society Symposium on Undergraduate Research in Chemistry at SUNY—Binghamton, May 17, 1980.

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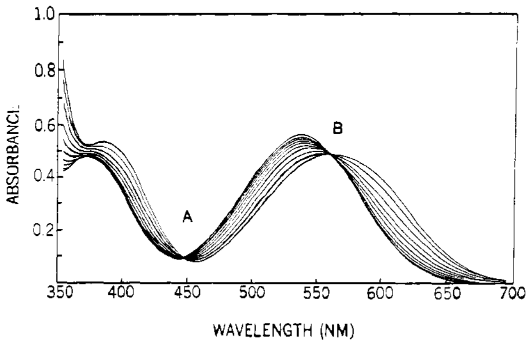

Figure 1. Spectral scans of $[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$ in formamide at 25 °C: A, $[Co(tren)Cl_2]^+$; B, $[Co(tren)Cl(form)]^{2+}$.

constants, have been described previously.[19] The reactions were carried out by either of the following procedures: (1) addition of the solid to the thermostated cell containing preheated or precooled solvent, using a device based on a Drummond micropipet, and mixing by compression of the pipet bulb; (2) withdrawing samples from solutions heated in a constant-temperature bath and quenching the reaction by cooling in ice before performing the absorbance measurements. Changes in absorbance were recorded on a Cary 14 recording spectrophotometer, a Cary 16 spectrophotometer, or a Beckman DU spectrophotometer. There was no difference in rate constants obtained by the two methods. Infinite time absorbances were obtained experimentally and triplicate runs generally agreed to better than 4%. Pseudo-first-order rate plots were linear for more than 3 half-lives.

(G) Ion-Pairing Constants (K_{IP}). These were determined with use of an Industrial Instruments Model RC-18 bridge with a variable-frequency oscillator as the source of the voltage. Ion-pairing constants were calculated by using the Fuoss equation[20]

$$\frac{F(Z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{C\Lambda(f\pm)^2}{K_{IP}\Lambda_0{}^2F(Z)}$$

where C is the unweighted molar concentration, Λ is the molar conductance, Λ_0 is the limiting molar conductance, $f\pm$ is the mean molar activity coefficient, K_{IP} is the ion-pairing constant, and $F(Z)$ is as defined previously.[20] Because of the low complex concentrations employed in this study, solvent densities and viscosities were used instead of solution values.

Results and Discussion

Solvolysis of $[Co(tren)Cl_2]^+$ and $[Cr(tren)Cl_2]^+$. The kinetics of solvolysis of both $[Co(tren)Cl_2]^+$ and $[Cr(tren)Cl_2]^+$ have been studied in Me_2SO, DMF, NMF, and formamide. Figure 1 shows the typical changes in the visible absorption spectra which accompany the primary solvolysis of chloride ion. The observed isosbestic points agree with those predicted from the spectra of the pure reactants and products and are indicative of simple stereoretentive solvolysis in each case (Table I).[16] Isomerization cannot occur due to the tripodal nature of the amine ligand, so the remaining chloride must be cis to the coordinated solvent molecule.

The lowest wavelength d–d band maximum of the product has a higher extinction coefficient than the starting material, which implies that the distortion of the complex has been increased. Theoretically, two isomers are possible for the solvolysis products, depending on whether the remaining chloride is cis or trans to the tertiary nitrogen. These two nonamine coordination sites are chemically nonequivalent.[21] The position cis to the tertiary nitrogen is in close proximity to several methylene protons, while the trans position is surrounded by amine protons. Replacement of the trans chloride would produce α-$[M(tren)Cl(solvo)]^{2+}$ (M = Cr(III), Co(III)), while replacement of the cis chloride would lead to β-$[M(tren)Cl(solvo)]^{2+}$ as the predominant product. A polar solvent molecule in the cis position would be subject to repulsive interactions with the aliphatic chains of the tren ligand. These interactions would induce more distortion in the amine, leading to a more intense ${}^1T_1 \rightarrow {}^1A_1$ band for β-$[Co(tren)Cl(solvo)]^{2+}$ and a more intense ${}^4T_{2g} \rightarrow {}^4A_{2g}$ band for β-$[Cr(tren)Cl(solvo)]^{2+}$. Although unequivocal assignment of the stereochemistry of the reaction products is impossible without a single-crystal X-ray study, these spectral data strongly suggest that the solvolysis product is the β isomer. Such spectral arguments have been used previously in the assignment of the structures of α- and β-$[Rh(tren)Cl(H_2O)]^{2+}$.[21]

The nonequivalency of these sites also provides some insight into the mechanism of these solvolysis reactions. The amine protons of tren are capable of attractive interactions with solvent molecules. Accordingly, the trans chloride in $[M(tren)Cl_2]^+$ is more susceptible to solvent interactions than the cis chloride. It is reasonable to assume, therefore, that an associative interchange (I_a) mechanism[22] would favor replacement of the trans chloride, while a dissociative (I_d) mechanism[22] would tend to occur at the position cis to the tertiary nitrogen. Our tentative assignment has the released chloride coming from the position cis to the tertiary nitrogen, so we have evidence that the solvolysis reactions of these two complexes proceed via dissociative mechanisms. The assignment is especially interesting in light of the fact that the aquation reactions of chromium(III) complexes are not believed to occur by means of an I_a mechanism. Our conclusion is not unique, however, as dissociative mechanisms have also been suggested for the solvolysis reactions of *cis*-$[Cr(en)_2Cl_2]^+$ and *cis*-$[Cr(en)_2Br_2]^+$ in DMF.[7,10]

Volumes of activation ($\Delta V^{\ddagger}$) are now often used as an aid in determining the mechanisms of ligand substitution reactions of octahedral metal complexes. These values correlate with the corresponding values of $\Delta S^{\ddagger}$. For aquation reactions, negative values of $\Delta V^{\ddagger}$ have been taken to indicate associative reactions. For the reactions presented here, the values of $\Delta(\Delta S^{\ddagger}{}_{Cr-Co})$ range from −10.2 to −17.9 cal mol^{-1} K^{-1}. In these solvents, however, the main contribution to $\Delta S^{\ddagger}$ should be the solvation of the leaving chloride ion. Thus, the more negative values of $\Delta(\Delta S^{\ddagger})$ need not be indicative of an associative mechanism but could be identified with an even more dissociated transition state. It is possible that in these solvents nucleophilic attack is hindered by the steric properties of tren and that these reactions are examples of the dissociative limit in chromium(III). If so, valuable information concerning parameter differences between I_a and I_d mechanisms at electronically similar centers could be obtained by the study of these systems. Further work on the nonaqueous chemistry of these and other metal–tren systems is in progress to determine pressure effects and other kinetic and thermodynamic data which may help in interpreting these parameters as they apply to substitution reactions in these media.

Under the conditions of the experiments reported here, the reactions of both complexes go to completion in NMF and form. However, when $[Co(tren)Cl_2]^+$ and $[Cr(tren)Cl_2]^+$ were reacted in Me_2SO and DMF, respectively, the limiting spectra indicated that the starting materials had not been completely converted to the solvolysis products. These limiting spectra are dependent on the added chloride concentration only for the chromium complex (Figure 2). The compositions of the mixtures obtained after limiting spectra had been reached were determined by the method of Drago[23] from the spectra of the pure products and reactants. All reactions in Me_2SO and

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Table II. Rate Constants (k_1 (s^{-1})) for Solvolysis of $[Co(tren)Cl_2]Cl \cdot {}^1/_2H_2O^a$

solvent	temp, °C 15.0	20.0	25.0	31.0	37.9	41.6	48.1	61.0
formamide		$(4.9 \pm 0.03) \times 10^{-4}$	$(8.27 \pm 0.01) \times 10^{-4}$	$(16.1 \pm 0.1) \times 10^{-4}$	$(34.5 \pm 0.5) \times 10^{-4}$			
Me_2SO			$(2.24 \pm 0.06) \times 10^{-5}$	$(4.89 \pm 0.03) \times 10^{-5}$		$(15.2 \pm 0.3) \times 10^{-5}$	$(32.5 \pm 0.3) \times 10^{-5}$	$(162 \pm 5) \times 10^{-5}$
DMF			$(1.18 \pm 0.05) \times 10^{-5}$	$(2.78 \pm 0.05) \times 10^{-5}$		$(11.4 \pm 0.2) \times 10^{-5}$	$(26.2 \pm 0.5) \times 10^{-5}$	$(120 \pm 4) \times 10^{-5}$
NMF	$(1.90 \pm 0.03) \times 10^{-3}$	$(3.39 \pm 0.05) \times 10^{-3}$	$(5.69 \pm 0.05) \times 10^{-3}$	$(9.83 \pm 0.08) \times 10^{-3}$				
H_2O		1.75×10^{-3}	2.96×10^{-3}					

^{a} [complex] = 7.3×10^{-4} M.

Table III. Rate Constants (k (s^{-1})) for Solvolysis of $[Cr(tren)Cl_2]Cl^a$

solvent	temp, °C 15.0	20.0	25.0	31.0	37.9	40.0	48.0	51.0	57.0	61.0
formamide		$(3.09 \pm 0.09) \times 10^{-3}$	$(4.86 \pm 0.05) \times 10^{-3}$	$(8.30 \pm 0.05) \times 10^{-3}$	$(14.6 \pm 0.3) \times 10^{-3}$					
Me_2SO			$(5.01 \pm 0.03) \times 10^{-5}$			$(18.9 \pm 0.5) \times 10^{-5}$		$(50.9 \pm 0.5) \times 10^{-5}$	$(95.3 \pm 0.6) \times 10^{-5}$	$(107 \pm 5) \times 10^{-5}$
DMF			$(1.62 \pm 0.04) \times 10^{-5}$			$(7.31 \pm 0.05) \times 10^{-5}$	$(34.1 \pm 0.6) \times 10^{-5}$		$(55.7 \pm 0.8) \times 10^{-5}$	$(77.6 \pm 0.6) \times 10^{-5}$
NMF	$(2.97 \pm 0.16) \times 10^{-2}$	$(4.31 \pm 0.09) \times 10^{-2}$	$(6.01 \pm 0.11) \times 10^{-2}$	$(8.39 \pm 0.18) \times 10^{-2}$						
H_2O			$(5.18 \pm 0.27) \times 10^{-2}$	$(8.46 \pm 0.28) \times 10^{-2}$						

^{a} [complex] = 7.3×10^{-4} M.

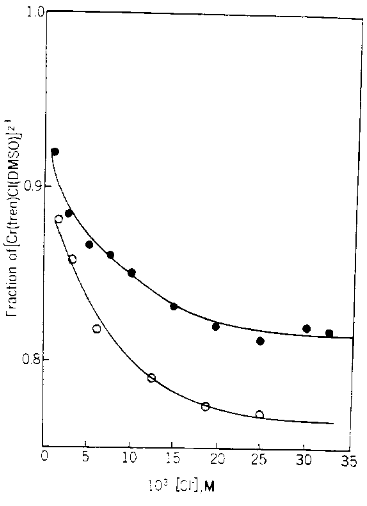

Figure 2. Fractions of $[Cr(tren)Cl(Me_2SO)]^{2+}$ (●, 57 °C) and $[Cr(tren)Cl(DMF)]^{2+}$ (○, 40 °C) present at equilibrium in the solvolysis of $[Cr(tren)Cl_2]Cl$ in Me_2SO and DMF as a function of the concentration of added chloride ion.

Table IV. Activation Parameters for Solvolysis of $[Co(tren)Cl_2]Cl \cdot {}^1/_2H_2O$ and $[Cr(tren)Cl_2]Cl$

	$[Co(tren)Cl_2]Cl \cdot {}^1/_2H_2O$		$[Cr(tren)Cl_2]Cl$	
solvent	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
formamide	20.1 ± 0.9	−4.9 ± 2.0	14.9 ± 1.0	−18.9 ± 2.0
Me_2SO	21.2 ± 1.1	−7.0 ± 2.0	17.7 ± 0.9	−18.5 ± 1.7
DMF	24.6 ± 1.0	4.0 ± 2.0	22.0 ± 0.9	−6.2 ± 1.5
NMF	17.1 ± 1.0	−11.2 ± 2.0	10.4 ± 1.1	−29.1 ± 2.0
$H_2O^{a,b}$	17.9	−10.4	12.3 ± 0.5	−23.0 ± 1.3

^{a} Reference 19. ^{b} Reference 14.

DMF were found to proceed to >75% completion. Experimental pseudo-first-order rate plots were linear for at least 3 half-lives, which indicate that interfrence from the opposing anation reactions was negligible. Previous calculations[24,25] have shown that, for reactions which proceed to 80–90% completion, calculations of rate constants which ignore the reverse reaction give results identical with those obtained by the complicated first-order-opposed-second-order method. Thus, all rate constants presented here were calculated as described previously.[19]

Tables II and III give the specific rate constants, k_1, for the reactions of $[Co(tren)Cl_2]^+$ and $[Cr(tren)Cl_2]^+$ in these solvents at various temperatures. The activation energies were calculated at 25 °C from the linear Arrhenius plots; these values were used to calculate the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, which are listed in Table IV. If uncertainties are taken into consideration, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ give accurate vaues of k_1 (25 °C).

For both complexes, correlations may be made between k_1 and the polarities of the solvents. The data in Table II and III show that the rate constants for replacement of chloride by a solvent molecule at 25 °C are in the order DMF < Me_2SO < form < H_2O < NMF. The dielectric constants of these solvents are in the order NMF > form > H_2O > Me_2SO > DMF. These results offer further support for a dissociative mechanism.

A solvent with larger dielectric constant will better facilitate the separation of charge in the transition state of dissociative-type reactions.[3] Thus, the rate constant for solvolysis should increase with increasing dielectric constant if the

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Table V. Rate Constants (s^{-1}) for Solvolysis of $[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$ and $[Cr(tren)Cl_2]Cl$ under Various Conditions of Added Electrolyte[a,b]

added electrolyte	$[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$		$[Cr(tren)Cl_2]Cl$	
	10^4k^c	10^3k^d	10^3k^c	10^2k^d
0.02 M $Mg(ClO_4)_2$	8.22 ± 0.06	3.35 ± 0.04	5.01 ± 0.04	6.15 ± 0.16
0.10 M $Mg(ClO_4)_2$	8.24 ± 0.08	3.33 ± 0.05	4.93 ± 0.03	6.02 ± 0.18
0.005 M NaCl	8.27 ± 0.05	3.40 ± 0.05	4.88 ± 0.06	5.94 ± 0.14
0.010 M NaCl	8.23 ± 0.06	3.32 ± 0.06	4.90 ± 0.05	6.07 ± 0.12

[a] [complex] = 7.3 × 10^{-4} M. [b] At 25 °C. [c] Solvent = formamide. [d] Solvent = NMF.

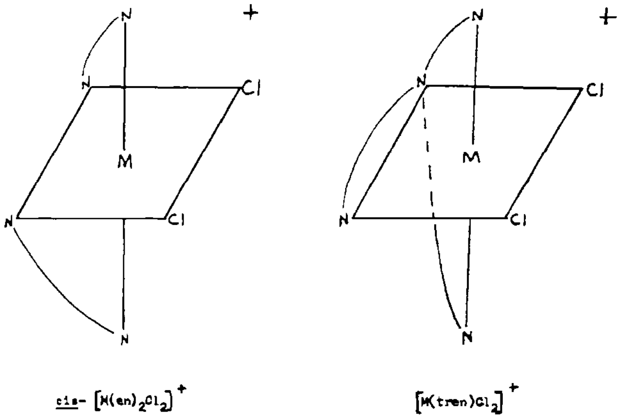

Figure 3. Structures of the *cis*-$[M(en)_2Cl_2]^+$ and $[M(tren)Cl_2]^+$ cations (M = Co(III), Cr(III)).

mechanism is I_d to be in complete agreement with the experimental results (Table II and III). The differences are larger for the Cr(III) complexes than for the Co(III) complexes contrary to what would be expected if Cr(III) centers were reacting more associatively and dielectric constants were less important.

In Table V are given the rate constants of solvolysis of both complexes in NMF and formamide under various conditions of added electrolytes. Increasing ionic strength has no effect on k_1, and the rate constants are independent of the free chloride concentration, results expected for reactions which go to completion. This completeness in H_2O, NMF, and formamide is due to the good solvating ability of these liquids, as well as their good ligating abilities.

Since previous studies[2,4,7,26] on similar systems have shown that ion pairing is significant in both Me_2SO and DMF, we have determined K_{IP} values for $[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$ and $[Cr(tren)Cl_2]Cl$ in these solvents at 25 °C. For the Co(III) complex these values are 278 ± 25 and 5341 ± 65 M^{-1} in Me_2SO and DMF, respectively, while the corresponding values for the Cr(III) complex are 211 ± 30 and 5057 ± 45 M^{-1}. Comparison with the analogous bis(ethylenediamine) species[27] shows that K_{IP} is significantly lower for the tren complexes. This can be rationalized on the basis of the differences in the structures of the two systems (Figure 3). It has been suggested[28] that *cis*-dihalo complexes form ion pairs in which the counteranion is located in the secondary coordination sphere, away from the complexed halide ions, and is hydrogen bonded to the amine protons. Clearly, the tren complexes, the favorable site for ion pairing is blocked by the C–C backbone of the tren ligand, and ion pairing should be reduced relative to the en complex.

Table VI. Rate Constants (s^{-1}) for Solvolysis of $[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$ and $[Cr(tren)Cl_2]Cl$ in DMF and Me_2SO under Various Conditions of Added Chloride Ion

$10^3[Cl^-]$, M	$[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O^a$		$[Cr(tren)Cl_2]Cl^a$	
	$10^3k^{b,e}$	$10^3k^{b,f}$	$10^4k^{c,e}$	$10^5k^{d,f}$
0.73	1.62 ± 0.05	1.20 ± 0.04	9.53 ± 0.05	7.31 ± 0.05
1.00			8.99 ± 0.08	7.17 ± 0.07
1.23			8.65 ± 0.11	7.06 ± 0.03
2.50			7.43 ± 0.06	6.87 ± 0.06
5.00	1.62 ± 0.04	1.21 ± 0.06	6.59 ± 0.08	6.62 ± 0.08
7.50			5.87 ± 0.10	6.50 ± 0.07
10.00	1.65 ± 0.07	1.23 ± 0.05	5.50 ± 0.03	6.43 ± 0.05
12.50			4.95 ± 0.06	6.39 ± 0.06
15.00			4.40 ± 0.04	6.37 ± 0.02
20.00			3.83 ± 0.07	6.48 ± 0.06
25.00			3.51 ± 0.01	
35.00			3.46 ± 0.05	
42.10			3.47 ± 0.02	
50.00			3.45 ± 0.06	6.39 ± 0.08

[a] [complex] = 7.3 × 10^{-4} M. [b] 61.0 °C. [c] 57.0 °C. [d] 40.0 °C. [e] Solvent = Me_2SO. [f] Solvent = DMF.

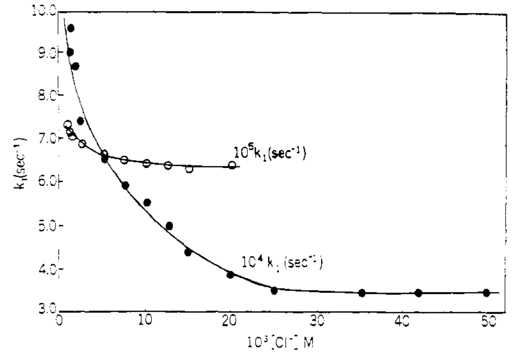

Figure 4. Pseudo-first-order rate constants (k_1) vs. $[Cl^-]$ for the solvolysis of $[Cr(tren)Cl_2]Cl$ in Me_2SO (●, 57 °C) and DMF (○, 40 °C).

Table VI lists the values of k_1 for both complexes in Me_2SO and DMF as a function of added chloride ion. The effect of chloride ion on the rates of solvolysis is due to the extensive ion pairing in these solvents. Conceivably, the ion pair could react faster, slower, or at the same rate as the free cation. For $[Cr(tren)Cl_2]Cl$, the attainment of a limiting rate constant at high chloride concentrations is due to complete formation of ion pairs, and this rate is that of solvolysis of the ion pair (Figure 4). The lack of chloride dependence for $[Co(tren)Cl_2]Cl\cdot{}^1/_2H_2O$ implies either that ion-pair formation is complete even at the lowest chloride concentrations used or that the free cation and ion pair react at the same rate.

It is significant that the equilibrium compositions in Me_2SO and DMF for the Cr(III) complex are chloride ion dependent (Figure 2). The attainment of a limiting composition is due to the stabilization of the solvo complexes by the formation of ion triplets. In the Co(III) systems, however, significant ion-triplet formation must occur even at low chloride concentrations, thus accounting for the lack of dependence of the equilibria on chloride ion.

For both complexes, solvolysis is more complete in Me_2SO than DMF. This result has been observed elsewhere[10,29] and is due to the relative solvating and ligating abilities of the two liquids. In addition, more solvo complex is present at equilibrium when $[Cr(tren)Cl_2]Cl$ is the starting material. This reflects the greater tendency of Cr(III) to form stable species with oxygen donor ligands.[30-32]

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Table VII. Values of k_{Cl} for the Anation of $[Co(tren)Cl(Me_2SO)]^{2+}$ [a]

T, °C	$10^3[Cl^-]$, M	10^3k_{Cl}, s^{-1}	T, °C	$10^3[Cl^-]$, M	10^3k_{Cl}, s^{-1}
50.00	80	1.32	60.00	50	2.93
60.00	5.0	1.64	60.00	60	3.14
60.00	7.5	1.83	60.00	70	3.15
60.00	15	2.02	60.00	80	3.17
60.00	30	2.42	65.00	80	5.42
60.00	40	2.67	70.00	80	8.09

[a] [complex] = 2.0×10^{-3} M. $\Delta H^{\ddagger} = 19.57 \pm 1.3$ kcal mol^{-1}.

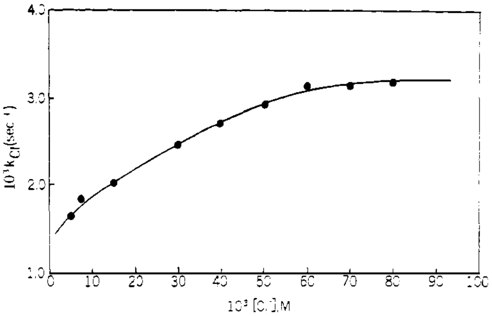

Figure 5. Pseudo-first-order rate constant (k_{Cl}) vs. $[Cl^-]$ for the chloride anation of $[Co(tren)Cl(Me_2SO)]^{2+}$ in Me_2SO at 60 °C.

The kinetics of the chloride anation of $[Cr(tren)Cl(Me_2SO)](ClO_4)_2$ were measured as a function of added chloride ion concentration and temperature. The results are presented in Table VII. A plot of k_{Cl} vs. $[Cl^-]$ is shown in Figure 5. The shape of Figure 5 is similar to that expected if anation occurs via an $(S_N1)_{IP}$ mechanism.[2,4,33] This provides further evidence that the solvolysis reactions of these complexes are essentially dissociative. By the principle of microscopic reversibility, both the solvolysis of $[Co(tren)Cl_2]^+$ in Me_2SO and the anation of $[Co(tren)Cl(Me_2SO)]^{2+}$ must pass through the same transition state. Since there is a great deal of bond breaking in the transition state of the anation reaction, the same must be true for the solvolysis reaction.

Synthesis of New Complexes and Spectral Studies. A number of new Co(III)- and Cr(III)-tren complexes containing neutral nonaqueous ligands have been synthesized via the Ag(I)-assisted solvolysis of the dihalo starting materials.

Pertinent infrared spectra data are presented in Table VIII.[16] All complexes containing a coordinated amide ligand exhibit carbonyl stretching frequencies in the range 1675–1640 cm^{-1}. These absorptions are of lower energy than in the free amides and are diagnostic of metal–oxygen bonding. Further evidence for oxygen coordination is found in the positions of the O–C–N deformation bands of the amides. These absorptions occur up to 100 cm^{-1} higher when the amide is coordinated to the metal. The compounds $[Co(tren)Cl(DMF)](ClO_4)_2 \cdot DMF$ and $[Co(tren)Br(DMF)](ClO_4)_2 \cdot DMF$ each show two carbonyl absorptions, one of which is the same as in the free ligand. This is indicative of a noncoordinated DMF molecule and is consistent with the results of elemental analysis.

The metal–Me_2SO complexes show sharp absorptions near 940 cm^{-1}, which can be assigned to the S–O stretching vibration. Again, coordination to the metal through the oxygen atom is indicated, since this band appears at 1055 cm^{-1} in neat Me_2SO.

The electronic spectral data for the new complexes are given in Table IX.[16] The data for the starting materials and the corresponding haloaquo species are included for comparison. There is a close similarity beween the electronic spectra of the solvo and haloaquo complexes. The metal–water bonds must be through the oxygen atom; the spectral similarities are a further indication that all the nonaqeous ligands are oxygen bonded to the metal center.

Examination of the data in Table IX reveals that the d–d band maxima for all solvo species occur at higher energies relative to the starting materials and at wavelengths similar to those observed for the aquo complexes. Thus, the ligand field strengths of all the solvo ligands are greater than those of the bromide and chloride ions. Comparisons among the individual solvent ligands are more difficult, though due to the small difference in the spectra of the complexes. Nevertheless, the λ_{max}'s appear to be roughly in the order NMF < form < Me_2SO < DMF. This is the reverse order of the dielectric constants of the solvents and may reflect the relative oxygen-donor capabilities of these liquids.

In summary, the solvolysis reactions of $[Co(tren)Cl_2]^+$ and $[Cr(tren)Cl_2]^+$ in NMF, formamide, Me_2SO, and DMF have been found to occur via dissociative mechanisms. Ion pairing is extensive in DMF and Me_2SO and exerts profound influence on the equilibria and solvolysis rates. The chloride anation of one solvolysis product, $[Co(tren)Cl(Me_2SO)]^{2+}$, occurs via an $(S_N1)_{IP}$ pathway. A number of these solvolysis products have been isolated and characterized.

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Registry No. $[Co(tren)Cl_2]Cl$, 20023-19-2; $[Cr(tren)Cl_2]Cl$, 57718-97-5; $[Co(tren)Cl(Me_2SO)](ClO_4)_2$, 75717-89-4; $[Co(tren)Cl(DMF)](ClO_4)_2$, 75717-91-8; $[Co(tren)Cl(NMF)](ClO_4)_2$, 75717-93-0; $[Co(tren)Cl(form)](ClO_4)_2$, 75717-95-2; $[Co(tren)Br(DMF)](ClO_4)_2$, 75717-97-4; $[Co(tren)Br_2]Br$, 23949-79-3; $[Co(tren)Br(NMF)](ClO_4)_2$, 75717-99-6; $[Cr(tren)Cl(Me_2SO)](ClO_4)_2$, 75732-06-8; $[Cr(tren)Cl(DMF)](ClO_4)_2$, 75732-08-0; $[Cr(tren)Cl(NMF)](ClO_4)_2$, 75732-10-4; $[Cr(tren)Cl(form)](ClO_4)_2$, 75732-12-6; Me_2SO, 67-68-5; DMF, 68-12-2; NMF, 123-39-7; form, 75-12-7.

Supplementary Material Available: Syntheses of new complexes of the general formula $[M(tren)X(solvo)](ClO_4)_2$ (solvo = Me_2SO, DMF, NMF, form; X = Cl, Br; M = Co, Cr), with their analyses and spectral data (Tables I, VIII, and IX) (9 pages). Ordering information is given on any current masthead page.

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