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Isomerization of Some *trans*-Chloro(solvent)bis(ethylenediamine)chromium(III) Complexes in Dimethylformamide and Dimethyl Sulfoxide

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trans-$Cr(en)_2(DMF)Cl^{2+}$ isomerizes completely to the cis isomer in dimethylformamide (DMF); $k_{tc} = 2.2 \times 10^{-5}$ sec^{-1} (50°), $\Delta H^\ddagger = 24.4$ kcal mol^{-1}, and $\Delta S^\ddagger = -4.5$ cal mol^{-1} deg^{-1}. Similarly, *trans*-$Cr(en)_2(DMSO)Cl^{2+}$ isomerizes to its cis form in dimethyl sulfoxide (DMSO); $k_{tc} = 3.7 \times 10^{-5}$ sec^{-1} (50°), $\Delta H^\ddagger = 22.3$ kcal mol^{-1}, and $\Delta S^\ddagger = -10.0$ cal mol^{-1} deg^{-1}. In the absence of added chloride ion and at lower temperatures (<60°), net ethylenediamine loss is not significant (<5%) in either isomerization reaction but becomes more important at higher temperatures; it is the dominant reaction in the presence of added chloride ion. At equilibrium, only cis isomers are observed; in DMSO, 5% chloride loss to *cis*-$Cr(en)_2(DMSO)_2^{3+}$ is found while there is no detectable chloride loss from the *cis*-$Cr(en)_2(DMF)Cl^{2+}$ complex in DMF. Evidence is presented to show that trans to cis isomerization proceeds through dissociation of a neutral leaving group, *i.e.*, *via* solvent exchange or a "one-ended" (unidentate) ethylenediamine intermediate. Reaction involving the direct exchange of solvent appears to require a large degree of nonretentive ligand substitution. Discussed are the factors related to the accumulation (and intermediacy) of trans solventochromium(III) and -cobalt(III) complexes in solvolysis and in particular the *trans*-chloro(solvento)chromium(III) isomers in the solvolysis reactions of *cis*- and *trans*-$Cr(en)_2Cl_2^+$ in DMF and DMSO.

Introduction

Recently the solvolyses of *cis*- and *trans*-$Cr(en)_2Br_2^+$ in DMSO[1] and DMF[2a] were studied. In that work the reactions of the trans isomer were shown to proceed exclusively through the *trans*-$Cr(en)_2(sol)Br^{2+}$ isomer, whereas only the *cis*-$Cr(en)_2(sol)Cl^{2+}$ ions were found in the corresponding reactions of the *trans*-$Cr(en)_2Cl_2^+$ complex in DMF[3] and DMSO.[4] Since the full range of *cis*- and *trans*-halo(solvento) complexes have been now isolated,[2-5] we initially examined the "intermediate" case of *trans*-(and *cis*-)$Cr(en)_2ClBr^+$ solvolysis in DMF and DMSO[2a] to resolve the apparent stereochemical anomaly. The present study of the *trans*-$Cr(en)_2(sol)Cl^{2+}$ isomers, found as the exclusive products in *trans*-$Cr(en)_2ClBr^+$ solvolysis but not observed as intermediates in the original dichloro systems,[1,2a] completes this work.[6,7] There are now sufficient data to rationalize the stereochemistry and sequence of reactions observed in chromium(III) solvolysis reactions in all these systems. Unfortunately the analogous trans solventocobalt(III) complexes have not been isolated but have been "seen"[8] and some rates of isomerization measured; their behavior is seen to be consistent with the rationale presented here.

Experimental Section

Complexes. *cis*- and *trans*-$[Cr(en)_2(DMF)Cl](ClO_4)_2$, *trans*-$[Cr(en)_2(DMSO)Cl](ClO_4)_2$, *cis*-$[Cr(en)_2(DMSO)Cl](NO_3)ClO_4$, *cis*-$[Cr(en)_2(DMF)_2](ClO_4)_3$ (and *cis*-$[Cr(en)_2(DMF)_2]NO_3(ClO_4)_2\cdot H_2O$), and *cis*-$[Cr(en)_2(DMSO)_2](ClO_4)_3$ were from batches used in concurrent work; complete characterization is given elsewhere.[2] All complexes used were freshly prepared.[5]

Solvents, Other Materials, and Kinetic Technique. Full details have been described.[2,9] All reactions were followed spectrophotometrically on an automatic recording Hitachi EPS-3T instrument by the continuous-scan technique. First-order rate constants were calculated in the usual way at wavelengths where the absorbance changes were greatest. Potentiometric titrations for free chloride were performed on equilibrated solutions as detailed earlier.[2a]

Table I. Observed and Calculated Isosbestic Points for the Isomerization of *trans*-$Cr(en)_2(sol)Cl^{2+}$ in sol

Obsd λ (ε)^{a,b}	Calcd λ (ε)
trans-$Cr(en)_2(DMSO)Cl^{2+} \xrightarrow{DMSO}$	*cis*-$Cr(en)_2(DMSO)Cl^{2+}$
436.5 (26.8)	436 (26.7)
458 (26.4)	458 (25.8)
592 (20.0)^c	589 (20.8)
trans-$Cr(en)_2(DMF)Cl^{2+} \xrightarrow{DMF}$	*cis*-$Cr(en)_2(DMF)Cl^{2+}$
432 (26.4)^d	431 (25.8)
445 (25.6)^d	446 (25.0)
579 (22.3)^e	579 (22.3)

^{a} λ, nm; ε, M^{-1} cm^{-1}. ^{b} Also an ill-defined isosbestic point in the range 350–360 nm. ^{c} $T = 64°$; temperature dependent. ^{d} Close to an "isosbestic line," 430–445 nm. ^{e} $T = 40°$; temperature dependent.

Results

Isomerization of *trans*-$Cr(en)_2(DMSO)Cl^{2+}$ in DMSO. In Figure 1 we show the spectral changes for this isomerization; in Figure 2, the pure component absorption spectra. Sharp isosbestic points were observed for at least 3 $t_{1/2}$ and the results (Table I) suggest simple isomerization. Slow (and only slight) Cl^- loss from the cis product occurs after several $t_{1/2}$'s and does not interfere. We note that, at the highest temperature studied (68°), the lowest energy isosbestic point is shifted some 3–5 nm to lower energies from that expected for simple isomerization. This is qualitatively what is expected for an ethylenediamine loss parallel reaction path,[2b] but it is clear (Table I) that this reaction path is minor (<5%).

Plots of ln $|D - D_\infty|$ were linear for (2–3)$t_{1/2}$, and the same value (±2%) for k_{tc} was obtained for calculations made at

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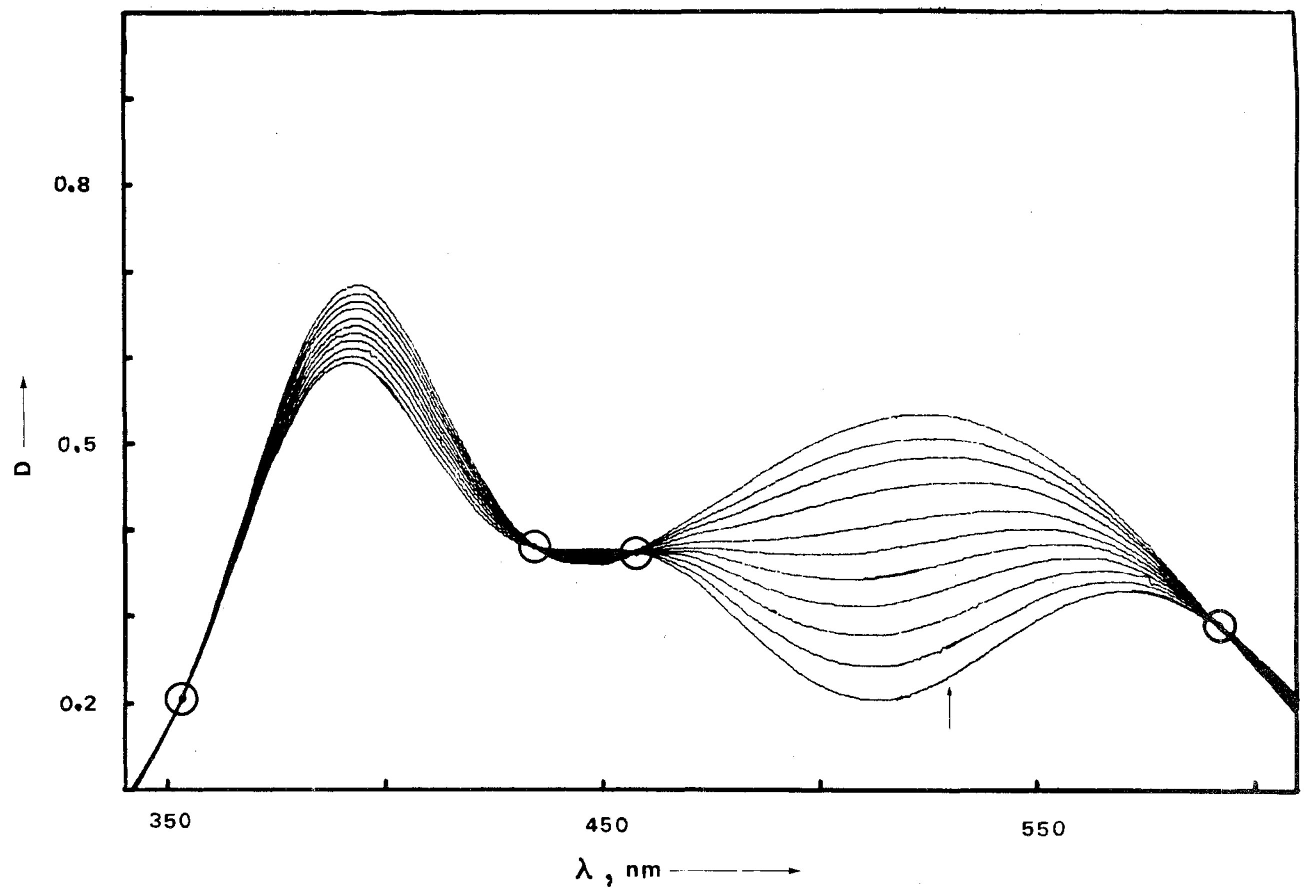

Figure 1. Spectral changes accompanying the isomerization of *trans*-$Cr(en)_2(DMSO)Cl^{2+}$ in DMSO. $[Complex]_0 = 1.45 \times 10^{-2}\ M$, 64°. Scans cover a period of approximately $1t_{1/2}$.

Table II. First-Order Rate Constants for the Reaction

$$trans\text{-}Cr(en)_2(DMSO)Cl^{2+} \xrightarrow[DMSO]{k_{tc}} cis\text{-}Cr(en)_2(DMSO)Cl^{2+}$$

$10^2[complex]_0, M$	T, °C	10^5k_{tc},[a,b] sec^{-1}	$10^2[complex]_0, M$	T, °C	10^5k_{tc},[a,b] sec^{-1}
1.61	49.65	4.03	1.42	58.75	10.7
1.54	54.5	6.88	1.44	63.0	16.3
1.15	57.6	9.30, 9.48[c]	1.42	66.1	22.7
1.15	57.6	9.65	1.04	68.05	27.7

[a] ±3%. [b] Calculated at 520 nm. [c] Calculated at 400 nm.

Table III. Activation Parameters for the Isomerizations

$$trans\text{-}Cr(en)_2(sol)Cl^{2+} \xrightarrow[sol]{k_{tc}} cis\text{-}Cr(en)_2(sol)Cl^{2+}$$

System (sol)	10^5k_{tc} (50°), sec^{-1}	$\Delta G^{\ddagger}$ (50°)[a]	E_a[a]	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]
DMSO	3.7	25.5	22.9	22.3	−10.0
DMF	2.2	25.9	25.0	24.4	−4.5

[a] kcal mol^{-1}; ±0.5 (DMSO), ±1.0 (DMF). [b] cal mol^{-1} deg^{-1}.

Table IV. First-Order Rate Constants for the Isomerization

$$trans\text{-}Cr(en)_2(DMF)Cl^{2+} \xrightarrow[DMF]{k_{tc}} cis\text{-}Cr(en)_2(DMF)Cl^{2+}$$

$10^2[complex]_0, M$	T, °C	10^5k_{tc},[a,b] sec^{-1}	$10^2[complex]_0, M$	T, °C	10^5k_{tc},[a,b] sec^{-1}
1.05	40.0	0.67	1.03	60.95	7.8
2.62	50.8	2.2	1.07	66.6	14.0[c]
1.83	56.7	7.0[c]	1.03	66.8	12.3
1.74	60.6	8.3[c]	1.35	68.95	26.7[c]
1.03	60.95	8.0, 7.8[d]			

[a] ±10%. [b] Calculated at 510 nm. [c] Rate constant too high; curved rate plots (see text). [d] Calculated at 500 nm.

several wavelengths (400, 510, 520, and 530 nm) on the assumption that *cis*-$Cr(en)_2(DMSO)Cl^{2+}$ is the only product and that back-reaction is negligible. The discrepancy is greater (±5%) at the highest temperatures; Cl^- loss from *trans*-$Cr(en)_2(DMSO)Cl^{2+}$ does not account for this observation, and undoubtedly en loss is occurring. We have made no attempt to isolate the mono(ethylenediamine) product since the path is barely significant, but it should be noted that in the reactions of *trans*-$Cr(en)_2(sol)_2{}^{3+}$ (in DMF and DMSO, no added halide ion) loss of en is a significant side reaction (~20%) to isomerization and there we have been able to account quantitatively for both reaction paths through the isolation of the mono(ethylenediamine) products, $Cr(en)(sol)_4{}^{3+}$. In this latter work we have shown[2] that en loss is more significant at higher temperatures.

Isomerization rate constants and activation parameters are given in Tables II and III. Rate constants were reproducible to ±3%; activation energies are ±0.5 kcal mol^{-1}.

After equilibrium is established, the spectrum of the product passes through the isosbestic points in the *cis*-$Cr(en)_2(DMSO)Cl^{2+}$ and *cis*-$Cr(en)_2(DMSO)_2{}^{3+}$ spectra; this spectrum is exactly reproduced by either *cis*-$Cr(en)_2(DMSO)Cl^{2+}$ or *cis*-$Cr(en)_2(DMSO)_2{}^{3+}$ plus 1 equiv of chloride ($N(C_2H_5)_4{}^+$) under equilibrium conditions (80°) and the composition 95 ± 1% *cis*-$Cr(en)_2(DMSO)Cl^{2+}$ and 5 ± 1% *cis*-$Cr(en)_2(DMSO)_2{}^{3+}$ is obtained through calculation at several wavelengths. Titration of free chloride confirmed this analysis (5%).[10]

Isomerization of *trans*-$Cr(en)_2(DMF)Cl^{2+}$ in DMF. This reaction is quite similar to its DMSO analog; the relevant data are given in Tables I, III, and IV. The reaction is simple isomerization with some evidence for en loss at higher tem-

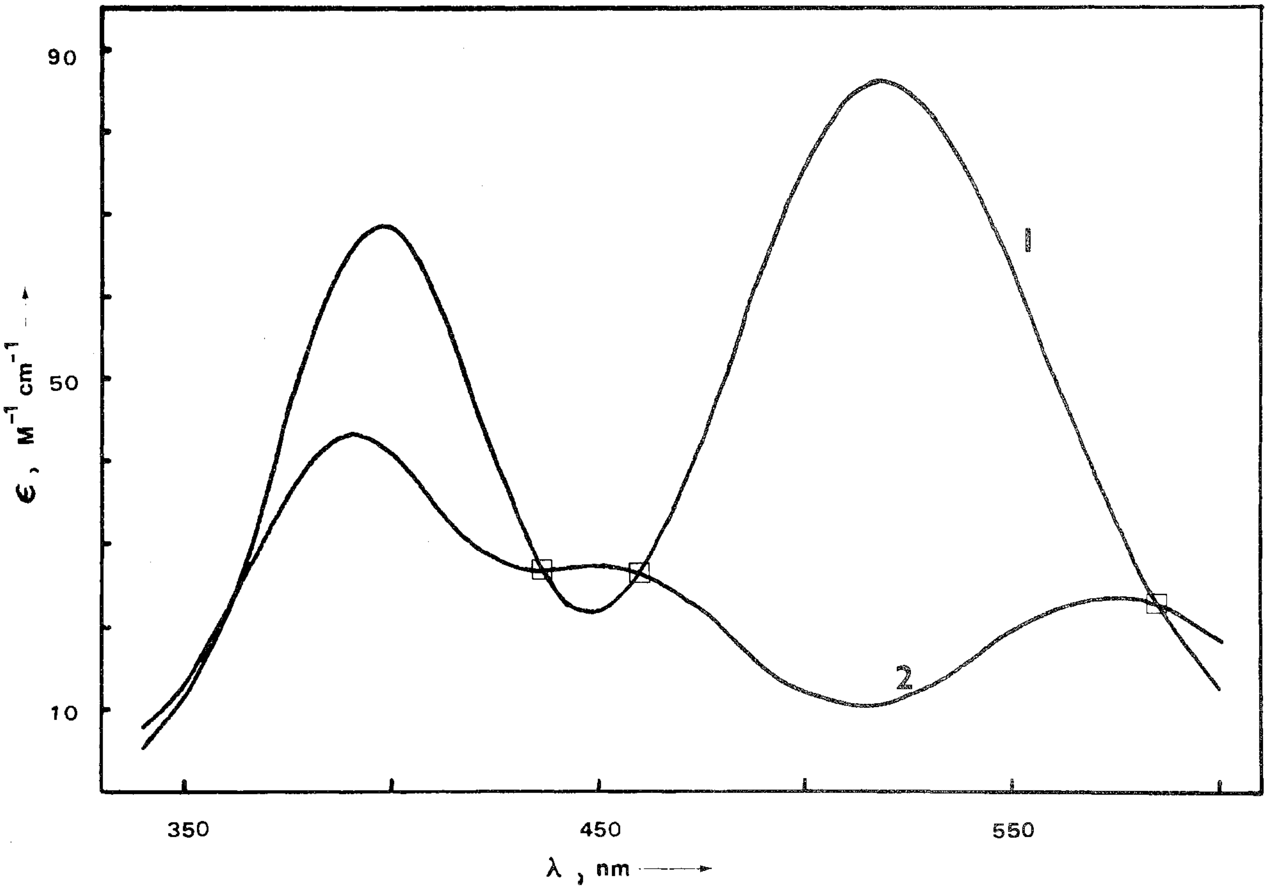

Figure 2. Visible spectra of *cis-* (1) and *trans*-Cr(en)$_2$(DMSO)Cl^{2+} (2) in DMSO at 25°.

peratures. Sharp isosbestic points were maintained up to $2t_{1/2}$; first-order rate plots were linear over this period. Problems associated with an uncharacterized catalysis[11] similar (although not as severe) to those reported[2b] for the reactions of *trans*-Cr(en)$_2$(DMF)Br^{2+} and *trans*-Cr(en)$_2$(DMF)$_2$$^{3+}$ in DMF were occasionally observed. This catalysis was apparent as a shift in the normally sharp isosbestic points and curved rate plots which led to high values for k_{tc} (Table IV); runs free from such complications were therefore fairly easily distinguished, although the kinetic data are less precise than for the DMSO reaction. Rate constants (uncatalyzed thermal reaction) are accurate to ±10% and activation energies to ±1 kcal mol^{-1}.

No detectable chloride loss occurs with *cis*-Cr(en)$_2$-(DMF)Cl^{2+} in DMF, at least before solvent decomposition is evident.

Reactions in the Presence of Added Chloride Ion. Both the DMF and DMSO reactions were completely different in the presence of added [N(C$_2$H$_5$)$_4$]Cl (greater than or equal to the stoichiometric amount). Known Cr(en)$_2$ complex spectra could not account for the product light absorption; it seems very likely that ethylenediamine is being liberated. Similar observations have been made with this same[7] and other trans-solvento complex reactions[1,2,7] in DMF and DMSO. Thus no stereochemical or kinetic information is available from these experiments other than to note that these reactions are reproducible and appear to be relatively rapid and that en is released.

Discussion

Equilibria. The equilibrium data are consistent with the now well-established trends in Cr(III)[1-4,7] and analogous Co(III) systems:[8,12] (i) the tendency to cis isomers in dipolar aprotic media and with increasing formal charge on the complex, (ii) more extensive solvolysis in DMSO over DMF, and (iii) more extensive solvolysis of bromo complexes over chloro complexes, particularly for Cr(III).[2a]

Isomerization. Both *trans*-Cr(en)$_2$(DMF)Cl^{2+} and *trans*-Cr(en)$_2$(DMSO)Cl^{2+} isomerize extremely slowly in their respective solvents ($t_{1/2}$ = 540 and 320 min, respectively, 50°); the *trans*-Co(en)$_2$(DMF)Cl^{2+} analog is reported[8] to isomerize in DMF with $t_{1/2}$ = 3.5 min (50°).[13] It is tempting to suggest that the Co–Cr rate differences (Co is faster by a factor of ~150) reflect in large part the stereochemistries of solvent exchange; Cr(III) is expected to be stereoretentive[2,14] while Co(III) undoubtedly exchanges with significant stereochemical change.[1,8] However, as will be seen, the precise explanation of the differences in the two metal systems is certainly more complicated than this and requires the recognition of many determining factors (see, for example, ref 15).

We pointed out previously[2b] that the isomerization rates of each of the *trans*-chloro(solvento)chromium(III) complexes are very nearly identical with their bromo analog rates. This seems to exclude rate-determining halide solvolysis (*i.e.*, isomerization *via* a bis(solvento) complex or halide-free pentacoordinate intermediate). Moreover, the reactions of the *cis-* and *trans*-bis(solvento) complexes[1,2,7] are not consistent with their being reaction intermediates.

Other results[2b] reveal that within the more general series *trans*-Cr(en)$_2$(sol)X^{n+} (X = Cl, Br, DMF, DMSO), where the complex formal charge is also varied, the isomerization rates are remarkably similar; these results are consistent with rate-determining dissociation of a neutral leaving group. Watts has reached a similar conclusion for *trans*-Cr(en)$_2$-(DMSO)Br^{2+} isomerization in DMSO, the rate of which was found to be insensitive to bromide ion association; this result is clearly inconsistent with rate-determining bromide dissociation.[1] By analogy with well-studied Co(III),[16] a

Table V. Relative Rates of Solvolysis and Subsequent Isomerization in $Cr(en)_2Cl_2^+$-sol Systems[a]

Substrate	Reaction	Solvent	$10^6k(50°)$, sec^{-1}
cis-$Cr(en)_2Cl_2^+$	Solvolysis[b]	DMSO	50.1
		DMF	23.3
trans-$Cr(en)_2Cl_2^+$	Solvolysis[b]	DMSO	3.7
		DMSO[c]	15.0
		DMSO[d]	31.3
		DMF	7.0
trans-$Cr(en)_2(sol)Cl^{2+}$	Isomerizn	DMSO	36.3[e]
			37.5
		DMF	22.0[e]

[a] No added chloride; data from ref 3, 4, and 7. [b] Statistically *un*corrected (factor of 2). [c] Cl^- exchange; k_{ex} *vs.* $[Cl^-]_0$ extrapolated to zero $[Cl^-]_0$. [d] Cl^- exchange; $[Cl^-]_0 = 36.8 \times 10^{-3}$ *M*. [e] This work.

solvent-exchange process would seem likely.

Preliminary results[2c] on the isomerization of *trans*-$Cr(en)_2(DMF)Cl^{2+}$ in DMSO show that *cis*-$Cr(en)_2(DMSO)Cl^{2+}$ is the exclusive product and that ethylenediamine loss is not significant. Moreover the rate of isomerization in DMF is essentially the same as in DMSO. Although it is conceivable that *trans*-$Cr(en)_2(DMF)Cl^{2+}$ isomerizes directly to *cis*-$Cr(en)_2(DMF)Cl^{2+}$ in DMSO which, at the very least, would preclude a solvent-exchange mechanism,[17] direct observation of this product is not possible since a faster (by a factor of ~50[2c]), subsequent solvent-interchange process leads to *cis*-$Cr(en)_2(DMSO)Cl^{2+}$. It is clear, however, that if solvent exchange is the means to isomerization, then it must occur with complete stereochemical change;[18] this is clearly uncharacteristic of Cr(III) substitution.[14]

The apparent facility with which *trans*-$Cr(en)_2$ complexes release amine in their reactions suggests an alternative mechanism, namely, the dissociation and rechelation of the complexed chelate. Note that the effect of acid in aqueous systems which can "trap" the unidentate chelate[19] is akin to the effect of added chloride in the present work; amine loss is promoted.[2,7] This supports the suggestion that en is dissociating although significant net loss of en is not observed except in the presence of added chloride ion. However, the question of whether the release of amine is simply a side reaction or whether it plays an important role in isomerization remains equivocal. The absence of acid in these dipolar aprotic solvent reactions must favor the rechelation of the amine which undoubtedly is dissociating, but this may simply be retentive and therefore play no part in the isomerization.

A recent result[2c] which supports a case for solvent exchange concerns the isomerization of *trans*-$Cr(NH_3)_4(DMSO)Cl^{2+}$ in DMSO. NH_3 loss is not observed, and, further, the en dissociation mechanism is not possible, yet we find a rate of isomerization ($k(58°) = 5.7 \times 10^{-5}$ sec^{-1}) very similar to that of the bis(ethylenediamine) analog. The reduced reactivity (by a factor of ~2) of the tetraamine is only slight and is fully consistent with the usual rate differences observed between the two tetraamine systems for the reactions of a variety of both cis and trans complexes in dipolar aprotic solvents.[2b]

Intermediacy of Trans Solventochromium(III) Complexes in Solvolysis. In Table V we give the solvolysis and isomerization rate constants in the dichlorochromium(III) systems. It can be seen that solvolysis of the cis isomers must proceed with retention in both solvents, since only the *cis*-chloro(solvento) products are observed[3,4] and since we now see that the trans isomers if formed would not isomerize sufficiently rapidly to escape detection. Both trans- to cis-solvento complex isomerizations are, however, more rapid than the generating *trans*-dichloro solvolysis reactions by a factor of ~12 (DMSO) or 3 (DMF). In part this results from a retentive chloride-exchange path for the solvolysis of the *trans*-$Cr(en)_2Cl_2^+$ complex in DMSO and possibly a similar situation pertains in DMF. The *trans*-chloro(solvento) complexes investigated in the present work were not detected in the original study[3,4] of the system, since it transpires that the spectra of *trans*-$Cr(en)_2Cl_2^+$ and *trans*-$Cr(en)_2(sol)Cl^{2+}$ are quite similar.[7] We note, however, that their presence should be evident in kinetic plots.[20,21] Thus quite possibly the reported trans solvolysis rates and stereochemistry (no added chloride) are in error since the data of Table V suggest[22] some accumulation of *trans*-$Cr(en)_2(sol)Cl^{2+}$ commencing with *trans*-$Cr(en)_2Cl_2^+$ (particularly in DMF).

The dichloro–DMSO system has recently been reinterpreted with a knowledge of *trans*-$Cr(en)_2(DMSO)Cl^{2+}$ reactivity.[7] Although the rates and stereochemistry of *trans*-$Cr(en)_2Cl_2^+$ solvolysis were not remeasured, it was suggested that the solvolysis could proceed through the *trans*-$Cr(en)_2(DMSO)Cl^{2+}$ complex at low or zero added chloride. Reaction through this same ion was specifically excluded for the added chloride reactions since en loss dominates the *trans*-chloro(solvento) ion but not the *trans*-dichloro complex solvolysis. Similar conclusions may now be drawn for the analogous DMF system,[3] although the precise stereochemistry of *trans*-dichloro substitution is not known and chloride-exchange data are not available.

Finally, we should note that since a significant Cr–N cleavage path exists in the *trans*-$Cr(en)_2Cl_2^+$ aquation,[24] this probably also exists in the even slower DMSO or DMF solvolysis, although net en loss is not observed in these latter two solvents except at higher temperatures. This may profoundly influence the stereochemistry of *trans*-dichloro substitution, as emphasized previously.[2a]

Accumulation of Trans Solventocobalt(III) and -chromium(III) Intermediates in Solvolysis. The stable cis Co(III) isomers are commonly observed intermediates in the isomerization reactions of *cis*- and *trans*-dihalo isomers in dipolar aprotic solvents. Little is known about the trans-solvento isomers since in addition to being unstable thermodynamically[8] they are not observed even transiently in these reactions.

Stereochemical change in Co(III) aquation is more the exception than the rule,[14] and thus, in view of the now emerging similarities between aquation and solvolysis,[2,16,25] it seems unlikely that the exclusive cis product in solvolysis is a consequence of a strong kinetic preference. Moreover, these trans-solvento species are not intrinsically labile since, for example, the isomerization rates of *trans*-$Co(en)_2(DMF)Cl^{2+}$ in DMF[8] and *trans*-$Co(en)_2(OH_2)Cl^{2+}$ in water[26] are almost identical. It would seem that the inability to detect any trans products in Co(III) solvolysis stems from their greatly reduced rate of formation in DMF and DMSO, since solvolysis is inevitably 1–2 orders of magnitude slower than aquation.[2,12] Therefore subsequent trans to cis isomerization becomes the limiting factor in their accumulation.

This rationale is consistent with results for the Cr(III) systems. Because of the greatly reduced tendency to isomerization,[14] as exemplified by this work, the selectively formed trans-solvento species may be readily observed when the generating solvolysis is sufficiently rapid, *e.g.*, in most aquation reactions and solvolyses of *trans*-$Cr(en)_2XBr^+$ (X = Cl, Br)[1,2] involving the relatively labile bromide leaving group.

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Registry No. *trans*-$Cr(en)_2(DMSO)Cl^{2+}$, 29844-97-1; *trans*-$Cr(en)_2(DMF)Cl^{2+}$, 46361-64-2; *cis*-$Cr(en)_2(DMSO)Cl^{2+}$, 46240-37-3.

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$$trans\text{-}Cr(en)_2Cl_2^+ \xrightarrow{k_s} trans\text{-}Cr(en)_2(sol)Cl^{2+} \xrightarrow{k_{tc}} cis\text{-}Cr(en)_2(sol)Cl^{2+}$$

reveals that the trans-solvento complex will represent 19% of the system at optimum time when $k_{tc} = 3k_s$ and 6.5% when $k_{tc} = 12k_s$.
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Amine Cleavage and Stereochemical Change in Octahedral Chromium(III) Substitution–Isomerization and Solvent-Interchange Reactions of Some *trans*-Bis(solvent)bis(ethylenediamine) Complexes in Dimethyl Sulfoxide

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The kinetics and stereochemistry of solvent interchange of *trans*-$Cr(en)_2(DMF)_2^{3+}$ and *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ (DMF = dimethylformamide) and the isomerization of *trans*-$Cr(en)_2(DMSO)_2^{3+}$ have been investigated in dimethyl sulfoxide (DMSO). In the two former reactions isomerization and solvent interchange are synchronous, and *cis*-$Cr(en)_2(DMSO)_2^{3+}$ is the only observed bis(ethylenediamine) product. Retentive solvent interchange followed by rapid isomerization is excluded by the results. In all three reactions significant net loss of ethylenediamine is observed (~20%; temperature dependent); there is no accumulation of unidentate ethylenediamine complex, and $Cr(en)(DMSO)_4^{3+}$ is the final product. A very slow subsequent rechelation of released diamine occurs; at equilibrium, isomerization and solvent interchange are complete (95 ± 1% *cis*-$Cr(en)_2(DMSO)_2^{3+}$ and 5 ± 1% $Cr(en)(DMSO)_4^{3+}$; 60°). Rate and stereochemical data and activation parameters are given for all reactions. The complete range of complexes which include *cis*- and *trans*-$Cr(en)_2(DMF)_2^{3+}$, *cis*- and *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$, *cis*- and *trans*-$Cr(en)_2(DMSO)_2^{3+}$, $Cr(en)(DMF)_4^{3+}$, and $Cr(en)(DMSO)_4^{3+}$ have been isolated. The role of the "single-ended" ethylenediamine complex intermediate in these reactions is considered.

Introduction

Recently we described solvolysis and isomerization reactions of bis(ethylenediamine)chromium(III) complexes in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).[1] The trans to cis isomerizations of *trans*-$Cr(en)_2(DMSO)Br^{2+}$ and -$Cr(en)_2(DMSO)Cl^{2+}$ in DMSO and of *trans*-$Cr(en)_2(DMF)Br^{2+}$, -$Cr(en)_2(DMF)Cl^{2+}$, and -$Cr(en)_2(DMF)_2^{3+}$ in DMF were shown to proceed *via* dissociation of a neutral leaving group, either (complexed) solvent or one end of the bidentate amine. It was apparent[2] that the former path must involve substitution with considerable stereochemical change, which is unusual for Cr(III). Other results[3,4] and the present work were alluded to in support of this conclusion. Clearly a knowledge of the rate and stereochemistry of solvent exchange is required to interpret fully these trans to cis isomerizations. As the first step in tackling this problem, we undertook a study of the closely analogous solvent-interchange reactions of a series of trans-solvento complexes. For reasons to become apparent we chose to study the *trans*-$Cr(en)_2(DMF)_2^{3+}$, -$Cr(en)_2(DMSO)(DMF)^{3+}$, and -$Cr(en)_2(DMSO)_2^{3+}$ series of cations in DMSO. We expected the stepwise DMSO substitution of coordinated DMF to be complicated by isomerization and net loss of ethylenediamine,[1-3] and thus for simplicity of reaction amenable to quantitative interpretation, we avoided complexes with replaceable anionic ligands (*e.g.*, Cl^-, Br^-). This proved to be an additional advantage in that the equilibria between the bis- and mono(ethylenediamine)solvento complexes could be accurately measured.

Experimental Section

Preparation of Complexes. *trans*-$[Cr(en)_2(DMF)_2](ClO_4)_3$ and *trans*-$[Cr(en)_2(DMSO)_2](ClO_4)_3$ were isolated previously.[2,5] Freshly prepared complexes for this work analyzed satisfactorily.

cis-$[Cr(en)_2(DMSO)_2](ClO_4)_3$ was synthesized according to Palmer and Watts[4] from the reaction between *cis*-$[Cr(en)_2Br_2]ClO_4$[1] or *cis*-$[Cr(en)_2Cl_2]ClO_4$[1] and excess $AgClO_4$ in hot DMSO. Some samples were also prepared from *cis*-$[Cr(en)_2(OH_2)_2](ClO_4)_3$[5] or *cis*-$[Cr(en)_2(DMF)_2](ClO_4)_3$[2] in hot DMSO (60°, 10 min). The analyses and absorption spectra of these samples, recrystallized from water (20°, $LiClO_4$) several times as pink needles, were identical. *Anal.* Calcd for $[Cr(en)_2(DMSO)_2](ClO_4)_3$: Cr, 8.3; C, 15.3; H, 4.6; N, 8.7; S, 10.2; Cl, 17.0. Found: Cr, 8.2; C, 15.7; H, 4.5; N, 8.7; S, 9.9; Cl, 17.0.

$[Cr(en)(DMF)_4](ClO_4)_3$ and $[Cr(en)(DMSO)_4](ClO_4)_3$ were from batches previously prepared and characterized.[2]

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