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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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$[Cr(DMSO)_6](ClO_4)_3$[6] was prepared from $[Cr(OH_2)_6](ClO_4)_3$ by recrystallizing three times from hot concentrated DMSO solution. Triethyl orthoformate was added in the first two crystallizations. The product was collected and washed quickly with a little DMSO–methanol (1:1), followed by methanol and finally ether. The freshly prepared and air-dried product showed only DMSO absorptions (and no H_2O) in the ir spectrum (Nujol mull), and its absorption spectrum in DMSO was essentially that reported.[6] *Anal.* Calcd for $[Cr(DMSO)_6](ClO_4)_3$: C, 17.6; H, 4.4; S, 23.5; Cl, 13.0. Found: C, 17.8; H, 4.9; S, 23.3; Cl, 12.9.

The new complex *trans*-$[Cr(en)_2(DMSO)(DMF)](ClO_4)_3$ was isolated by a slight modification of the usual method; the bromo complex was induced to solvolyze using excess $AgClO_4$ or $Hg(ClO_4)_2$. We describe the more convenient $AgClO_4$ method. A concentrated solution of *trans*-$[Cr(en)_2(DMF)Br](ClO_4)_2$[5] in DMSO (20°) was treated with a 5 molar excess of $AgClO_4$ in DMSO. The initially violet solution which had become red after 45 min at 20° in the dark was filtered to remove AgBr and poured slowly with stirring into a large volume of ethanol–ether (1:4) to give a red oil. The supernatant liquid was decanted, and the oil was dissolved in a minimum volume of water (20°) and was filtered. A crystal of $Na_2S_2O_3 \cdot 5H_2O$ was added to the filtrate followed by excess $LiClO_4$. The pink needles which deposited on cooling (5°) and standing (3 hr) were recrystallized twice more from water. The collected product was washed with cold methanol and then ether and was air-dried.

Following the above method and using *trans*-$[Cr(en)_2(DMSO)Br](ClO_4)_2$[4a] in DMF containing the excess $AgClO_4$ (5–10°, 1 hr), a similar yield (70–80%) of *trans*-$[Cr(en)_2(DMSO)(DMF)](ClO_4)_3$ was obtained.

The visible spectra (see Figure 4) of this complex prepared by both methods were identical (ϵ, ±1%). This is distinctly a trans spectrum and is quite different from that of the known cis isomer.[7] The ir spectrum showed the usual oxygen-bonded DMSO and DMF absorptions (ν(CO) 1660 cm^{-1}, ν(SO) 982 cm^{-1}; KBr disk). *Anal.* Calcd for $[Cr(en)_2(DMSO)(DMF)](ClO_4)_3$: C, 17.3; H, 4.7; N, 11.3; S, 5.1; Cl, 17.1. Found: C, 17.3; H, 4.0; N, 11.0; S, 5.2; Cl, 17.1.

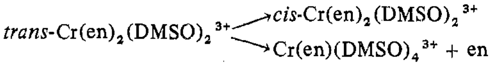
All complexes were recrystallized to constant spectrum (ϵ, ±1%) from water, water–DMF, or water–DMSO unless noted otherwise. Isomeric purity was checked and elemental analyses were performed as described earlier.[5,8] Complexes used were always freshly prepared. *trans*-$[Cr(en)_2(DMSO)_2](ClO_4)_3$ noticeably decomposes on prolonged dark storage; it isomerizes to the cis form under laboratory lighting. Therefore we routinely stored complexes for short periods of time in sealed tubes in the dark after briefly drying (100°, or at 25° *in vacuo* over $Mg(ClO_4)_2$).

Solvents, Other Reagents, and Kinetic Technique. DMSO and DMF were dried, purified, and handled under dry N_2 as done previously.[1-3] All chemicals were reagent grade, except $LiClO_4 \cdot 3H_2O$ (carbonate free), which was prepared from Li_2CO_3 and AR $HClO_4$, and ethylenediamine, which was purified by drying (KOH) and distillation.[8]

All reactions were followed on a Hitachi EPS-3T recording spectrophotometer by the repetitive-scan technique (340–700 nm) or by using the constant-wavelength continuous-scan mode. Most runs were performed by directly following the reaction in 1-cm silica spectrophotometer cells housed in a thermostated cell block, the temperature of which was controlled to ±0.05° by an external water bath using a Haake thermostat and pump control. Temperatures were measured in the cell,[8] but only at higher temperatures (70°) was there any appreciable drop (~0.4°) from that of the bath. To check for possible photochemical reaction, some runs were carried out using standard sampling techniques and blackened reaction vessels. Individual aliquots sealed in ampoules or a bulk solution sampled by syringe was thermostated in an oil bath. Temperature control was achieved (±0.02°) with a mercury–toluene regulator. Samples withdrawn at convenient times were freeze-quenched. All spectra were recorded following a run by quickly thawing. Results obtained in this way were identical with those for reaction solutions exposed to spectrophotometer light. Therefore all rate and stereochemical data reported here refer to thermal reaction.

Results

Reaction Course and Stereochemistry. 1. *trans*-$Cr(en)_2(DMSO)_2^{3+}$ in DMSO. In Figure 1 are shown the changes in absorption spectra for this reaction (54°). Sharp isosbestic points are maintained for almost the entire primary reaction (4$t_{1/2}$). In Table I are given the observed and calculated isosbestic point data. It is apparent that the two higher energy isosbestic points are in reasonable agreement with those expected for simple isomerization. However, the discrepancy in the observed and calculated lowest energy isosbestic point is outside experimental error (ϵ, ±1%; λ, ±1 nm), particularly at the upper temperature extreme studied. These results suggest that another product is produced in constant proportion together with *cis*-$Cr(en)_2(DMSO)_2^{3+}$, and indeed if one assumes the reaction



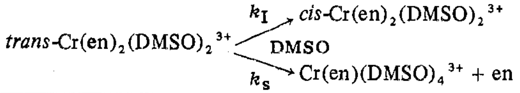
$$trans\text{-}Cr(en)_2(DMSO)_2^{3+} \rightarrow cis\text{-}Cr(en)_2(DMSO)_2^{3+};\quad trans\text{-}Cr(en)_2(DMSO)_2^{3+} \rightarrow Cr(en)(DMSO)_4^{3+} + en$$

then the agreement between the observed and calculated isosbestic points for the lowest and highest temperature studied is excellent (Table I). The pure-component absorption spectra used in this analysis are shown in Figure 2. Note that these and all other spectra measured in this work were carefully checked for temperature dependence in the range 20–70°; none was observed (±1%). Table II summarizes the observed isosbestic points and calculated product proportions for all temperatures investigated.

We have excluded a unidentate en complex intermediate as a product present in significant proportions (<5%) on the basis of the high internal consistency of the results (*vide infra*). The assumption is that a CrN_3O_3 chromophore will have a spectrum quite different from that of CrN_2O_4 ($Cr(en)(DMSO)_4^{3+}$), and its presence would therefore lead to obvious inconsistencies in our analyses which involve several wavelengths.

The stereochemical results have been put on a more precise

Table I. Observed and Calculated Isosbestic Points for the Reaction

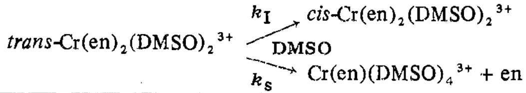


$$trans\text{-}Cr(en)_2(DMSO)_2^{3+} \xrightarrow[\text{DMSO}]{k_I} cis\text{-}Cr(en)_2(DMSO)_2^{3+};\quad trans\text{-}Cr(en)_2(DMSO)_2^{3+} \xrightarrow[\text{DMSO}]{k_s} Cr(en)(DMSO)_4^{3+} + en$$

Isosbestic points λ (ϵ)[a] Obsd	Isosbestic points λ (ϵ)[a] Calcd	T,[b] °C	% *cis*-$Cr(en)_2$-$(DMSO)_2^{3+}$ in products[c]
423 (29.2)	423 (29.6)		
446 (30.2)	447 (30.3)	41.35	90 ± 2
577 (21.2)	576 (21.4)		
	420.5 (29.6)		
	446 (30.5)		100
	572.5 (21.9)		
424 (29.0)	424 (28.9)		
449 (29.7)	449 (30.0)	68.4	81 ± 2
583 (19.8)	582 (20.0)		

[a] λ, nm; ϵ, M^{-1} cm^{-1}. [b] Two temperature extremes studied. [c] ±5% (isosbestic point method); ±2% (other methods see text).

Table II. Isosbestic Points, Product Ratios, and Their Temperature Dependence for the Reaction



$$trans\text{-}Cr(en)_2(DMSO)_2^{3+} \xrightarrow[\text{DMSO}]{k_I} cis\text{-}Cr(en)_2(DMSO)_2^{3+};\quad trans\text{-}Cr(en)_2(DMSO)_2^{3+} \xrightarrow[\text{DMSO}]{k_s} Cr(en)(DMSO)_4^{3+} + en$$

Obsd isosbestic points λ[a]			T, °C	R[b]	% *cis*-$Cr(en)_2$-$(DMSO)_2^{3+}$ in products[c,d]
583	449	423.5	68.4	4.2	81
581	447	422	66.6	4.9	83
582.5	449	423	64.3	4.9	83
582.5	448.5	423	59.25	5.3	84
580	448	422	54.25	6.2	86
577	446	422	48.75	9.0	90
577	447	423	41.35	9.0	90
572.5	446	420.5			100[e]

[a] nm. [b] $R = k_I/k_s$. [c] ±2%. [d] $10^2R/(1 + R)$. [e] Calculated for simple isomerization.

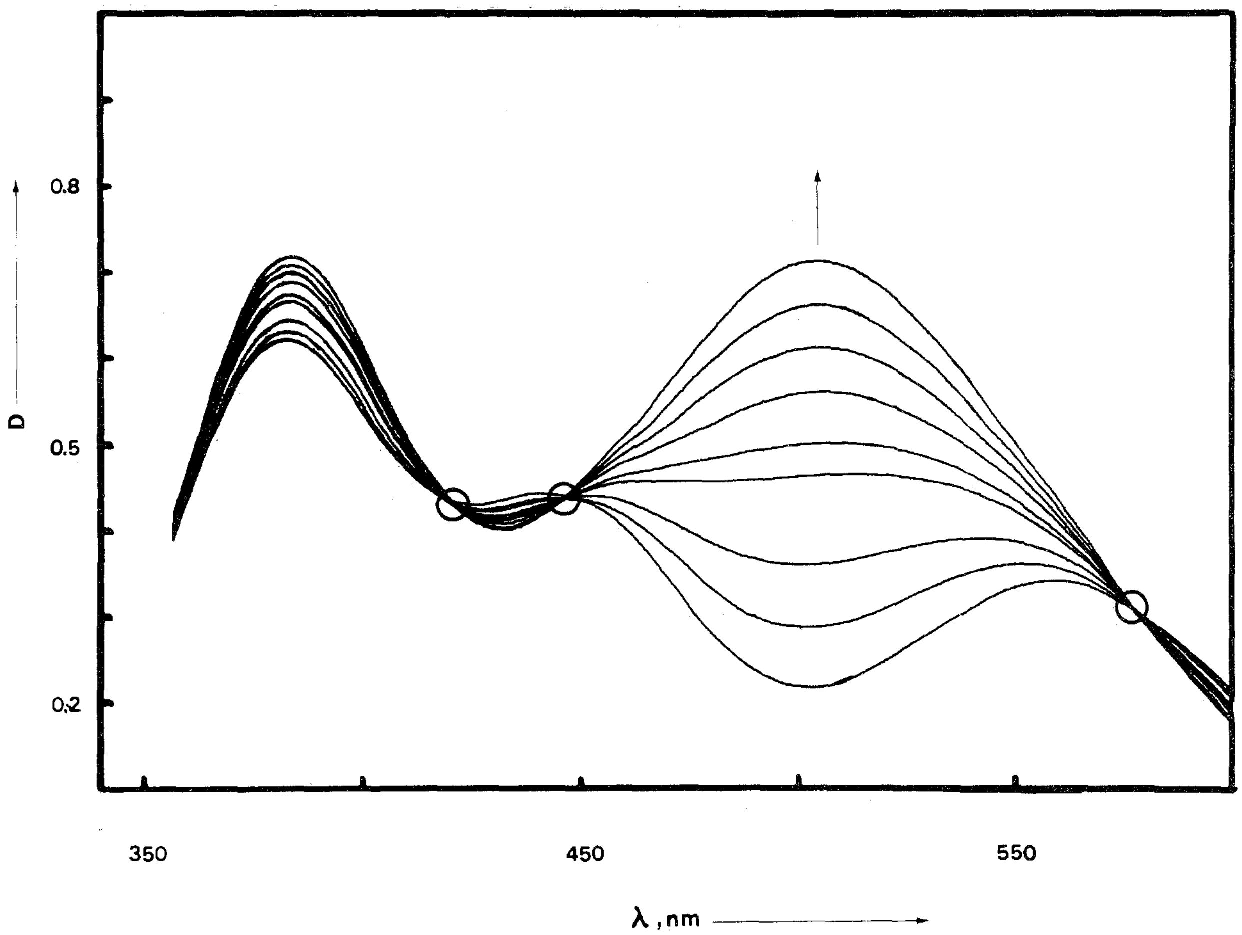


Figure 1. Changes in visible absorption spectra for the reaction of *trans*-$Cr(en)_2(DMSO)_2^{3+}$ in DMSO. $[Complex]_0 = 1.70 \times 10^{-2}$ *M*, *T* = 54.0°.

quantitative basis as follows: (a) complete spectrophotometric analysis of the reacting system for the three light-absorbing species, (b) the constancy (±2%) of k_0[19] calculated at several wavelengths on the assumption of a fixed product ratio (*R*) derived from the isosbestic point data, and (c) the constancy and consistency of the product ratio *R* (derived from ϵ_∞) calculated at several wavelengths from first-order kinetic fits[20] where both ϵ_∞ and k_0 could be used as parameters, or where only ϵ_∞ was used as a variable and k_0 was fixed at the value found from data collected at an *cis*-$Cr(en)_2(DMSO)_2^{3+}$–$Cr(en)(DMSO)_4^{3+}$ isosbestic point (538 nm).

Methods (b) and (c) are considered ahead; method (a) warrants some comment.[21] We stress that in analyzing absorbance data for three light-absorbing species by the method of simultaneous equations[9] the selection of suitable wavelengths is not straightforward; indeed spurious results are readily obtained even for a well-defined reaction with large changes in absorbance. We used two criteria to establish accuracy: (a) at any time *t*, $\sum_i c_i = c_0$;[19] (b) the independence of results (c_i, *t*) from the set of three wavelengths chosen. We have found that criterion (a) by itself is not a sufficient condition for meaningful results.

This type of analysis is exemplified by the data given in Table III for *trans*-$Cr(en)_2(DMSO)_2^{3+}$ reaction in DMSO at 64.3°. At all temperatures we have reproduced these results (to ±2%) using at least three sets of three wavelengths (criterion (b)) and in Table III it can be seen $\sum_i c_i = c_0$ for each *t* (criterion (a)). Of course, the product ratios determined at early times are not accurate, being indeterminate at zero reaction time. Accuracy is maximum at complete reaction. We have found a nearly constant product ratio (as % *cis*-$Cr(en)_2(DMSO)_2^{3+}$, ±2%) between $1t_{1/2}$ and $4t_{1/2}$. These data, together with the sharp isosbestic points, which give the same product ratio (Tables I and II), clearly show that secondary reaction does not interfere until at least $4t_{1/2}$ in the temperature range studied.

Table III. Typical Results of Complete Spectral Analysis of the *trans*-$Cr(en)_2(DMSO)_2^{3+}$ Reaction in DMSO[g]

Time, min	10^2 [trans],[a] *M*	10^2 [cis],[b] *M*	10^2 [mono],[c] *M*	$10^2 \Sigma_i C_i$[d]	*R*[e]	% cis in products[f]
0	1.505	0	0	1.505		
10.0	1.18	0.20	0.095	1.475	2.10	68
15.0	1.04	0.335	0.10	1.475	3.35	77
20.0	0.915	0.44	0.125	1.48	3.5	78
25.0	0.795	0.545	0.14	1.48	3.9	79.5
30.0	0.685	0.64	0.16	1.485	4.0	80
35.0	0.61	0.71	0.165	1.485	4.25	81
40.0	0.53	0.78	0.175	1.485	4.45	81.5
45.0	0.465	0.84	0.18	1.485	4.65	82.5
50.0	0.41	0.89	0.185	1.485	4.8	83
55.0	0.355	0.94	0.19	1.485	4.95	83
100.0	0.105	1.15	0.235	1.49	4.9	83
2500	0	1.415	0.075	1.49	18.9	95

[a] trans = *trans*-$Cr(en)_2(DMSO)_2^{3+}$. [b] cis = *cis*-$Cr(en)_2(DMSO)_2^{3+}$. [c] mono = $Cr(en)(DMSO)_4^{3+}$. [d] Sum of concentrations (*M*). [e] *R* = [cis]/[mono]. [f] 10*R*/(1 + *R*). [g] Analysis wavelengths 520, 430, 380 nm; $[trans]_0 = 1.51 \times 10^{-2}$ *M*;[a] *T* = 64.3°.

After about $4t_{1/2}$, the isosbestic points drift and a single new point is established at ~540 nm at later times. Thus a second reaction is occurring. Analysis shows an initial composition (at $4t_{1/2}$) of 5 ± 2% *trans*-$Cr(en)_2(DMSO)_2^{3+}$, 79 ± 2% *cis*-$Cr(en)_2(DMSO)_2^{3+}$, and 16 ± 2% $Cr(en)(DMSO)_4^{3+}$ and a final composition of 95 ± 1% *cis*-$Cr(en)_2(DMSO)_2^{3+}$ and 5 ± 1% $Cr(en)(DMSO)_4^{3+}$ (64.3°, several days). There is

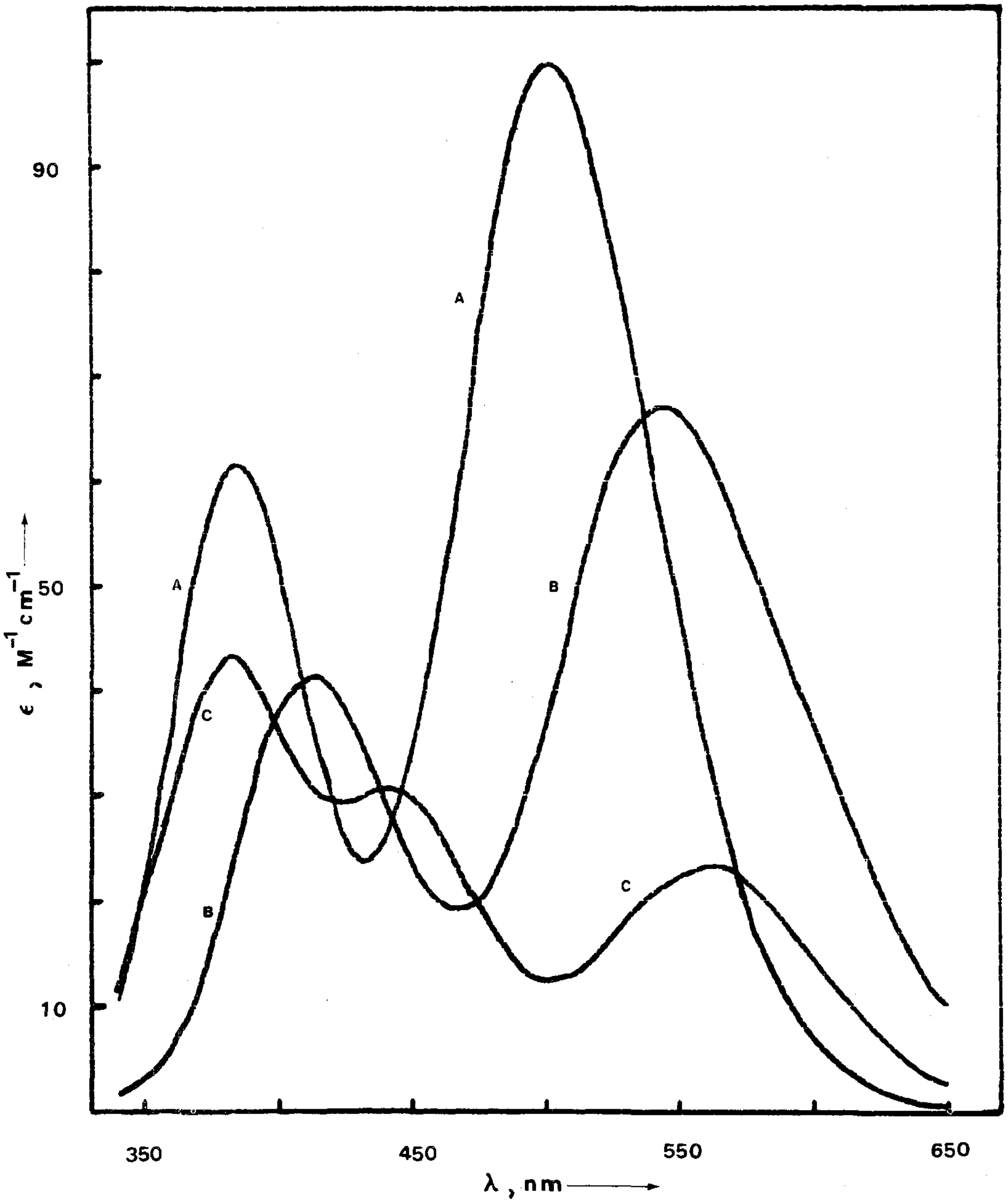


Figure 2. Pure absorption spectra in DMSO at 25°: A, *cis*-$Cr(en)_2(DMSO)_2^{3+}$; B, $Cr(en)(DMSO)_4^{3+}$; C, *trans*-$Cr(en)_2(DMSO)_2^{3+}$.

no residual *trans*-$Cr(en)_2(DMSO)_2^{3+}$; thus isomerization goes to completion and the second reaction observed is substantial rechelation (15%), of the initially liberated ethylenediamine (20%). These results were qualitatively confirmed by monitoring the free amine concentration using an acid–base colorimetric indicator method[10] adapted to DMSO. We have not studied the equilibrium temperature dependence or the kinetics of this rechelation process.

2. *cis*-$Cr(en)_2(DMSO)_2^{3+}$ in DMSO. The cis complex only very slowly changes its spectrum at 60°. After several days, a 1.70×10^{-2} *M* solution has the composition 95 ± 1% *cis*-$Cr(en)_2(DMSO)_2^{3+}$ and 5 ± 1% $Cr(en)(DMSO)_4^{3+}$. Because there is only 5% reaction, isosbestic points are not well developed but the light absorption is accurately accounted for by only the above two complexes at all times. There is no detectable cis to trans isomerization.

3. $Cr(en)(DMF)_4^{3+}$ in DMSO. At 25° initial reaction is rapid. After several hours, an approximately constant spectrum is obtained which is closely "midway" between the $Cr(en)(DMF)_4^{3+}$ and $Cr(en)(DMSO)_4^{3+}$ spectra in DMSO. Sharp isosbestic points are held for about 30% of this spectrum change. We have not attempted to follow the kinetics of these stepwise solvent-interchange reactions nor attempted to isolate the mixed $Cr(en)(DMF)_{4-n}(DMSO)_n^{3+}$ ($n = 1–3$) complexes, but by analogy with the thoroughly investigated reactions of *cis*-$Cr(en)_2(DMF)_2^{3+}$ and *cis*-$Cr(en)_2(DMSO)(DMF)^{3+}$ in DMSO,[7] it appears that two coordinated DMF molecules are replaced rapidly to give $Cr(en)(DMF)_2(DMSO)_2^{3+}$. Subsequent reaction of this complex is extremely slow; a final spectrum which is exactly that of $Cr(en)(DMSO)_4^{3+}$ is obtained only after several days at 60°. Thus solvent interchange goes to completion and the last two complexed DMF ligands are substituted much more slowly than the first two. Both the $Cr(en)(DMF)_4^{3+}$ and $Cr(en)(DMSO)_4^{3+}$ complexes are thermally stable to amine solvolysis.

4. *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ in DMSO. This reaction is analogous to that of *trans*-$Cr(en)_2(DMSO)_2^{3+}$, *i.e.*

$$trans\text{-}Cr(en)_2(DMSO)(DMF)^{3+} \begin{cases} \rightarrow cis\text{-}Cr(en)_2(DMSO)_2^{3+} \\ \rightarrow Cr(en)(DMSO)_3(DMF)^{3+} + en \end{cases}$$

Sharp isosbestic points are observed over a period of just over

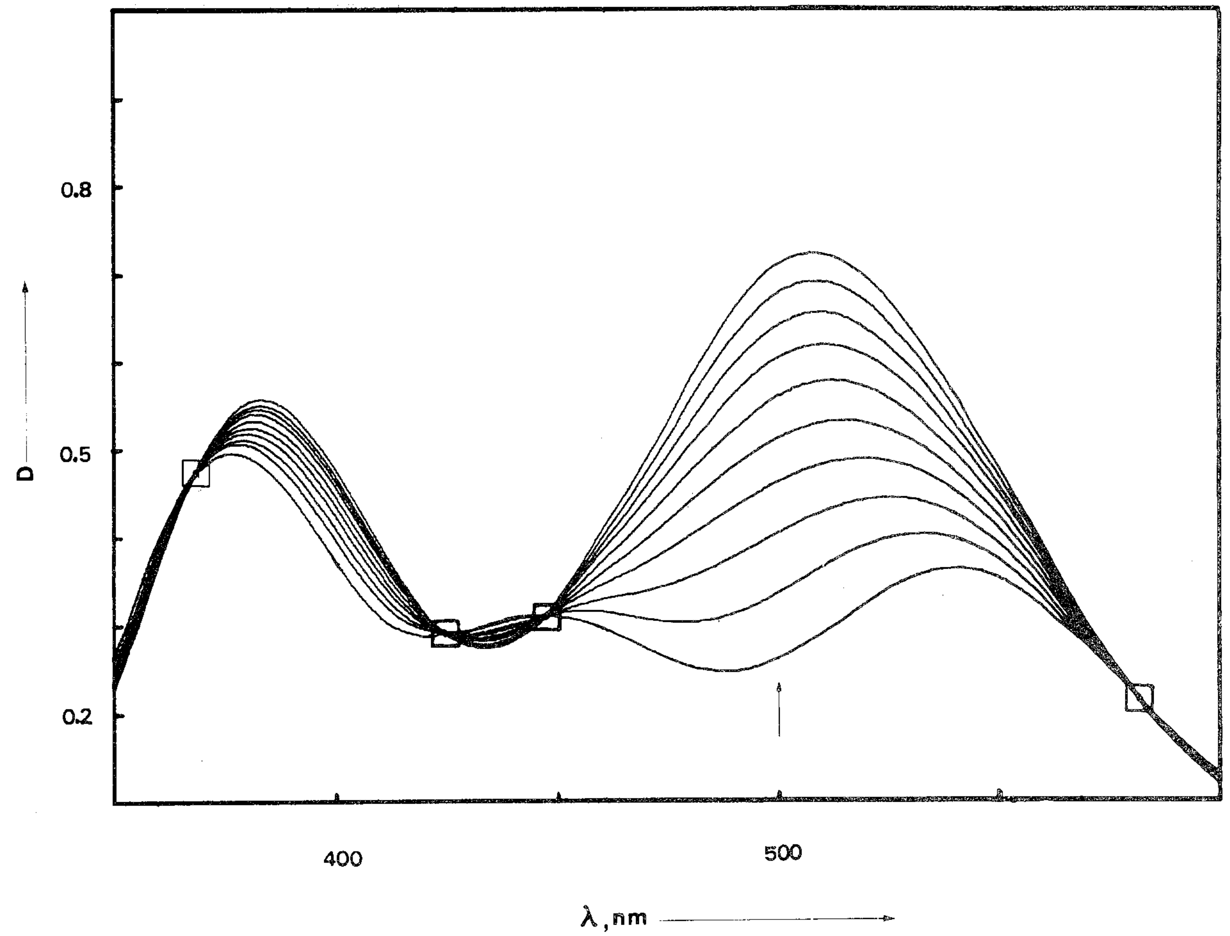


Figure 3. Spectral changes accompanying the solvent interchange, amine solvolysis, and isomerization of *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ in DMSO. $[Complex]_0 = 1.10 \times 10^{-2}$ *M*, $T = 63.0°$.

Table IV. Product Proportions (Kinetic) and Their Temperature Dependence for the Reactions of *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ and *trans*-$Cr(en)_2(DMF)_2{}^{3+}$ in DMSO

Obsd isosbestic points λ[a]				*T*, °C	*R*[b]	% *cis*-$Cr(en)_2(DMSO)_2{}^{3+}$ in products[c,d]
trans-$Cr(en)_2(DMSO)(DMF)^{3+}$ $\xrightarrow[DMSO]{k_I}$ *cis*-$Cr(en)_2(DMSO)_2{}^{3+}$; $\xrightarrow{k_S}$ $Cr(en)(DMSO)_3(DMF)^{3+}$ + en						
581	448	424.5	369	62.7	6.7	87
582	448	424.5	369	62.6	6.1	86
580	447	424	369	58.7	9.0	90
577	446	425	369	44.45	15.7	94
trans-$Cr(en)_2(DMF)_2{}^{3+}$ $\xrightarrow{k_I}$ *cis*-$Cr(en)_2(DMSO)_2{}^{3+}$; $\xrightarrow{k_S}$ $Cr(en)(DMSO)_2(DMF)_2{}^{3+}$ + en						
449.5	428	373.5		67.05	4.0	80
449	428	373.5		60.55	3.0	75
449	427.5	373.5		60.25	3.0	75
453	424	379		42.6	1.5	60

[a] nm. [b] $R = k_I/k_S$. [c] $10^2R/(1 + R)$. [d] ±3% top reaction, ±10% bottom reaction; "best values" from a combination of methods of determination.

$2t_{1/2}$ (Figure 3). The product ratio was calculated as described above and results at several temperatures are given in Table IV. Although *cis*-$Cr(en)_2(DMSO)_2{}^{3+}$ is the only observed bis(ethylenediamine) product, *cis*-$Cr(en)_2(DMSO)(DMF)^{3+}$ may well be the initial and exclusive cis species since it is known[7] (see Table V) that

$$cis\text{-}Cr(en)_2(DMSO)(DMF)^{3+} \xrightarrow{DMSO} cis\text{-}Cr(en)_2(DMSO)_2{}^{3+}$$

is about 50 times as fast as the rate of cis formation from *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$. Thus *cis*-$Cr(en)_2(DMSO)(DMF)^{3+}$, if formed, would not be detected. The retentive solvent interchange reaction

$$trans\text{-}Cr(en)_2(DMSO)(DMF)^{3+} \xrightarrow{DMSO} trans\text{-}Cr(en)_2(DMSO)_2{}^{3+}$$

was not observed. Significant reaction (<5%) through this path can be excluded by our results since (a) *trans*-$Cr(en)_2(DMSO)_2{}^{3+}$ does not isomerize rapidly enough to escape detection (Table V), (b) the product distributions for

Table V. Comparison of Solvent-Interchange Reactions of *cis*- and *trans*-Bis(ethylenediamine)chromium(III)–Solvento Complexes in DMSO at 50°

Reactant	Rate constants[a]			Stereochemistry,[b] % cis in products
	10^5k_0[c]	10^5k_I[d,f]	10^5k_s[e]	
trans-$Cr(en)_2(DMSO)_2^{3+}$	10.0	8.8	1.2	
trans-$Cr(en)_2(DMSO)(DMF)^{3+}$	7.1	6.5	0.6	100 ± 5
trans-$Cr(en)_2(DMF)_2^{3+}$	4.1	2.7	1.4	100 ± 5
cis-$Cr(en)_2(DMSO)_2^{3+}$			8	
cis-$Cr(en)_2(DMSO)(DMF)^{3+}$	450	450	5	100 ± 2
cis-$Cr(en)_2(DMF)_2^{3+}$	1020	1020	8	100 ± 2

[a] sec^{-1}. [b] Refers to k_I path. [c] Total rate of reactant consumption, ±2%. [d] Maximum (see text) total rate of solvent interchange (=isomerization rate for trans reactants), ±5%. [e] Minimum (see text) amine solvolysis rates, ±10%; not generally observed for cis substrates but *upper* estimates given.[7] [f] Statistically *un*corrected (factor of 2).

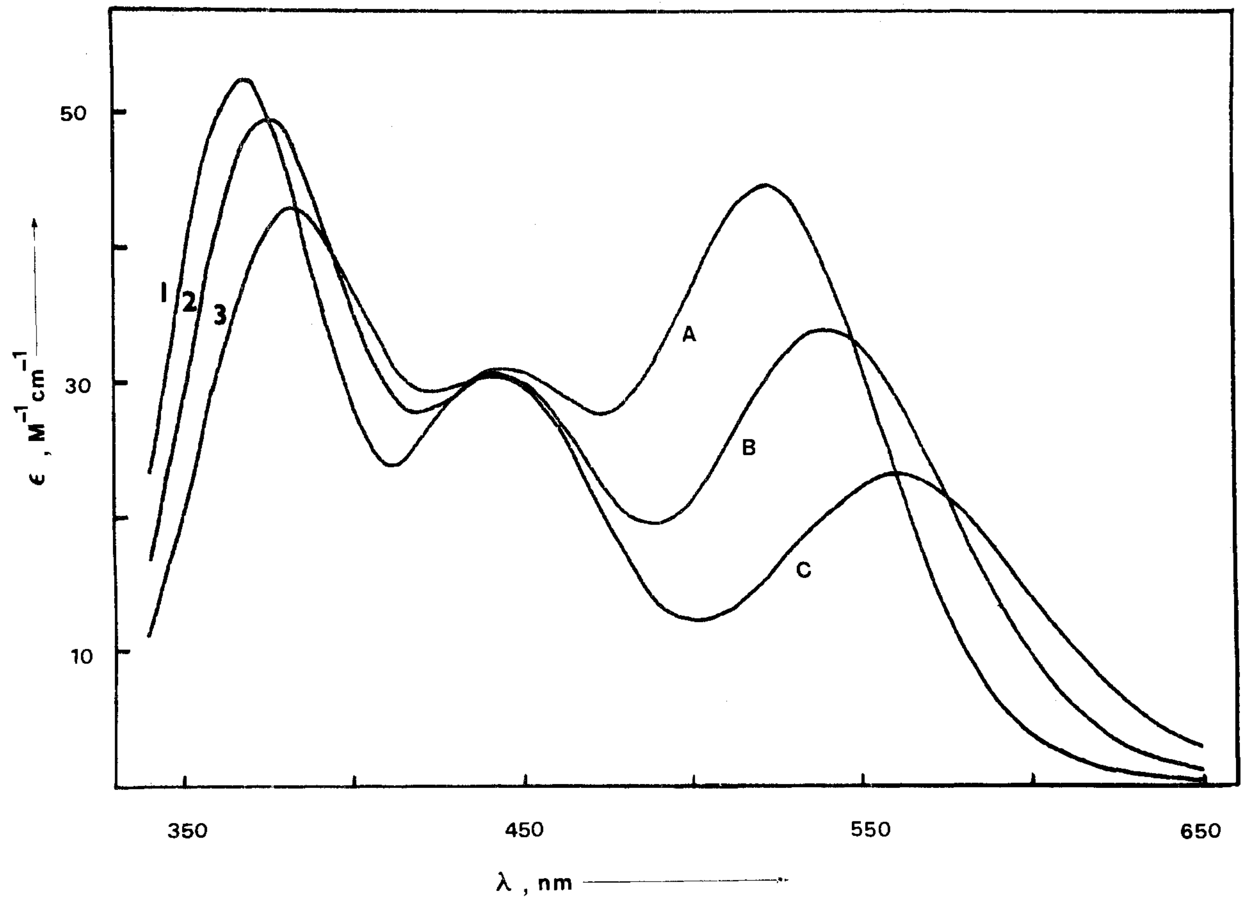


Figure 4. Pure absorption spectra in DMSO at 25°: *trans*-$Cr(en)_2(DMF)_2^{3+}$ (A); *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ (B); *trans*-$Cr(en)_2(DMSO)_2^{3+}$ (C).

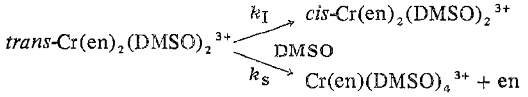
trans-$Cr(en)_2(DMSO)_2^{3+}$ and *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ are different (Tables II and IV) (they should be identical if reaction proceeded exclusively *via* *trans*-$Cr(en)_2(DMSO)_2^{3+}$), and (c) the spectra of *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ and *trans*-$Cr(en)_2(DMSO)_2^{3+}$ are quite different (Figure 4). The cis spectra[7] are even more different, and thus the reaction products are readily identified spectrophotometrically by the methods described.

Although we have calculated consistent product ratios by the various methods mentioned earlier, the *nature* of the initial mono(ethylenediamine) product is not known with certainty—it may be $Cr(en)(DMSO)_3(DMF)^{3+}$ or $Cr(en)(DMSO)_4^{3+}$. The spectrum of $Cr(en)(DMSO)_3(DMF)^{3+}$ has been approximated by using the well-known rule of "average environment" ($^3/_4Cr(en)(DMSO)_4^{3+}$ + $^1/_4Cr(en)(DMF)_4^{3+}$) and this is probably substantially correct, since, for example, the *cis*-[7] and *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ spectra (Figure 4) are almost precisely an "average" of their respective $(DMF)_2^{3+}$ and $(DMSO)_2^{3+}$ spectra. Partly because the spectrum of $Cr(en)(DMSO)_3(DMF)^{3+}$ does not differ greatly from that of $Cr(en)(DMSO)_4^{3+}$ and partly because the en release reaction is only some 20% of the total *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ reaction, we obtain only slightly more self-consistent results assuming a $Cr(en)(DMSO)_3(DMF)^{3+}$ rather than $Cr(en)(DMSO)_4^{3+}$ product. Our independent investigations of $Cr(en)(DMSO)_3(DMF)^{3+}$ (section 3) suggest that this product, if formed, would not readily solvolyze to $Cr(en)(DMSO)_4^{3+}$. Our analysis is further substantiated by the drift in isosbestic points after $2t_{1/2}$ of the *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ reaction, at which time $Cr(en)(DMSO)_3(DMF)^{3+}$ solvolysis is evident. Complete interpretation of this secondary reaction is complicated by simultaneous recomplexing of free amine.

At equilibrium (63°) we again find the composition of 95 ± 1% *cis*-$Cr(en)_2(DMSO)_2^{3+}$ and 5 ± 1% $Cr(en)(DMSO)_4^{3+}$. Thus isomerization and solvent interchange eventually go to completion.

5. ***trans*-$Cr(en)_2(DMF)_2^{3+}$ in DMSO.** Following analyses

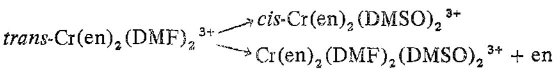
Table VI. First-Order Rate Constants for the Reaction


$$trans\text{-}Cr(en)_2(DMSO)_2{}^{3+} \xrightarrow[DMSO]{k_I} cis\text{-}Cr(en)_2(DMSO)_2{}^{3+}; \quad trans\text{-}Cr(en)_2(DMSO)_2{}^{3+} \xrightarrow[DMSO]{k_s} Cr(en)(DMSO)_4{}^{3+} + en$$

T, °C	10^5k_0,[a] sec^{-1}	10^5k_I,[b] sec^{-1}	10^5k_s,[c] sec^{-1}
68.6	69.5	56.3	13.2
68.4	65.5	53.0	12.5
66.7	58.3	48.3	10.0
66.6	58.3	48.3	10.0
64.3	44.2	36.7	7.5
59.2	28.5	24.0	4.5
54.25	15.8	13.7	2.1
48.75	8.65	7.8	0.85
41.35	3.85	3.45	0.40

[a] $k_0 = k_I + k_s$; ±2%. [b] ±5%. [c] ±10%.

similar to those already mentioned, the initial reaction was established as


$$trans\text{-}Cr(en)_2(DMF)_2{}^{3+} \rightarrow cis\text{-}Cr(en)_2(DMSO)_2{}^{3+}; \quad trans\text{-}Cr(en)_2(DMF)_2{}^{3+} \rightarrow Cr(en)_2(DMF)_2(DMSO)_2{}^{3+} + en$$

Spectral changes are shown in Figure 5. Isosbestic point data from which product ratios were calculated are given in Table IV for several temperatures; again, results were confirmed by an analysis of reaction mixtures for the (initially) three light-absorbing species (over ~$1t_{1/2}$).

Kinetics. In this work we have only investigated the reaction rates for the trans complexes; complete results for the cis isomers will be reported elsewhere.[7] First-order rate constants were calculated from plots of ln $|D - D_\infty|$ against time at several wavelengths. At a suitable isosbestic point between the two products (*e.g.*, *cis*-$Cr(en)_2(DMSO)_2{}^{3+}$ and $Cr(en)(DMSO)_4{}^{3+}$, 538 nm; Figure 2), k_0 could be directly determined. At other wavelengths, the calculation of D_∞ requires a knowledge of the product ratio in addition to the relevant extinction coefficients. Provided (a) D,t data covering a period of $2t_{1/2}$ or greater were used, (b) the product ratio was constant over this period, and (c) secondary reaction had not set in (*i.e.*, in all reactions except those of *trans*-$Cr(en)_2(DMF)_2{}^{3+}$), both k_0 and D_∞ could be computed from the data by fitting the usual first-order rate expression with these parameters. The constancy of k_0 (±2%) and the product ratio (obtained from D_∞, ±2% as per cent cis) for calculations at several wavelengths were taken as criteria of meaningful results. The values of k_0 so obtained were identical with those found more directly using absorbance data collected at the product isosbestic point. As a further check, k_0 was computed from plots of ln [complex] against time, where [complex] data came directly from complete spectrophotometric analyses of reaction mixtures (see, for example, Table III). The results were identical (±3%).

k_0 ($=k_s + k_I$) was divided into the constants for amine solvolysis (k_s) and isomerization (k_I) using the product ratio R ($=k_I/k_s$) determined at the same temperature.

First-order rate constants are given in Tables VI and VII and activation parameters in Table VIII for all reactions.

Equilibria. We have confirmed the equilibrium results given above by equilibrating the following mixtures at 60°: (a) $Cr(DMSO)_6{}^{3+}$ + 2 equiv of en; (b) $Cr(en)(DMSO)_4{}^{3+}$ + 1 equiv of en ([complex]$_0$ = 1.70×10^{-2} M). The complete stability of $Cr(en)(DMSO)_4{}^{3+}$ with respect to en loss was verified by reproducing its spectrum with mixture (a) using only 1 equiv of diamine. When amine (in DMSO) is added carefully to complex and equilibrated, there is no detectable disproportionation. Only the *cis*-$(en)_2$ (95 ± 1%) and en (5 ± 1%) species are found at equilibrium with 2:1 = en:Cr; there is no detectable standing concentration of unidentate en complex.

Table VII. First-Order Rate Constants for the Reactions of *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ and *trans*-$Cr(en)_2(DMF)_2{}^{3+}$ in DMSO

T, °C	10^5k_0,[a] sec^{-1}	10^5k_I,[b] sec^{-1}	10^5k_s,[c] sec^{-1}
	trans-$Cr(en)_2(DMSO)(DMF)^{3+}$		
62.7	30.8	26.8	4.0
62.7	30.5	26.8	3.7
62.7	31.0	26.8	4.2
62.7	31.7	27.5	4.2
62.6	30.7	26.3	4.4
58.7	18.8	17.0	1.8
58.65	18.3	16.5	1.8
44.45	3.58	3.37	0.21
44.5	3.70	3.45	0.25
	trans-$Cr(en)_2(DMF)_2{}^{3+}$		
67.05	44.2	35.3	8.9
60.55	18.5	13.8	4.7
60.25	16.5	12.3	4.2
42.6	1.36	0.82	0.54

[a] $k_0 = k_I + k_s$; ±2%. [b] ±5% (top); ±10% (bottom). [c] ±10% (top); ±20% (bottom).

Table VIII. Activation Parameters for DMSO Reactions

Reactant	10^5k (50°)[a]	$\Delta G^\ddagger$ (50°)[e]	ΔE_a[e]	$\Delta H^\ddagger$[e]	$\Delta S^\ddagger$[f]
trans-$Cr(en)_2(DMSO)_2{}^{3+}$	10.0[b]	24.8	22.7	22.1	−8.0
	8.8[c]	25.0	21.8	21.2	−12.0
	1.2[d]	26.2	27.6	27.0	+2.5
trans-$Cr(en)_2(DMSO)(DMF)^{3+}$	7.1[b]	25.1	24.6	24.0	−3.5
	6.5[c]	25.2	23.8	23.2	−6.0
	0.6[d]	26.7	30.6	30.0	+10.0
trans-$Cr(en)_2(DMF)_2{}^{3+}$	4.1[b]	25.5	30.3	29.6	+12.5
	2.7[c]	25.7	32.8	32.2	+20.0
	1.4[d]	26.1	25.5	24.9	−4.0

[a] sec^{-1}. [b] $k_0 = k_I + k_s$. [c] k_I. [d] k_s. [e] kcal mol^{-1}; $\Delta H^\ddagger(k_0)$, ±0.5; $\Delta H^\ddagger(k_I)$, ±1.0; $\Delta H^\ddagger(k_s)$, ±2.0. [f] cal mol^{-1} deg^{-1}.

Discussion

trans-$Cr(en)_2(DMF)_2{}^{3+}$ has been studied previously in DMF.[2] The isomerization rate ($k_I = 7.3 \times 10^{-5}$ sec^{-1}, 50°) is remarkably similar to that reported here for DMSO (8.8×10^{-5} sec^{-1}, 50°; Table V). Amine solvolysis also occurs at similar rates in the two solvents (DMF,[2] $k_2 = 1.25 \times 10^{-5}$ sec^{-1}; DMSO, $k_s = 1.20 \times 10^{-5}$ sec^{-1}; 50°). Clearly the reaction pathways in each solvent are very similar.

trans-$Cr(en)_2(DMSO)_2{}^{3+}$ in DMSO has been investigated earlier in connection with Cl^- and Br^- anation work at 30°.[4a] en loss from this complex was not previously detected, and our results show that amine solvolysis is quite significant at higher temperatures (~15%) and it represents about 8% reaction at 30° (no added halide). It is surprising to us that en loss is not evident in the added halide reaction,[4a] particularly as halide usually further promotes the loss of amine[2-4] (there are exceptions[4b]). The reported[22] activation parameters for isomerization ($\Delta H^\ddagger$ = 22.2 kcal mol^{-1}, $\Delta S^\ddagger$ = 9.5 cal mol^{-1} deg^{-1})[4] are similar to ours (Table VIII).

Isomerization and Solvent Interchange. In earlier work on other trans solventochromium(III) complexes in DMF and DMSO we concluded that isomerization proceeded by a common mechanism, namely, dissociation of a neutral leaving group, but we were unable to establish whether this was solvent or amine.[3] The present work was aimed at examining the paths involving solvent substitution and ethylenediamine solvolysis more closely.

If dissociation of coordinated solvent is the means to isomerization, then our results (Table V) show quite clearly that *every act of solvent interchange leads to isomerization*, at least for *trans*-$Cr(en)_2(DMF)_2{}^{3+}$ in DMSO. We previously reported that *trans*-$Cr(en)_2(DMF)Cl^{2+}$ substituted DMF with total stereochemical change in DMSO.[3] This result is re-

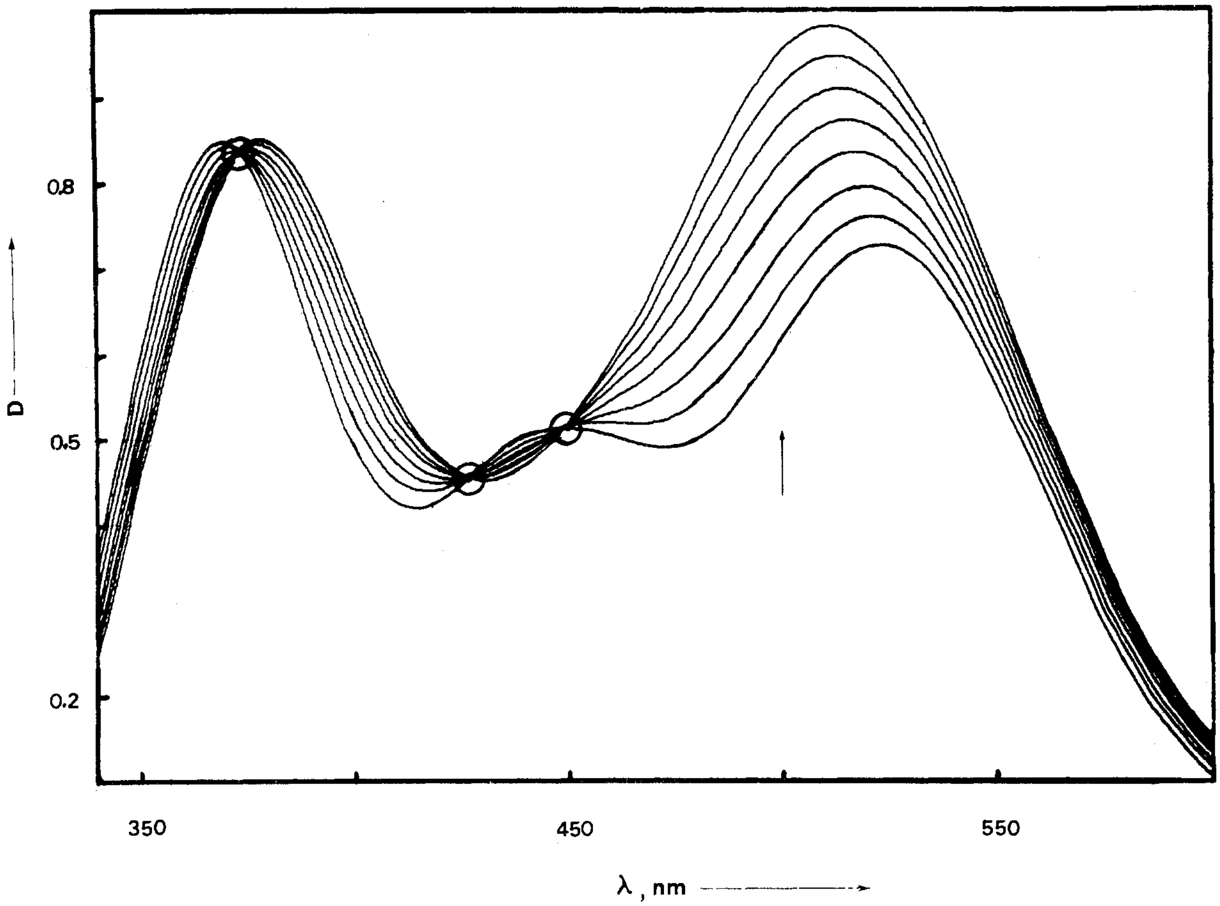


Figure 5. Changes in absorption spectra during the reaction of *trans*-$Cr(en)_2(DMF)_2^{3+}$ in DMSO. $[Complex]_0 = 1.65 \times 10^{-2}$ *M*, $T = 60.0°$. A period of less than $1t_{1/2}$ is shown.

markable since aminechromium(III) complexes normally substitute with strict retention of configuration.[11] It seems likely that DMSO exchange in *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ (and *trans*-$Cr(en)_2(DMSO)_2^{3+}$) is also largely nonretentive; we have monitored only DMF substitution which fits this pattern.

As discussed below, en dissociation and rechelation can lead simply to nonretentive solvent interchange (or exchange). This possibility implies that our k_I values (Table V) represent only the *maximum* rates of direct solvent interchange for the trans isomers.

It is apparent that the cis isomers are at least 50 times more reactive in solvent interchange than the corresponding trans forms (Table V). Such a difference in cis–trans reactivity is unusual; we find this is a general result for reactions of triply charged tetraminechromium(III) complexes involving neutral leaving groups.[7] Previously[1] we have considered cis–trans lability and its solvent dependence in connection with solvolysis and aquation of singly charged complexes involving anionic leaving groups; the reactivities of the two isomers are more comparable there (within a factor of 10). Both cation and leaving group solvation would seem to play a major role in determining which isomer is the more reactive (and to what extent).[1]

It should be pointed out that while the cis isomers are the more reactive, they are also the more stable isomers in these solvents. Thus the reaction of a cis and its trans isomer cannot proceed through a common transition state, as the common stereochemistry of substitution in solvent interchange (100% cis product, Table V) might suggest.

Equilibria. The exclusive presence of the cis isomer of $Cr(en)_2(DMSO)_2^{3+}$ at equilibrium is in accord with previous trends;[12] there is a marked tendency to cis isomers as the formal charge and dipole moment of the complex, as well as solvent dipole moment, are increased.[2]

Solvent interchange in DMSO goes to completion (>99%) with the $(DMF)_2$ and $(DMF)_4$ complexes since DMF and DMSO differ little in their ligand properties and under our conditions bulk solvent was always in large excess. Solvent interchange of the corresponding DMSO complexes in DMF goes to completion.[7]

Earlier[2] we alluded to the significance of the results reported here for the thermodynamics of en loss from the $Cr(en)_2$ moiety in DMSO. We suggested that the bare stability of $Cr(en)_2(DMSO)_2^{3+}$ to amine solvolysis (at equilibrium, 95 ± 1% *cis*-$Cr(en)_2(DMSO)_2^{3+}$, 5 ± 1% $Cr(en)(DMSO)_4^{3+}$ + en at 60°, $[complex]_0 \doteq 1.0 \times 10^{-2}$ *M*) reflected the inherently weak Cr–N bond; detectable solvolysis does occur despite the enhanced stability of the diamine complex through chelation. More significant is the lack of any tendency to disproportionation, as found in DMF,[2] and this recently has acquired importance in the ready synthesis of tetraaminechromium(III) complexes in DMF and DMSO.[13,14]

Ethylenediamine Solvolysis. The observation of significant net en loss from the trans-solvento complexes is undoubtedly connected with the relatively weak Cr–N bond. Co–N cleavage is rarely encountered in Co(III) systems.

The ~20% accumulation of free amine for the *trans*-bis(solvento) complex reactions in DMSO (and in DMF[2]) would seem to be a kinetic phenomenon since at equilibrium only 5% amine remains uncomplexed. It should be emphasized that while loss of amine from Cr(III) complexes is quite generally observed,[11b] it is not because Cr–N cleavage is particularly facile but rather because reaction is particularly slow (solvent interchange in the present work). Linck[15] has made a similar point in connection with *trans*-$Cr(en)_2X_2^+$ aquation. The fact that the cis but not the trans isomers are stable to en loss undermines this point in the present work.

In acid hydrolysis of en an intermediate unidentate en complex usually appears (in its protonated form) and then slowly liberates the diamine (see, for example, the two well-studied en aquation reactions, $Cr(en)(OH_2)_4^{3+}$ [16] and *trans*-$Cr(en)_2F_2^{+}$ [15]). It should be noted that these rates of the stepwise cleavage of the Cr–N bonds do not differ greatly. These observations are important for two reasons. First in this and earlier work[2] in DMF and DMSO there is no evidence for unidentate en complex intermediates when surely en loss proceeds through such species. Second, there is evidence that Cr–N cleavage can occur without net loss of amine in dipolar aprotic media.[2] This suggests that rechelation is occurring and this suppresses the accumulation of the intermediate. Indeed, it has been shown that rechelation occurs, although slowly, even in acid medium.[15] We have noted significantly different spectral changes for reacting solutions of *trans*-$Cr(en)_2(DMSO)_2^{3+}$ in DMSO 0.1 *M* in $HClO_4$, thus supporting this suggestion.

A result of interest is the appearance of $Cr(en)(DMSO)_2(DMF)_2^{3+}$ [18] rather than $Cr(en)(DMSO)_4^{3+}$ as the en solvolysis product of *trans*-$Cr(en)_2(DMF)_2^{3+}$. Thus DMF is not significantly exchanged in the (unobserved) intermediate unidentate en (eN) complex $Cr(en)(eN)(DMSO)(DMF)_2^{3+}$. A similar conclusion may be drawn from results for *trans*-$Cr(en)_2(DMSO)(DMF)^{3+}$ solvolysis. It follows that rechelation with retention will regenerate the reactant and it is therefore unobservable. Ring closure with stereochemical change will lead to the observed *cis*-$Cr(en)_2(DMSO)_2^{3+}$ since DMF in any *cis*-$Cr(en)_2(DMSO)(DMF)^{3+}$ formed is rapidly substituted by DMSO.[7] Thus all our observations may be explained in terms of a dissociating chelate.

Finally we should note that since it appears that dissociated en is substantially rechelating, our values for amine solvolysis (k_s, Table V) represent only the *minimum* rate of cleavage of the first Cr–N bond in the *trans*-$Cr(en)_2$ complexes. The activation parameters (Table VIII) are therefore only apparent since they may be composite quantities. We may note however that for en aquation reactions high activation energies have been reported;[11b,17] these values are probably realistic since rechelation problems have not been encountered in acidic medium. Our $\Delta H^{\ddagger}$ values for en loss in DMF[2,3] and DMSO follow these trends.

Conclusions

The *cis*-$Cr(en)_2(DMSO)_2^{3+}$ product common to the three reactions studied can arise either through direct solvent interchange or through ring closure in the intermediate unidentate en complex. If direct solvent interchange is the reaction path, it must occur largely with stereochemical change.

The en-loss path gives mono(ethylenediamine) product without the interchange of trans-coordinated solvent, and the accumulation of the intermediate "one-ended" en complex appears to be prevented by rechelation. Whether rechelation leads to isomerization is not established. Clearly the role of the chelate in these reactions can only be fully elucidated through the isolation and independent investigation of the unidentate en complex intermediates.

Acknowledgment. W.G.J. is grateful for financial support through a Commonwealth Postgraduate Research Grant.

Registry No. *trans*-$[Cr(en)_2(DMSO)(DMF)](ClO_4)_3$, 53586-60-0; *trans*-$Cr(en)_2(DMSO)_2^{3+}$, 29845-01-0; *trans*-$Cr(en)_2(DMF)_2^{3+}$, 29845-00-9; *cis*-$Cr(en)_2(DMSO)(DMF)^{3+}$, 53626-26-9; *cis*-$Cr(en)_2(DMSO)_2^{3+}$, 37095-05-9; *cis*-$Cr(en)_2(DMF)_2^{3+}$, 46935-03-9; $Cr(en)(DMSO)_4^{3+}$, 53586-57-5.

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(17) See, for example, D. A. Kamp, R. L. Wilder, S. Tang, and C. S. Garner, *Inorg. Chem.*, **10**, 1396 (1971), and references therein.
(18) The geometry of these product mixed-solvento complexes is not known but they probably retain the parent trans configuration.
(19) k_0 is the first-order rate rate constant for disappearance of reactant, c_i is the concentration of complex i, $i = 1$–3, and c_0 is the total complex concentration (=initial complex concentration at $t = 0$); other symbols used have their usual meaning or are defined where necessary.
(20) Least-squares fittings were carried out on an IBM 7044 computer.
(21) The sensitivity of the method was gauged from analysis for (known) concentrations in synthetic mixtures of the complexes.
(22) $\Delta S^{\ddagger}$ appears misprinted in ref 4b but is corrected in ref 4a.